Seaweed drying characterization via serial statistical criteria analysis

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Abstract. In drying seaweeds, it is important to describe its drying behavior using semi-theoretical models. Predicting the best drying model for the seaweed was commonly done by testing the goodness of the curve for seaweed drying models by calculating the coefficient of determination $R^2$, the reduced chi square $\chi^2$, root means square error (RMSE) and mean bias error (MBE). However, it is essential to rank the drying models before selection by assessing its performance index $\Phi$ and mean relative deviation (MRD). It is also necessary to test the normality by evaluating the skewness and kurtosis statistics using the D’Agostino Pearson test which is the best test for goodness of fit. The simple sample run test statistics and confidence interval must also be satisfied. These are the conditions that should be met under the serial statistical criteria analysis. This study utilized it to choose the best drying model for seaweeds. Employing this statistical analysis for testing commonly used drying models, Modified Page model emerged as the best model that depicts the drying behavior of the seaweeds with accuracy of 99.98% and highest performance index of 452.1967.

1. Introduction

Drying is composed of heat and mass transfer from the product. The drying process can be modelled mathematically in which derived equations can predict drying characteristics of air in various products [1]. The idea of thin layer drying applies to an assumed temperature distribution of the material, whole or part is exposed freely to drying air and there is variation in the material’s thickness [2]. To determine drying characteristics of different types of porous materials, thin-layer equations are frequently used. The thin-layer equations can be categorized into theoretical, semi-theoretical and empirical models [3]. Theoretical models depend on Fick’s second law which correlate diffusion coefficient to the local moisture content of the material assuming that the resistance to the moisture flow is uniformly distributed throughout the interior of the homogeneous isotropic material and the volume shrinkage is negligible. Simplifying the general series solution for Fick’s second law, semi-theoretical models can be developed. These models can also be derived from simplified models with valid constraints on drying parameters such as temperature, relative humidity, air velocity and moisture content [4, 5]. Most of the common drying models used for seaweed drying were the Modified Page [6,7], Page [8,9], Wang and Singh [10], Newton [10,11] and Henderson and Pabis [11]. In order to pinpoint the best drying model, the behavior of the moisture ratio (MR) must be obtained, and its best fit curve must be estimated. Statistical analysis is conducted to test the goodness of the best fit curve of MR compared to existing models. The commonly used statistical tools in testing the goodness of the curve for seaweed drying
models are coefficient of determination (R²), the reduced chi square (χ²), root means square error (RMSE) and mean bias error (MBE) [6, 8, 12]. However, to ensure goodness of fit, it is necessary to rank the drying models using other parameters such performance index Φ and mean relative deviation (MRD). The study will employ another statistical approach of testing for the best drying model using serial statistical criteria analysis. This analysis was used to determine the drying behavior of banana [13] and moisture sorption isotherms for chayote, almond powder, and yogurt [14]. This consists of four (4) criteria. The first criterion composed of the six statistical tools mentioned earlier. The D’ Agostino - Pearson test of normality is the second criterion for testing the best fit curve and also considered as the best test for goodness of fit. [13, 14]. This involves solving for the skewness test statistic z₁ and kurtosis test statistic z₂. Using these the test statistic D’ Agostino Pearson, χ²_{DAP} can be calculated. The third criterion for serial statistical criteria is using single sample run test which uses z as its test statistics for randomness of moisture residual series. For the fourth and last criterion, the significance and precision of drying parameters via creation of confidence interval of individual parameters will be conducted.

There is lack of literature that employed serial statistical criteria analysis in thin dry modelling for seaweeds. This study will provide benchmark approach to analyze and test the goodness of fit of the curves and select the best drying model. The models should satisfy the four criteria and the top model will be chosen with the highest performance index in the rankings.

2. Materials and Methods
The seaweed species Eucheuma cottonii was used in the experiment. In order to obtain the initial moisture content, the seaweeds loss on drying procedure [15] was performed using microwave oven with temperature setting of 105°C. This is the same temperature used by [16]. 100g of seaweeds were placed in an aluminum foil and dried at constant temperature. For monitoring the mass reduction of the seaweeds, the aluminum foil is pulled every 10 minutes. Three same successive mass readings can safely assume that the seaweeds are totally dried. The initial moisture content of the seaweed is obtained using the formula below:

\[ \text{Initial Moisture Content} = \frac{m_i - m_f}{m_i} \times 100\% \]  \hspace{1cm} (1)

One kilogram of seaweeds was placed in the solar dryer in each tray location. Load cells were used to monitor and measure the mass of the seaweed with the use of Arduino Software for data gathering. The moisture ratio of the seaweeds has been calculated. The moisture ratio was plotted, and best fit curve was being approximated in describing each drying model using Minitab 18 and employing Microsoft Excel Real Function Tool for statistical calculations

2.1. Moisture ratio
The moisture ratio is defined as the ratio of the change of moisture at any given moisture M with the equilibrium moisture content Mₑ over the difference of the initial M₀ to the equilibrium moisture content Mₑ and expressed in the equation:

\[ MR = \frac{M - M_e}{M_0 - M_e} \]  \hspace{1cm} (2)

However due to relative humidity fluctuations in the dryer [17, 18] and the moisture ratio is simplified as

\[ MR \approx \frac{M}{M_0} \]  \hspace{1cm} (3)

2.2. Semi-theoretical drying models
The common widely used semi-theoretical models were given below and utilized in the study to approximate the best fit curve for MR. The Page Model is one of the commonly used thin drying model for seaweeds and expressed as

\[ MR = e^{-kt^n} \]  \hspace{1cm} (4)
where \( t \) is the time, \( M \) is the material moisture content, \( M_O \) is the initial moisture content and \( M_e \) is the equilibrium moisture content with \( k \) and \( n \) as empirical coefficients.

Modified Page model is one of the commonly used thin drying model for seaweeds. It is the revised version of the Page Model. Modified Page model are better fit to drying models for seaweeds compared to the Page Model [6]. The formula was stated as

\[
MR = e^{-(kt)^n}
\] (5)

Henderson and Pabis model was the first term of the general series solution of Fick’s Second Law and described by

\[
MR = ae^{-kt}
\] (6)

where \( t \) is the time while \( a \) and \( k \) are drying parameters.

The simplified version for the Henderson and Pabis model is the Lewis Model or sometimes called Newton model and described by the equation

\[
MR = e^{-kt}
\] (7)

The Wang and Singh Model is described by the equation

\[
MR = at^2 + bt + 1
\] (8)

where \( t \) is the time \( a \) and \( b \) are drying constants.

2.3. Serial Statistical Criteria Analysis

Table 1 shows the summary of Serial Statistical Criteria Formulas. For the first criterion \( MR_{exp,i} \) is the \( i \)th experimentally observed moisture ratio, and \( MR_{pre,i} \) is the \( i \)th predicted moisture ratio. \( N \) is the number of observations and \( n \) is the number of constants. \( M_i \) is the moisture content and \( M_e \) is the mean moisture content. \( \Phi \) is ratio of \( R^2 \) to the product of RMSE and MRD. The second criterion is meant for the calculation of the D’Agostino test statistic \( \chi^2_{DAP} \). \( SE_m \) is the auxiliary variable for the computation of the normality test statistic where \( m \) = 2, 3, 4. The error about the residual mean is denoted by \( \epsilon_i \) while \( m_3 \) is the third moment of the mean for residual population and \( m_4 \) is fourth moment of the mean for residual population while \( s \) is the standard deviation of the individual mean. Equations (20) and (22) to (27) are applied in solving for skewness statistics \( z_1 \) in (33) while the kurtosis test statistics \( z_2 \) in (34) are obtained using equations (21) and (28) to (32). The resulting values in (33) and (34) are used to determine \( \chi^2_{DAP} \). To accept the drying model for curve fitting, \( \chi^2_{DAP} \) in (35) should be compared with critical chi square \( \chi^2_{crit} \) at \( \alpha = 0.05 \) with \( df = 2 \) or \( \chi^2_{crit} = 5.99 \). The drying model for best fit curve will be selected if \( \chi^2_{DAP} < \chi^2_{crit} \). The simple sample run test is the third criterion in which the test statistics \( z_r \) is determined. This test statistics is depended to \( n_1 \) which is the number of positive residuals, \( n_2 = \) the number of negative residuals and \( g = \) the number of times the sequence of residual changes sign. Using equations (36) and (37), \( z_r \) in (38) is calculated. The value of \( z_r \) will be compared with critical value of \( z \), \( z_{crit} \), at significant level \( \alpha = 0.05 \) or \( z_{crit} = 1.96 \). If \( z_r < z_{crit} \), hence accept the drying model for best fit curve otherwise discard it. The fourth and final criterion is based on the creation of the confidence interval of individual drying parameters. The drying model is accepted if the drying parameters are within the 95% confidence interval or else the model will be eliminated.
Table 1. Summary of Serial Statistical Criteria Formulas

| Criteria | Parameters | Formulas | Interpretation |
|----------|-----------|----------|----------------|
| First Criterion | $R^2$, $\chi^2$, RMSE, MBE, $\Phi$, $\text{MRD}$ | $R^2 = 1 - \frac{\sum_{i=1}^{N} (\text{MR}_{\text{prei}} - \text{MR}_{\text{ri}})^2}{\sum_{i=1}^{N} (\text{MR}_{\text{expi}} - \text{MR}_{\text{prei}})^2}$ | The higher value of $R^2$ and Lower values for $\chi^2$, RMSE and MBE will imply better curve fit for the drying model [13, 14]. |
| | | $\chi^2 = \frac{\sum_{i=1}^{N} (\text{MR}_{\text{expi}} - \text{MR}_{\text{prei}})^2}{N-n}$ | |
| | | $\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{N} (\text{MR}_{\text{expi}} - \text{MR}_{\text{prei}})^2}{N}}$ | |
| | | $\text{MBE} = \frac{\sum_{i=1}^{N} (\text{MR}_{\text{expi}} - \text{MR}_{\text{prei}})}{N}$ | |
| | | $\text{MRD} = \frac{1}{n} \sum_{i=1}^{N} \left| \frac{E_i}{M_i} \right|$ | |
| | | $E_i = M_i - \bar{M}_i$ | |
| Second Criterion | $\chi^2_{\text{DBAP}}$ | $\bar{M}_i = \frac{1}{n} \sum_{i=1}^{N} M_i$ | |
| | | $\phi = \frac{\text{RMSE}}{(\text{MRD})}$ | |
| | | $SE_m = \sum_{i=1}^{n} \epsilon_i^m$ | |
| | | $\epsilon_i = E_i - \bar{E}_i$ | |
| | | $s = \frac{SE_2}{n-1}$ | |
| | | $m_3 = \frac{nSE_3}{(n-1)(n-2)}$ | |
| | | $m_4 = \frac{n(n+1)SE_4}{(n-1)(n-2)(n-3)SE_2^2}$ | |
| | | $A_1 = \frac{nSE_3}{s^3(n-1)(n-2)}$ | |
| | | $B_1 = \frac{3(n^2+27n-70)(n+1)(n+3)}{(n-2)(n+5)(n+7)(n+9)}$ | |
| | | $C_1 = \sqrt{2B_1 - 1} - 1$ | |
| | | $D_1 = \sqrt{C_1}$ | |
| | | $E_1 = \frac{1}{\ln(D_1)}$ | |
| | | $F_1 = \frac{A_1\sqrt{C_1} - 1}{\sqrt{E_1}}$ | |
| | | $G_2 = \frac{24(n-2)(n-3)}{(n+1)^2(n+3)(n+5)}$ | |
| | | $H_2 = \frac{s^4(n-1)(n+1)\sqrt{G_2}}{m_4}$ | |
| | | $J_2 = \frac{6(n^7-5n-2)}{(n+7)(n+9)}\sqrt{\frac{6(n+3)(n+5)}{n(n-2)(n-3)}}$ | |
| | | $K_2 = 6 + \frac{8J_2}{J_2 + \sqrt{1 + \frac{4}{J_2}}}$ | |
| | | $L_2 = 1 - \frac{2}{K_2}/(1 + H_2\sqrt{2/K_2-4})$ | |
| | | $z_1 = E_1\ln(F_1 + \sqrt{F_1^2 + 1})$ | |
\[ z_2 = \left( \frac{2}{\sqrt{K_2}} \right)^2 \left( 1 - \frac{z}{2K_2} - \frac{L}{L_2} \right) \]

\[ \chi^2_{DAP} = z_1^2 + z_2^2 \]

Third Criterion

\[ g_1 = \frac{2n_1n_2 + 1}{n_1+n_2} \]

\[ \sigma_r = \frac{2n_1n_2(2n_1n_2-n_1-n_2)}{(n_1+n_2)^2(n_1+n_2-1)} \]

\[ z_r = \frac{|g-g_1|-0.5}{\sigma_r} \]

The value of \( z_r \) will be compared with critical value of \( z \), \( z_{\text{crit}} \), at significant level \( \alpha=0.05 \) or \( z_{\text{crit}} = 1.96 \). If \( z_r < z_{\text{crit}} \) hence accept the drying model for best fit curve otherwise discard it.

Fourth Criterion

CI

Confidence Interval

The drying model is accepted if the drying parameters are within the 95% confidence interval or else the model will be eliminated.

### 3. Results and Discussion

The mass of the seaweeds was reduced from 100g to 11.2g for 0.5920 g/min drying rate at 105°C with initial moisture content of 89.8%. The mass reduction of the seaweeds in the drying experiment was also determined. It took 311 minutes or approximately 5 hours and 19 minutes to reach the moisture content of 40%. The falling drying rate highly dominates at a rate of 1.42 g/min while the constant drying rate on the other hand is at 1.12 g/min. The moisture ratio was also calculated per drying time and plotted as shown in Figure 1.

![Figure 1. Actual Moisture Ratio per drying time](image-url)
Table 2 Summary of Drying Model Curve Fitting via serial statistics criteria for the whole dryer

| Thin drying models | Constant s | Value | CI | $R^2$ | RMS E | MBE | $X^2$ | MRD | $\Phi$ | $\chi^2_{app}$ | $z_\alpha$ |
|-------------------|-------------|-------|----|------|------|-----|------|-----|-------|-------------|--------|
| Modified Page*    | k           | 0.146 | 9  | 0.145 | 0.148 | 0.999 | 0.0034 | 0.000 | 0 | 0.649 | 452.196 | 0.763 | 1.486 |
|                   | n           | 1.299 | 9  | 1.277 | 1.322 | 0.999 | 8      | 2    | 0     | 9          | 4.06   |
| Page              | k           | 0.082 | 7  | 0.079 | 0.085 | 0.999 | 0.0036 | 0.000 | 0 | 0.649 | 428.989 | 2.177 | 1.428 |
|                   | n           | 1.299 | 9  | 1.277 | 1.322 | 0.999 | 8      | 2    | 0     | 9          | 4.06   |
| Henderson and Pabis | a           | 1.051 | 9  | 1.003 | 1.099 | 0.986 | 0.0298 | 0.002 | 0.001 | 0.118 | 279.664 | 0     | 2     |
|                   | k           | 0.148 | 6  | 0.134 | 0.162 | 0.986 | 2      | 0.002 | 0 | 0.649 | 428.989 | 2.177 | 1.428 |
| Wang and Singh    | a           | 0.002 | 3  | 0.001 | 0.003 | 0.997 | 0.0125 | 0.002 | 0 | 0.649 | 118.929 | 0.040 | 0.977 |
|                   | b           | 0.106 | 8  | 0.113 | 0.100 | 0.986 | 2      | 0.002 | 0 | 0.649 | 118.929 | 0.040 | 0.977 |
| Newton            | k           | 0.138 | 3  | 0.126 | 0.149 | 0.978 | 0.0375 | 0.007 | 0.001 | 0.571 | 45.6633 | 0.763 | 0.959 |

With this data, the curve fitting for each drying model has been conducted. Afterwards, serial statistical criteria analysis was applied to obtain the best drying model. It can be observed in Table 2 that all drying models satisfied the four criteria. The most accurate were the Page and Modified Page model with $R^2=0.9998$. The Modified Page model has the lowest RMSE = 0.0034. Ranking $\Phi$, it was evident that the Modified Page model has highest value of 452.1967 followed by the Page Model with $\Phi = 428.9897$. The least accurate was the Newton model with $R^2=0.9782$ and $\Phi = 45.6633$. The Modified Page model was the top choice for the best semi-theoretical seaweed drying model as denoted by the asterisk (*) symbol and agrees with the studies of [6, 7].

Using non-linear regression tool in Minitab 18, the best fit curve of MR for each drying model was plotted and shown in Figure 2.
Figure 2. Best fit curve of MR for the drying model a) Modified Page b) Page c) Henderson and Pabis d) Wangh and Singh and e) Newton

The resulting equation for the Modified Page model with accuracy of 99.98% is expressed in the equation below

\[ MR = e^{-(0.1469t)^{1.2999}} \]  \hspace{1cm} (39)

From the above data, it can be noted that the Modified Page model is the top model for predicting the moisture content reduction in dried seaweeds under solar drying with an accuracy of 99.98%. This model was also used to observe drying behavior in mint leaves and basil leaves [2, 22]

4. Conclusion and Recommendation

It can be concluded in the study that the Serial Statistical Criteria Analysis is an effective way of selecting the potential drying model in seaweeds from which they were ranked in terms of performance indices. The Modified Page model was selected to be the best model for predicting the drying behaviour of the seaweeds having an accuracy of 99.98% with highest performance index of 452.1967. The researchers would like to recommend validating the findings of this study and compare them to the results of applying theoretical and empirical models.

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