STATISTICAL EVALUATION OF FOUR-PARAMETER MOISTURE SORPTION ISOTHERM MODELS

STATISTIČKA OCENA NEKIH ĆETIRI PARAMETARSKIH MODELA SORPCIONIH IZOTERMI

In the scientific and engineering literature, there are various mathematical methods for modelling the equilibrium moisture content of agricultural and food materials. The objective of the present study was to statistically evaluate a total of thirty-two four-parameter moisture sorption isotherm models and subsequently compare their goodness of fit. The moisture sorption isotherm models considered were either originally developed or taken from the reference literature. The coefficient of determination and the graphical evaluation of residual randomness were utilized as the main assessment criteria for statistical evaluation of the moisture sorption isotherm models examined. The statistical performance of the models was tested according to the equilibrium moisture content of quinces. On the basis of the statistical analyses performed, the Popovski&Mitrevski model, i.e. the model with the reference numbers M25 and M30, and the McLaren&Rowen model were found to have the best statistical performance of all the models considered.

Key words: sorption isotherms, four-parameter models, statistical evaluation.

INTRODUCTION

In the scientific and engineering literature, there are numerous mathematical models for approximating the moisture sorption of agricultural and food materials. Depending on the number of parameters included, such models are referred to as one-parameter, two-parameter, three-parameter, or multi-parameter models.

The moisture sorption isotherm data, as a function of two or more temperatures, are important for the thermodynamic analysis, drying kinetics modelling and evaluation of food stability during storage (Vega-Galvez et al., 2007).

Over the past two decades, an increasing number of studies have been concerned with methods for sorption and/or desorption isotherm determination (Mitrevski et al., 2015; Mitrevski et al., 2018), sorption isotherm temperature dependence (Popovski&Mitrevski, 2004), sorption heat determination (Kaymak-Ertekín and Gedik, 2004) and the development of mathematical models for approximating moisture sorption data (Mitrevski et al., 2012; Mitrevski et al., 2015a).

In engineering calculations, the simplicity of a mathematical model (namely a model with a smaller number of parameters) is of great importance. Provided a sorption isotherm model is incorporated into a mathematical model for calculating the drying process of certain products or used to predict the shelf-life of packaged dried products, approximations of the experimental data on the equilibrium moisture content of such products are highly significant (Boquet et al., 1978).

The objective of the present study was to statistically evaluate a total of thirty-two four-parameter sorption isotherm models for approximating the data on the equilibrium moisture content of quinces and to subsequently compare their goodness of fit using the coefficient of determination.

MATERIAL AND METHOD

In this study, the equilibrium moisture contents of the quince samples were determined at temperatures of 15, 30, 45 and 60 °C using the static gravimetric method (Mitrevski et al., 2018, Boquet et al., 1978)
Mitrevski et al., 2019). A total of ten saturated salt solutions (namely LiCl, CH₃COOK, MgCl₂, K₂CO₃, Mg(NO₃)₂, NaBr, SrCl₂, NaCl, KCl and BaCl₂) were utilized to obtain the constant equilibrium relative humidity in the glass jars ranging from 0.110 to 0.920. Two dry samples were placed on holders in each of the ten glass jars and exposed to atmospheres of various relative humidity.

The glass sorption jars were placed and kept in the temperature controlled SANYO MCO-15AC cabinet (SANYO Electric Co., Ltd. Refrigeration Products Division 1-1-1, Sakata Ozumi-Machi, Ora-Gun, Gunma 370-0596 Japan) and maintained at temperatures 15, 30, 45 and 60 °C (with an accuracy of ± 0.1 °C). Three replications were made at each temperature and equilibrium relative humidity in the glass jars, using two samples per replication, and the average values of the equilibrium moisture content were calculated (Mitrevski et al., 2018, Mitrevski et al., 2019). Changes in the sample masses were recorded every 7 days using the electrical balance KERN PLJ360-3M (Kern&Sohn GmbH, Ziegelei 1, 72336 Balingen, Germany) with a precision of 0.001 g.

The equilibrium between the samples and their environments was reached after 21 days as evidenced by the constant mass of the samples after two successive measurements. The equilibrium moisture content of the samples was determined gravimetrically by oven drying for 24 h at a temperature of 105 °C and atmospheric pressure.

**RESULTS AND DISCUSSION**

The equilibrium moisture content values of the quince slices Xₑ (Table 1), obtained at different water activity values aₑ and four different temperatures (Mitrevski et al., 2018, Mitrevski et al., 2019), were fitted with thirty-two four-parameter sorption isotherm models M01-M32 (Table 2).

### Table 1. Equilibrium moisture content of the quince samples*

| Temperature | aₑ | Xₑ [kg/kg d.b.] | aₑ | Xₑ [kg/kg d.b.] |
|-------------|----|----------------|----|----------------|
| 15°C        | 0.113 | 0.008±0.000  | 0.113  | 0.013±0.001  |
| 30°C        | 0.113 | 0.008±0.000  | 0.113  | 0.013±0.001  |
| 45°C        | 0.113 | 0.008±0.000  | 0.113  | 0.013±0.001  |

*mean and standard deviation based on N = 3 replications

### Table 2. Mathematical models for approximating the sorption data

| Num. model | Name of model | Model | References |
|------------|---------------|-------|------------|
| M01        | Enderby       | Xₑ = −aₑ + Cₑ + Dₑ + aₑ * Cₑ  | Enderby, 1955 |
| M02        | Kollmann      | Xₑ = Aₑ + Cₑ + Dₑ + aₑ * Cₑ  | Kollmann, 1962 |
| M03        | McClaren & Rowen | Xₑ = Aₑ + Cₑ + Dₑ + aₑ * Cₑ  | McClaren & Rowen, 1951 |
| M04        | Peleg         | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Peleg, 1993 |
| M05        | Polynomial equation | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Castillo et al., 2003 |
| M06        | Popovski & Mitrevski | Xₑ = exp(Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ)  | Popovski and Mitrevski, 2004 |
| M07        | Popovski & Mitrevski | Xₑ = exp(Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ)  | Popovski and Mitrevski, 2004 |
| M08        | Popovski & Mitrevski | Xₑ = exp(Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ)  | Popovski and Mitrevski, 2004 |
| M09        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M10        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M11        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M12        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M13        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M14        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M15        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M16        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M17        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M18        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M19        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M20        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M21        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M22        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M23        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M24        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M25        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M26        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M27        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M28        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M29        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M30        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M31        | Popovski & Mitrevski | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | Popovski and Mitrevski, 2004 |
| M32        | Riedel        | Xₑ = Aₑ + Bₑ + Cₑ + Dₑ + aₑ * Cₑ  | van den Berg and Bruin, 1981 |
The statistical evaluation of sorption isotherm models depends on the nature of the model itself. The following statistical criteria are used for determining the goodness of fit of an isotherm model: the coefficient of determination ($R^2$), the root-mean-squared error (RMSE) and the mean relative deviation (MRD).

Sorption isotherm models with the graphical evaluation of residual randomness are also commonly used (Mitrevski et al., 2012). Plotting the residuals against independent variables is a measure of error distribution. If the sorption model is correct, then the residuals should be random independent errors with a zero mean, constant variance and arranged in a normal distribution. If the residual plots indicate a clear pattern, the model should not be accepted (Basu et al., 2006; Ruiz-Lopez et al., 2009). In this study, the coefficient of determination ($R^2$) and the graphical evaluation of residual randomness were the main statistical indicators for selecting the best four-parameter sorption isotherm model.

As regression methods (both indirect nonlinear and direct nonlinear regression methods), estimation methods, initial step sizes, initial parameter values, convergence criteria and function forms exert significant effects on the accuracy of the parameters estimated, a large number of numerical experiments were performed (Mitrevski et al. 2015). The method of indirect nonlinear regression analysis and the estimation methods such as the quasi-Newton, Simplex, Simplex-and quasi-Newton, Hooke-Jeeves pattern moves, Hooke-Jeeves pattern moves and quasi-Newton, Rosenbrock pattern search, Rosenbrock pattern search and quasi-Newton, Gauss-Newton and Levenberg-Marquardt from computer software Statistica (Statsoft Inc., Tulsa, OK, http://www.statsoft.com) were used to approximate the sorption isotherm model.

The statistical evaluation of sorption isotherm models used for approximating quince sorption data (Mitrevski et al., 2019).

Of all the models considered, the model with the reference number M21 (Popovski&Mitrevski, 2005) had the lowest value of the coefficient of determination ($R^2 = 0.97819$; rank 32), i.e. the worst statistical performance.

The A, B, C and D parameter values of the models M03, M25 and M30 were estimated by fitting the models to the experimental equilibrium moisture content of quinces using estimation methods which minimize the sum squares errors. The estimated parameter values are shown in Table 4.

### Table 3. Model Ranking

| Model | $R^2$ | Rank | Model | $R^2$ | Rank |
|-------|-------|------|-------|-------|------|
| M01   | 0.99119 | 17   | M17   | 0.99115 | 18   |
| M02   | 0.99148 | 6    | M18   | 0.98943 | 30   |
| M03   | **0.99157** | 3    | M19   | 0.99114 | 19   |
| M04   | 0.99147 | 8    | M20   | 0.99113 | 22   |
| M05   | 0.98480 | 31   | M21   | 0.97819 | 32   |
| M06   | 0.99113 | 24   | M22   | 0.99112 | 25   |
| M07   | 0.99156 | 4    | M23   | 0.99108 | 26   |
| M08   | 0.99147 | 7    | M24   | 0.99119 | 16   |
| M09   | 0.99113 | 23   | **M25** | **0.99157** | **2** |
| M10   | 0.99124 | 13   | M26   | 0.99065 | 29   |
| M11   | 0.99114 | 21   | M27   | 0.99121 | 14   |
| M12   | 0.99102 | 27   | M28   | 0.99152 | 5    |
| M13   | 0.99114 | 20   | M29   | 0.99129 | 12   |
| M14   | 0.99073 | 28   | **M30** | **0.99157** | **1** |
| M15   | 0.99131 | 11   | M31   | 0.99138 | 9    |
| M16   | 0.99121 | 15   | M32   | 0.99131 | 10   |

As can be seen in Table 3, the Popovski&Mitrevski models with the reference numbers M25 and M30 (Popovski&Mitrevski, 2005b) and the McLaren&Rowen model (McLaren and Rowen, 1951) had the highest coefficient of determination value ($R^2 = 0.99157$; rank 1). Consequently, these models correlate the experimental values of quince sorption better than other models. Moreover, the highest coefficient of determination value was obtained when two-parameter sorption isotherm models were.
Fig. 1c Experimental and predicted sorption isotherms for the quince samples at 45 °C in the case of the M30 model

Fig. 1d Experimental and predicted sorption isotherms for the quince samples at 60 °C in the case of the M30 model

As can be seen in Figures 1a-1d, the M30 model exhibited a good agreement between the experimental and predicted values of the equilibrium moisture content of quinces.

The regression analyses for the models M03, M25 and M30 indicate that the residual plots obtained show no abnormal distribution relative to the predicted values. Figures 2a-2c show the residual plots for the M03, M25 and M30 models relative to the experimental values.

CONCLUSIONS

In this paper, the statistical performance of a total of thirty-two four-parameter sorption isotherm models was studied according to the equilibrium moisture content of quinces. The coefficient of determination and the graphical evaluation of residual randomness were utilized as the main assessment criteria for statistical evaluation of the sorption isotherm models considered. Of all the models considered, the Popovski&Mitrevski M25 and M30 models and the McLaren&Rowen M03 model exhibited the best statistical fit between the experimental and predicted equilibrium moisture contents of quinces at different water activity values.

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