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Study of uncertainty in the fitting of diffusivity of Fick's Second Law of Diffusion with the use of Bootstrap Method

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ABSTRACT

Through appropriate considerations, Fick's Second Law of Diffusion admits analytical solution. A model based on this law was proposed and its analytical solution in series was obtained for mathematically modeling the soybean hydration process. The diffusivities were fitted to experimental data by nonlinear regression. The Bootstrap method was used to assess uncertainties that occur in the estimation of diffusivity. The study was based on the analysis of the influence that the amount of terms of the series (analytical solution) exerts on the variability of the diffusivity values adjusted. The results showed that the variability of these values decreases considerably as more terms of the series are considered in analytical solution. From ten terms considered in the series, the variability of the diffusivity becomes stable. The results also showed that the number of terms of the series may compromise the correct interpretation of the influence of temperature in the diffusivity values.

1. Introduction

One of the most widespread ways in literature to describe the mass and heat diffusion in transient regime is using the Fick's Second Law of Diffusion. Its deduction and examples of its use can be found in textbooks of transport phenomena, for example. Once solved, it describes how heat and mass is transported in a medium as a function of position and time (Bird et al., 2002; Welty et al., 2008).

The method of separation of variables is widely used for the solution of the diffusion equation. Such method is also widely used for the description of the mass diffusion process during hydration and drying food, usually by truncating the solution in the first term of the series with the main purpose of estimating the mass effective diffusivity. This parameter is very important in diffusive processes since it provides the order of magnitude with which diffusion occurs. Analytical solutions of the diffusion equation in terms of infinite series have already been applied in hydration processes of white and brown rice (Engels et al., 1986), pigeon pea (Kader, 1995), soybean (Gowen et al., 2007), cereal (Tütüncü and Labuza, 1996), hazel (Martinez-Navarrete and Chiralt, 1999) and vegetables in general (Seyhan-Gürtas et al., 2001).

Examples of application of infinite series solutions are also found in food drying such as meat (Trujillo et al., 2007), potato (Hassini et al., 2007), tomato (Fiorentini et al., 2015). All these works make use of analytical solutions in series considering the geometry that best suits the original shape of the food analyzed. The work of Liu et al. (2012) stands for presenting a theoretical analysis of adjustment of effective diffusion coefficients for drying problems as a whole, using the solution proposed by Crank (1975) for diffusion into an infinite rod. In their work the authors analyzed the quality of the effective diffusivities fitted and the factors that most affect the quality of its estimates.

A common practice present in some of the above cited works is the consideration only of the first term of the series that composes the analytical solution. This allows the linearization of the solution, by applying the natural logarithm in both sides of the equality, and causes the obtaining of effective diffusivity to be reduced to obtaining the slope of the resulting straight line (Hassini et al., 2007; Liu et al., 2012; Martinez-Navarrete and Chiralt, 1999; Tütüncü and Labuza, 1996). However, this practice discards the

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remaining terms of the series, which has infinite terms.

During the parameter estimation procedure is important to infer the error made in obtaining the values of these parameters. Generally these errors are computed as the standard deviation of the obtained value and the confidence interval in which the value is present. These calculations provide an idea of the quality of the fitting of the model parameters, as well as inform how reliable the obtained values can be (Englezos and Kalogerakis, 2000; Montgomery and Runger, 2014). One of the ways to make the inference of uncertainty in parameter estimation is through the bootstrap method.

In its original formulation, the bootstrap is a variation of the Monte Carlo method that numerically determines the shape of the distribution (Chernick, 1999; Diaconis and Efron, 1983). Given a random and independent sample, the method consists of the following steps (Olea and Pardo-Igúzquiza, 2010):

1. Obtain a sample at random with replacement of the original sample;
2. Calculate and save the statistics of interest;
3. Return to step 1 and repeat the process at least 1000 times;
4. Correctly present the values obtained for each statistic;
5. Stop.

However, in the presence of temporal correlation step 1 is inappropriate since the resampling may result in a sample containing non-correlated data.

One of the first solutions for the bootstrap problem with correlated data has been proposed by Solow (1985). The basic idea of this work was to turn correlated data into non-correlated data. Journel (1994) proposed a conditional resampling method based on the error distribution. Berkowitz and Kilian (2007) presented a bootstrap resampling in block for data with time dependence. Liang et al (2013) proposed a resampling method through sub samples, however, applicable only in large databases. Other approaches can be verified in Olea and Pardo-Igúzquiza (2010) and Chrysikopoulos and Vogler (2004).

Cribari-Neto and Zarkos (2001, 2004) presented a series of application advantages of bootstrap methods including the ease of obtaining new estimates, construction of confidence intervals and bias correction.

The bootstrap method has widespread use as part of processes involving food analysis. By tracking changes in quality and development stages of two types of ponkan via an “e-nose” and an “e-tongue”, Qiu et al. (2015) used the bootstrap method to process the data collected in their studies. In the study of the concentration of phenols in sliced fruits to be stored, Amodio et al. (2014) used the bootstrap to infer the distribution of the values of the parameters present in the models proposed in their work. In proposing a model to relate the shell color and quality of fresh mango, Fukuda et al. (2014) used the Random Forests method for evaluating its results, being the bootstrap method part of the calculation of Random Forests. Cafarelli et al. (2014) have classified different types of Italian bread for microtomography. In the models proposed in this work the authors used the bootstrap to increase the accuracy of the classification procedure. Arias-Mendez et al. (2013) proposed an optimized design for the process of frying potato chips. In this work the authors used the bootstrap for obtaining robust confidence intervals for the parameters present in the optimization model.

In this context the aim of this study was to mathematically model the hydration of soybeans using the analytical series solution of the Fick's Second Law of Diffusion. It was intended to also study the uncertainty in obtaining these parameters using the bootstrap method, mainly by analyzing how the number of terms of the series influences the variability of fitted effective diffusivity and model prediction intervals. The results show that from five terms considered in analytical solution, the effective diffusivity tends to stay constant, while the confidence intervals tend to become almost constant only after ten terms. The correct estimation of the variability of the parameter was decisive to correctly infer the influence of temperature in the behavior of effective diffusivity values.

2. Theory

Fick's Second Law of Diffusion was obtained from a transient mass balance in a differential volume element of a soybean considered spherical. Equation (1) presents Fick's Second Law of Diffusion, which, for the present work, had the effective diffusivity (D) considered constant. Equation (2) is the initial condition of the problem and states that at the beginning of hydration the grains have known and evenly distributed moisture content. Equation (3) it is the symmetry condition in the center of the sphere and Equation (4) is the boundary condition at the surface and establishes that at this point the equilibrium moisture content is reached immediately.

$$\frac{\partial X}{\partial t} = D\left(\frac{2}{r}\frac{\partial X}{\partial r} + \frac{\partial^2 X}{\partial r^2}\right) \quad (1)$$

$$X(r,0) = X_0 \quad \forall r \quad (2)$$

$$\left.\frac{\partial X}{\partial r}\right|_{r=0} = 0 \quad t>0 \quad (3)$$

$$X(R,t) = X_{eq} \quad t>0 \quad (4)$$

where X is the moisture on a dry basis, X_0 the initial moisture on a dry basis, X_{eq} the equilibrium moisture content on a dry basis, r the radial coordinate, R the radius of the grain, t the time coordinate and D the effective diffusivity.

Equation (5) presents the analytical solution of the model composed by Equations (1)–(4).

$$X*(r,t) = \frac{2R}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\sin\left(\frac{n\pi r}{R}\right)e^{\left[-D\left(\frac{n\pi}{R}\right)^2 t\right]} \quad (5)$$

where

$$X*(r,t) = \frac{X(r,t) - X_{eq}}{X_0 - X_{eq}}$$

The boundary condition represented by Equation (3) causes an indetermination in the form of 0/0 when applied to the analytical solution (Equation (5)). When $r \to 0$ the term $sin(n\pi r/R)/r$ tends to this indetermination. To avoid this problem and obtain a valid solution in the center of spherical grains ($r = 0$), the limit of Equation (5) when $r \to 0$ was evaluated using L'Hôpital rule (Smith, 1987). Equation (6) presents the resulting equation which is valid for $r = 0$.

$$X*(0,t) = 2\sum_{n=1}^{\infty}(-1)^{n+1}e^{\left[-D\left(\frac{n\pi}{R}\right)^2 t\right]} \quad (6)$$

Usually in particulate systems the average moisture as a function of time is measured experimentally. Thus, in order to compare the model results with the average experimental values of moisture, average moisture content was calculated by the model using Equation (7). This equation calculates the average moisture over the