DRYING KINETICS OF SILICA-GEL DISCRIMINATION STATISTICS EQUATIONS

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Abstract. *The use of mathematical models to predict drying kinetics the thin layer process of various products has been the objective of many studies. The literature presents semi-empirical drying kinetics equations, generally based on the diffusional model. Most semi-empirical drying kinetics equations presented in the literature are nonlinear, thus care should be taken when estimating parameters, since in some situations the estimators may not be appropriate. There are procedures available to validate the statistical properties of the least squares (LS) estimators of nonlinear models. Bates and Watts developed new measures of nonlinearity based on the geometric concept of curvature, dividing it into two components: intrinsic (IN), which is characteristic of the model; due to the effect of parameters (EP) that depends on how the parameters appear in the model. Box presented a useful formula for estimating the bias in the LS estimators. In this study, three semi-empirical drying kinetics equations were considered (Henderson-Henderson; Page; Overhults), examining an experimental data set by the nonlinearity measures of Bates and Watts and the bias of Box. Was utilized a central composite design with four replications at the center, they studied temperatures 35.8, 40, 60, 80, 84.2°C and the superficial velocities 0.9, 1.1, 2.2, 3.3, 3.5m s-1. The relative humidity of the experiments ranged from 37 to 69%. As soon as the desired conditions were reached, the measuring cell was inserted into the equipment, initiating the experiment (zero time). The initial temperature of the silica-gel blue (withdrawn from the humidifier) was equal to that of the drying air. The measuring cell was periodically withdrawn and its mass determined on an analytical balance. At the end of experiment was measured and the dry mass determined using an oven (105+2ºC for 24 h), thereby calculating the final moisture (dry basis) of the material. The equilibrium moisture content used to calculate the dimensionless moisture content was obtained at the end of each experiment so considering the dynamic method. The results of the experiments were used to estimate the parameters of equations by LS using the Gauss-Newton. It was found that the three equations analyzed IN curvature measures were not significant. The measure of curvature in the equations of PE and Page of Overhults was not significant, as well as the distribution of residuals of these equations is better. In the equation of Henderson-Henderson observed the nonlinear behavior of the first parameter, as indicated by values of bias of Box. Among the equations of Page Overhults and observed that the values presented Overhults not an bias of Box and presented the F ratio greater than that of Page, thus being considered the best equation to represent the drying kinetics in thin layer of silica gel.*

Keywords*: nonlinear regression, drying kinetics, nonlinearity measures.*

1. INTRODUCTION

Obtaining the drying kinetics is of utmost importance to determine the parameters that control the phenomena of heat and mass transfer. The classic mode of approaching the problem is through drying experiments in thin layer (Prado, 1999). Literature reports semi-empirical drying kinetics equations, generally based on the “diffusive” method, which is a simplification of Luikov theory (1966) for drying in porous media. These equations, in general, are non linear, and the parameters are estimated from experimental results by the least square method (Gauss-Newton, Marquadt). Statistical validation of the results obtained from the estimates by least squares is done by some procedures found in the literature. Bates and Watts (1980) developed a non linearity measure based on the concepts of differential geometry, dividing it in two components: 1) intrinsic (IN), which is characteristic of the model; 2) that due to effect of parameters (PE), which depends on the manner in which the parameters appear in the model (reparametrizations). These measures are based on the magnitude of the second derivative of the model in relation to the parameters, which differs between the linear and non linear models. In contrast, Box (1971) developed a methodology to determine the biases of the estimators of the least squares for non linear models. This study evaluated drying kinetics equations found in the literature, considering the methods developed by Box and by Bates e Watts to identify which is the best equation to represent the drying kinetics in silica-gel.

2. EQUATIONS OF DRYING KINETICS

A number of empirical and semi-empirical equations have been proposed in the literature. Most kinetics studies described in the literature were done in thin layer, where several empirical and semi-empirical models are presented to describe the drying kinetics. Table 1 presents the most used empirical and semi-empirical equations to predict the drying kinetics of several materials.

Table 1. Drying kinetics equations

Equation		Reference
MR = *c* [exp (-Kt)+1/9 exp (-9Kt)], sendo K = *a* exp (-*b*/TF)	(1)	Henderson and Henderson (1968)
MR = exp (-Kt^n), were K = *a* exp (-*b*/TF)	(2)	Page (1949)
MR = exp [(-Kt)^n], where K = exp (*a* + *b*/TF)	(3)	Overhults et al. (1973)

Source: BARROZO (1995)

Equation (1) is derived based on theoretical model (Fick's second law) but is simplified and added with empirical coefficients (Henderson and Henderson, 1968); the Page (1949) and Overhults et al. (1973) equations originated from empirical modifications of the Lewis (1921) equation (Lewis (1921) - proposed equation using an analogy with Newton's law of cooling). In equations of Tab. 1, MR is the moisture dimensionless number:

$$MR = \frac{M - M_{eq}}{M_0 - M_{eq}} \tag{4}$$

M_{eq} is the equilibrium moisture, M is the solid moisture, M_0 is the initial moisture of the solid. The parameter K presented in the equations is known as drying constant and varies with temperature, according to Arrhenius like function, for eq. 1 and 2, while for eq. 3 the function that represents this variation is different. The letters *a*, *b*, *c* and *n* are parameters of these equations. The letters *t* and *TF* are the time and temperature of the fluid (air).

3. NON LINEARITY MEASUREMENTS

Non linearity measurements are known in the literature as expressions used to evaluate adequability of the linear approximation and their effects on the inferences. One of the first relevant attempts to quantify the non linear of a non-linear regression was presented by Beale (1960), who proposed four measures. According to Guttman and Meeter (1965), these measures should not be used in practice, since they tend to underestimate the true non linearity (Bates; Watts, 1980).

A non-linear regression model is considered "intrinsically linear" if it can be reduced to a linear model by means of an appropriate reparametrization. The term "intrinsically linear" can be used to refer to models that can be linearized by some transformation. In practice, in general, a non-linear model is linearized to facilitate the breadth of the parameters' estimates. When an appropriate transformation or reparametrization is not feasible to "linearize" the model, this is called "intrinsically non linear" model.

3.1. Obtaining the estimates of least squares

Several iterative methods to obtain estimates of least squares parameters of a non-linear regression method are proposed in the literature. The most used are the method of Gauss-Newton, or linearization method, and Marquardt's method (Bates; Watts, 1988 *apud* Mazucheli; Achcar, 2001). The least square estimators of linear regressions are non biased, normally distributed, and present the least possible variance among any other classes of estimators. However, for non-linear regressions, these properties are valid only when the sample size is large enough (Jennrich, 1969 *apud* Mazucheli; Achcar, 2001). Consequently, it can be stated that the results become more applicable as the sample size increases. When the least square estimators present small bias, near normal distribution and almost constant variances, it can be stated that the estimators present a near linear behavior and, consequently, the inferences will be more reliable. The extent of non-linear behavior is evaluated through non-linearity measures.

3.2. Bates and Watts' curvature measures

Bates and Watts (1980) detailed Beale concepts (1960) using concepts of differential geometry and developed non-linearity measures based on the concept of geometric concept of curvature. These authors demonstrated the a model's non-linearity can be decomposed in two components: intrinsic non-linearity (IN), which is characteristic of the model; and the non-linearity due to the effect of parameters (PE), which depends on the sequence that the parameters appear in the model (reparametrizations).

Intrinsic non-linearity (IN) measures the curvature of all possible solution for the problem of least squares in the sampled space. The solution of least squares is the point in estimation space that is nearest to the vector of response variables. A linear regression model presents a nil (IN) measure, since the estimation space is a straight line, a plane or a hyperplane. In contrast, the estimation space of non-linear model is curved, and (IN) measures the extent of such curvature. Bates and Watts (1980) and Ratkowsky (1983) concluded that, for most non-linear models of practical interest, the measure (IN) is generally small.

Non-linearity due to parameter effect is a consequence of the lack of uniformity of the coordinate system in the estimation space. In the linear case, the parameter lines are parallel. The measure (PE) is a scale quantity that represents the maximum value of the parametrization effect, obtained from a tri-dimensional vector, known as acceleration vector. The acceleration matrix in a linear model is made of zeros, thus resulting in (PE) equal to zero. In contrast, in a non-linear model, with a given (IN) value, the value of (PE) increases as its behavior deviates from the linear behavior, since (PE) measures the extent of the non-linear behavior caused by parametrization. When the non-linearity is mostly due to the effects of parameters, a reparametrization becomes important.

The statistical significance of IN and PE may be assessed by comparing these values with the radius of the confidence region, 100(1-α)%, which is equal to: $1/2\sqrt{F(p;n-p;\alpha)}$, where F = F(p;n-p;α) was obtained from a table of the F-distribution (significance level α), with *n* is the data number and *p* is the dimension of parameter.

3.3. Box bias measure

Box (1971) proposed an statistics to evaluate the bias of least square estimators of parameters of a univariate non-linear regression model, given by:

$$Bias\left(\hat{\theta}\right) = -\frac{\sigma^2}{2}\left[\sum_{i=1}^{n} F\left(\hat{\theta}\right) F^t\left(\hat{\theta}\right)\right]^{-1} \sum_{i=1}^{n} F\left(\hat{\theta}\right) \; traço \left[\left(\sum_{i=1}^{n} F\left(\hat{\theta}\right) F^t\left(\hat{\theta}\right)\right) H\left(\hat{\theta}\right)\right] \tag{5}$$

where F(θ) is the vector (p x 1) of the first derivatives of f (xi ; θ), also known as velocity vector, and H(θ) is a matrix (p x p) of second derivatives in relation to each element of θ. In practice, the computation of (2), is done using $\hat{\theta}$ and $\hat{\sigma}^2$ as the true values of θ and σ^2, respectively; and *t* is the transposed.

It is common to express the value of bias estimate in percentage:

$$\%Bias\left(\hat{\theta}\right) = \frac{100Bias\left(\hat{\theta}\right)}{\hat{\theta}} \tag{6}$$

where an absolute value in excess of 1% indicates nonlinear behaviour (Ratkowsky, 1983).

4. EXPERIMENTAL METHODOLOGY

The experimental procedures were done with blue silica-gel, with $dp=2.6x10^{-3}$m. The material was previously moistened and placed in a saturated environment for 24 hours at 60°C, reaching approximately 0.28 kg water/kg dry solid. Around one hour before the beginning of the experiment, the silica-gel was placed at the experiment temperature to minimize heat transfer during the initial stages of the trial. The experimental conditions were chosen to analyze the effect of air velocity and temperature on drying kinetics. Therefore, the selected design used a central composite organization (Box et al., 1978) with four replications in the center, and temperatures 35.8, 40, 60, 80 and 84.2ºC and surface velocities 0.9, 1.1, 2.2, 3.3 and 3.5m s^{-1}.

After the experiment conditions were reached, the measuring cell was inserted in the unit and the experiment time was computed (time zero). The cell was removed periodically and its mass determined in an analytical scale. At the end of the experiment, the dry mass of the sample subjected to drying in thin layer was determined by the oven method (105±2ºC), thus calculating the final moisture (dry basis) of the material. The equilibrium moisture used for the calculation the dimension-less moisture (MR), Eq 4, was obtained at the end of each experiment, considering the dynamic method.

5. RESULTS

The results obtained in the experiments (321 observations) were used in the estimation of the parameters of equations found in the literature, Tab. 2, to obtain the best model adjusting to the dry kinetics data with non-linear regression. The parameters were estimated by least squares using Gauss-Newton's method, using the software STATISTICA 7.0.

The statistical significance of the effects (IN) and (PE) was evaluated comparing the values obtained with the radius of the curvature of the confidence region 100(1-α)%, which is given by $1/2\sqrt{F(p;n\text{-}p;\alpha)}$, where F is Fisher's statistic (tabled), α the significance level. For α=0.05, if (IN)< $1/2\sqrt{F}$ and (PE)< $1/2\sqrt{F}$, there is a satisfactory linear approximation on the confidence region of 95%. A non-linear behavior of the parameters is found when the bias is above 1% for Box measures, i.e., this measure can indicate which parameter of the model is responsible for non-linearity. It can be seen in Tab. 2 that the intrinsic curvature (IN) of all equations analyzed was not significant. In contrast, for the curvature measure due to effects of parameters (PE) only Page's and Overhults's equations had values below $1/2\sqrt{F}$.

Table 2. Results of least squares and curvature and Box bias measures for the drying equations in thin layer silica-gel

Equation	R^2 and F	Curvature	Parameter	Estimated Value	Box's bias (%)	Estimated Standard Error(2)
Henderson-Henderson(1)	R^2=97.7 F=11657	IN=0.0170 PE=0.7510	a b c	66.415 2299.026 0.801	1.96 0.00 0.00	0.0477
Page(1)	R^2=99.2 F=33836	IN=0.0470 PE=0.2979	a b n	15.913 1404.802 0.601	0.27 -0.01 -0.03	0.0281
Overhults(1)	R^2=99.2 F=33841	IN=0.0013 PE=0.0027	a b n	4.61 -2338.92 0.60	0.00 0.00 0.00	0.0281

(1): $1/2\sqrt{F(3;318;0.95)} = 0.3081$; (2): Estimated Standard Error => $ESE = \sqrt{\frac{\sum(Obs\text{-}Est)^2}{DFR}}$

Therefore, it can be stated that, for these two equations, non-linearity due to parametrization was small, indicating that the inference results based on asymptotic approximations for the estimators of least squares were valid. The non-linear behavior of the equation of Henderson-Henderson was associated to the parameter *a*, while Arrhenius' equation, as shown by the bias values of Box, there is a probable need of reparametrization of the drying constant with temperature. The value of R^2 (99.2%) and the distribution of the residues of Page and Overhults equations were also best, while the distribution of the residues of the other model presented a lack of randomization (Figure 1). Comparing the equations of Page and Overhults, Overhults' had no values of Box bias and presented greater F proportion than Page.

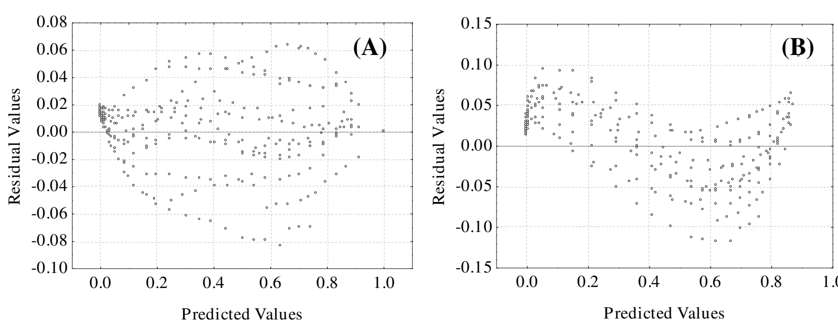

Figure 1. (A) Distribution pattern of residues as a function of MR values predicted by the equations of Overhults and Page; (B) Distribution pattern of residues as a function of MR values predicted by the equations of Henderson-Henderson.

Therefore, Overhults' equation was considered as the best equation in which the statistical inferences of least square estimators can be assured. Thus, the intervals of confidence (95%) of its parameters for t(min), T (K) and M (g water/g dry solid), are the following: a = 4.61 ± 0.46; b = -2338.92 ± 150.84; n = 0.60 ± 0.01.

Figure 2 shows the good agreement between the results predicted by Overhults' equation and the experimental data. The difference between the results measured and those computed was in the range 0.06 – 6.37%.

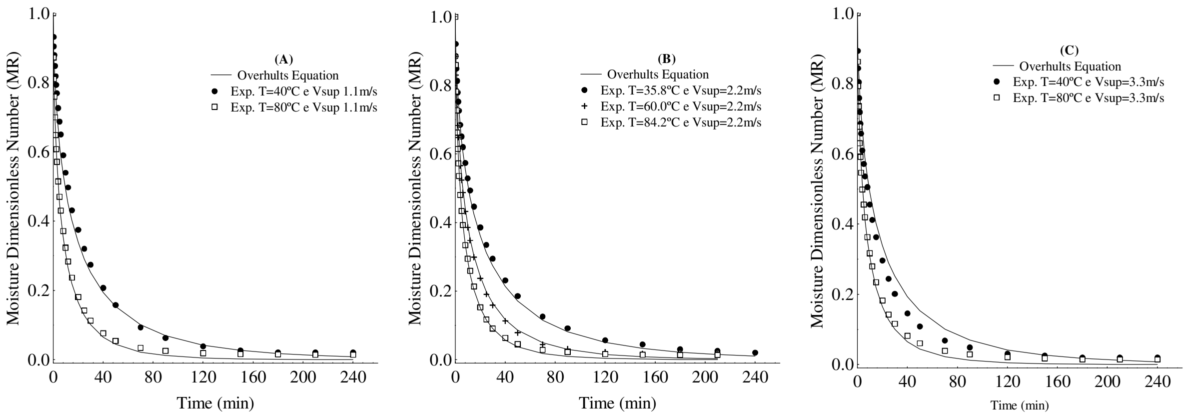

Figure 2. Drying curves of the experiments compared with the responses obtained by Overhults equation.

6. CONCLUSIONS

It can be concluded, from the results obtained in the present study, that:

- the values of R^2 and F proportion in conjunction with the distribution of the residues of Page and Overhults equations indicate them as adequate to represent the kinetics of silica-gel drying; however, the analysis of non-linearity indicated that Overhults equation was better, and should be indicated to best represent the present study.

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