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Equations of drying curves

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Abstract—A new method is suggested for obtaining, on the basis of experimental data, an approximate equation of the drying curve in the form of error functions which satisfy an ordinary second-order differential equation associated with a diffusion equation. Examples of calculations are given which are carried out from the data on the drying of grain and low-pressure polyethylene.

INTRODUCTION

THE DYNAMICS of the process of drying is described by a system of differential heat and mass transfer equations solved under corresponding boundary conditions [1]. Using the solutions of ref. [1] and making the conversion from the local functions of moisture content and temperature to their integral values, the basic differential equation for the kinetics of drying was obtained (see p. 460 of ref. [2]). The solutions of this equation determine a wide class of theoretical drying curves.

ANALYSIS

When a researcher has no necessary thermophysical and mass transfer characteristics for solving heat and mass transfer equations (a situation occurring, for example, in the drying of materials involving modern technology), he makes use of approximate equations of the drying curves, although they are less informative. Surveys, analyses and estimations of the advantages of many approximate equations of drying curves can be found, for example in ref. [3]. It is seen from this survey that these approximate equations are usually based on the ordinary differential equation

$$\frac{\mathrm{d}w}{\mathrm{d}\tau} = -F(w). \qquad (1)$$

In this equation, the function $F(w)$ is linear, power-law or fractionally-rational, depending either on the binomial $(w-w_e)^n$, or on the ratio w/w_e, where w is the instantaneous moisture content, w_e the equilibrium moisture content of the material and τ the time.

When solving equation (1), which depends on the binomial $(w-w_e)^n$, a simple exponential time function of moisture content results only at $n = 1$. When $n = 2$, a non-linear equation—the so-called logistic equation—results, which is successfully applied, for example, in biology, ecology and in the theory of drying [4]. Its solution is usually represented in the form $\tau = f(w)$. When $n > 2$, especially when n is fractional, the solution of equation (1) becomes rather difficult.

We believe it is more advisable and simple to seek an approximate solution to the drying curve equation straightaway as an explicit time function of the form $w = \varphi(\tau)$ following the logic of a drying experiment. Such an approach was realized in ref. [5] and is extended in this paper.

Our analysis of experimental curves for a wide class of materials subjected to drying in different modes and by different techniques showed that the ratio of drying acceleration $\mathrm{d}^2w/\mathrm{d}\tau^2$ to its rate $\mathrm{d}w/\mathrm{d}\tau$ is proportional at any time instant to a certain linear function of time. The process of drying is quite satisfactorily described by

$$\frac{\mathrm{d}^2w}{\mathrm{d}\tau^2} + 2p^2(\tau - t_0)\frac{\mathrm{d}w}{\mathrm{d}\tau} = 0 \qquad (2)$$

and, in special cases, by

$$\frac{\mathrm{d}^2w}{\mathrm{d}\tau^2} + kf(\tau - t_0)\frac{\mathrm{d}w}{\mathrm{d}\tau} = 0$$

where p, τ_0 and k are constants and $f(\tau-\tau_0)$ is a non-linear function.

Equation (2) describes reliably the most general process which includes heating, and periods of constant and falling rates of drying when the drying curves are S-shaped. These are monotonically decreasing curves without extrema, with one inflexion point and two horizontal asymptotes—the upper ($w = w_a$) and the lower ($w = w_e$). The inflexion point divides the drying curve into two segments, over the first of which $\mathrm{d}^2w/\mathrm{d}\tau^2 < 0$ and over the second $\mathrm{d}^2w/\mathrm{d}\tau^2 > 0$.

The general solution of equation (2) is the function

$$W = A(1 - \mathrm{erf}\,(p(\tau - \tau_0))) + B \qquad (3)$$

where

$$A = 1/2(w_e - w_a) < 0 \quad (\text{since } w_e < w_a) \qquad (4)$$

$$B = w_a. \qquad (5)$$

Calculations by equation (3) are made easier because the error function

NOMENCLATURE

A, B, D, k, n, p, w_a	constants
u	linear function of time
U	function of substance transfer
w	instantaneous moisture content of material
w^d	instantaneous moisture content in terms of dry substance
w_e	equilibrium moisture content.

Greek symbols

δ, τ_0	constants
σ	r.m.s. deviation
τ	time
$\Phi(\tau)$	integral of probabilities.

$$\operatorname{erf}(u) = \frac{2}{\sqrt{\pi}} \int_0^u e^{-t^2} \, dt$$

has been tabulated, for example in ref. [6] and, in more detail, in refs. [7, 8]. In addition to constant quantities A and B, the meaning of which is clear from equations (4) and (5), equation (3) involves two parameters: p and τ_0. The analysis of the moisture conduction equation shows that the quantity, which is proportional to $1/p^2$, is connected linearly with the average (over the process) moisture diffusion coefficient a_m. On the other hand, with the probabilistic nature of the erf-function taken into account, it becomes evident that $1/p^2$ is associated with the variance of the random quantity studied. The parameter τ_0 is the abscissa of the drying curve inflexion point.

Each point of the experimental curve carries important information about the factors that jointly influence the process of drying. The accumulation of the values of p and τ_0 for each specific material and their further analysis may allow one to elucidate new and interesting correlations.

Equation (3) yields the following expression for the rate of drying:

$$\frac{dw}{d\tau} = -\frac{2Ap}{\sqrt{\pi}} e^{-p^2(\tau-\tau_0)^2}. \qquad (6)$$

Equations (3) and (6) may turn out to be useful in creating a system of automatic control of drying.

We will now consider, in a general form, two techniques for finding the parameters p and τ_0. Both of these parameters are based on the assumption that the drying curve is centrally symmetric with respect to the inflexion point, with its imaginary continuation beyond the ordinate axis taken into account.

First technique

The parameter τ_0 is found as the inflexion point abscissa which corresponds to the ordinate $w_0 = 1/2(w_a + w_e)$. The parameter p is determined in the following way. Solve equation (3) for the erf-function

$$\operatorname{erf}(p(\tau-\tau_0)) = \frac{A+B-w}{A} \qquad (7)$$

where τ_0, A and B are already known. Instead of the variables τ and w in equation (7), substitute in turn the coordinates of several experimental points selected on the curve on each side of the inflexion point. Each time this will yield a certain constant value of the erf-function on the right-hand side of equation (7). Given this value, we use the table of erf-functions (or of their inverse functions) to find the corresponding value of the argument containing the unknown p. The latter is easily calculated. For example, for the first selected point (τ_1, w_1), the table gives the argument of the form $u_1 = p(\tau_1 - \tau_0)$, from which p is calculated. Analogously, the values of p for the second, third and following selected points are obtained. The arithmetic mean of all these values of p is taken to be the value of the parameter sought.

Second technique

The determination of the parameters p and τ_0 is based on the linear relationship between the arguments of the normalized and non-normalized erf-functions. It is evident that $\operatorname{erf}(u) = \operatorname{erf}(p(\tau-\tau_0))$ only in the case when

$$u = p(\tau - \tau_0) \qquad (8)$$

i.e. when u depends linearly on τ. It is this relation which is used as a basis for both graphical and analytical determinations of the parameters.

Consider the graphical method. Represent equation (7) in the form

$$\operatorname{erf}(u) = \frac{A+B-w}{A}. \qquad (9)$$

Substitute into this equation any two experimental values of w_1 and w_2 which are far enough apart, but preferably not the limiting values for better approximation. From the two numerical values of the erf-function, we find, with the aid of the table, the corresponding arguments u_1 and u_2. Plot the points $M_1(\tau_1; u_1)$ and $M_2(\tau_2; u_2)$ in a system of rectangular coordinates $\tau 0 u$ and pass through them a straight line which will represent the curve of function (8). The point $(\tau_0; 0)$ of the intersection of this line with the abscissa determines the value of the parameter τ_0, whereas the tangent of the slope of this line determines the parameter p calculated with the scales on the axis and tangent sign taken into account. By virtue of the fact that the erf-function is associated with the normal distribution law, the rest of the experimental points fall either on this line or close to it.

The parameters p and τ_0 can be found purely analytically from the two points $M_1(\tau_1; u_1)$ and $M_2(\tau_2; u_2)$ with the aid of equation (8), since this leads to a system of linear equations

$$\tau_0+\frac{1}{p}u_1=\tau_1$$
$$\tau_0+\frac{1}{p}u_2=\tau_2 \qquad (10)$$

which yield

$$\frac{1}{p}=\frac{\tau_1-\tau_2}{u_1-u_2} \qquad (11)$$

$$\tau_0=\tau_1-\frac{1}{p}u_1=\tau_2-\frac{1}{p}u_2. \qquad (12)$$

It is also possible to find the equation of the straight line which passes through these two points and reduce it to the form of equation (8), from which the values of the parameters p and τ_0 are evident.

Taking into account the normal nature of the erf-function, the plot of which is identified with the drying curve, it is natural to assume that to the period of constant rate there approximately corresponds the time interval

$$\tau_0-\delta<\tau<\tau_0+\delta \qquad (13)$$

where

$$\delta=\frac{1}{|p\sqrt{2}|}$$

or

$$0<\tau<\tau_0+\delta \qquad (14)$$

when the drying curve begins with the period of the constant rate of drying. For quartiles, this corresponds to $u_N=\pm 0.8427$ when erf $(u_N)=\pm 1$.

The basic idea behind the proposed method for obtaining an approximate equation of the drying curve is that experimental points are superposed with the entire plot or with a portion of the plot of the function erfc (τ) (or of the function $1-\Phi(\tau)$, where $\Phi(\tau)$ is the probability integral) with the parameters selected, so that variance of nonadequacy be made as small as possible.

When selecting the parameters for the drying curve equation, it is necessary that the portion of the curve which is located to the left of the inflexion point be considered as symmetric with its right-hand side with respect to this point and as if continued to the left beyond the ordinate axis. As a result, the value of the upper horizontal asymptote $w=w_a$ will nearly always be greater than the measured value of the initial moisture content w_H of the material. In those cases when the heating segment on the experimental drying curve is very small and cannot be detected in measurements

Table 1. Experimental and computational values of moisture content in drying of low-pressure polyethylene

τ (min)	w (%)	$\tilde{w}$ (%)
0	60	60.3
2.5	55	55.4
5	49	49.1
7.5	35	34.4
10	17	18.1
12.5	6	7.1
15	2.5	2.4
17.5	1.2	1.2
20	1	1
22.5	1	1
25	1	1

(drying of cloth, paper, etc.) and the curve begins with a linear period, which corresponds to the constant rate of drying, it is recommended that the experimental curve be represented as a truncated plot of the appropriate function erfc (τ). When the time τ_f of the end of the linear period is distinct, it is possible to assume that $\tau_0=0.5\ \tau_f$; otherwise τ_0 is determined as suggested above. The analytical technique for estimating the parameters p and τ_0 from two experimental points seems to be the most simple and effective. Some examples will be considered.

Example 1

One can find the equation of the curve from the data on the drying of low-pressure polyethylene borrowed from curve 1 of ref. [4]. Assume that $w_a=61$ and $w_e=1$. Then $A=-30$, $B=61$ and $w_0=31$, to which there corresponds $\tau_0=8$ (Fig. 1). From the coordinates of the second, third, fifth and sixth points, we calculate that $p=-20$. The approximate equation of the drying curve is

$$\tilde{w}=-30(1+\text{erf}\,(0.20(\tau-8)))+61;$$

the non-adequacy variance is $\sigma^2=1.08$ ($\sigma=1\%$).

We will apply to this example the method of estimation of the parameters p and τ_0 on the basis of two points. The coordinates of the experimental points will be taken to be (5; 49) and (15; 2.5). Replacing w

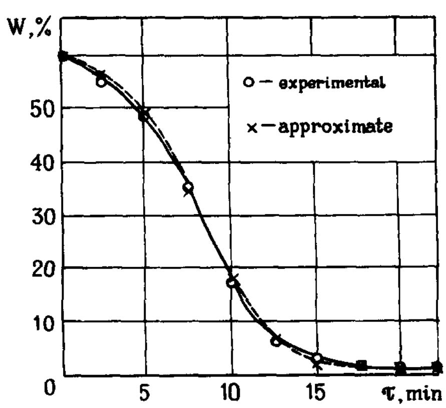

FIG. 1. Experimental and approximate drying curves.

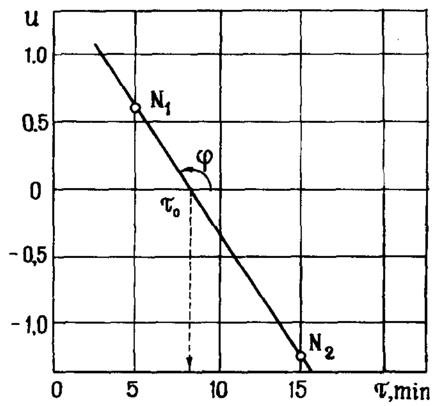

FIG. 2. Graphical determination of p and τ_0 by two points.

in equation (9) by $w_1 = 49$, $w_2 = 2.5$, we will obtain erf $(u_1) = 0.6$, erf $(u_2) = -0.95$, whence $u_1 = 0.595$, $u_2 = -1.386$. Equations (11) and (12) will yield

$$\frac{1}{p} = -5.048, p = 0.198; \quad \tau_0 = 8.004.$$

By using the coordinates of the same two experimental points, we will obtain two points $N_1(5; +0.595)$ and $N_2(15; -1.386)$ in the system of coordinates $\tau 0 u$ (Fig. 2). The equation of the line N_1N_2, reduced to the form $u = p(\tau - \tau_0)$, will have the form

$$u = -0.198(\tau - 8.008).$$

Consequently, $p = -0.198$ and $\tau_0 = 8.008$. The time interval during which the drying rate is approximately constant is $4.4 < \tau < 11.6$ min.

Example 2

The characteristic feature of this example is that the drying curve of wheat grain, plotted from the experimental data of ref. [9], has no distinct heating segment and graphically begins with a linear period of the constant drying rate (drying in a shaft grain dryer, the temperature of the drying agent 130°).

We construct the drying curve from the experimental data and determine visually that $w_e = 15.5$. To the portion of constant drying rate there corresponds the time interval $0 < \tau < 21$ and the moisture content range $28 > w > 19$, the middle values of which are taken to be the coordinates of the inflexion point: $\tau_0 = 10.5$; $w_0 = 23.5$. Since the difference $w_0 - w_e = 8$, $w_a = w_0 + 8 = 31.5$ is the upper asymptote. For further calculations, we have $A = -8$, $B = 31.5$. From the coordinates of the first four experimental points we find that $p = -0.05$. An approximate equation of the drying curve will be

$$\tilde{w}^d = -8(1 + \text{erf}(0.05(\tau - 10.5))) + 31.5.$$

The non-adequacy variance is $\sigma^2 = 0.028$ ($\sigma = 0.17\%$). The estimation of the parameters p and τ_0 by the coordinates of two points (7; 0.168), (21; −0.549) in the system of coordinates $\tau 0 u$ leads to the result $p = -0.051$, $\tau_0 = 10.28$.

Comparison of the parameters calculated by the different techniques shows that they differ insignificantly in each example.

Table 2. Change of moisture content of wheat grain in industrial drying

τ (min)	w^d (%)	$\tilde{w}^d$ (%)
0	28	27.8
7	25	25.1
14	22	21.9
21	19	19.2
28	17.2	17.2
35	16	16.2

CONCLUSION

Several general comments will now be appropriate.

(1) When the drying curve differs from the plot of the function erfc (τ) by the inflexion point (drying of nutrient yeast, vegetables, apple purée, cream, etc.) being considerably shifted from the middle of the curve and when it has positive or negative asymmetry, which is indicated by a convex or concave shape of the line plotted by several points according to equation (8), it is possible to use Captain's distribution [10]. In some cases, replacing the variable τ by an appropriate function $g(\tau)$ (for example, log τ, $\sqrt{\tau}$, etc.), it is possible to eliminate the asymmetry and to obtain a curve which would be close to the normal one and then to use the proposed procedure for selecting the drying curve equation.

(2) In the majority of cases, the proposed technique for obtaining simple relations to describe the drying kinetics gives quite satisfactory results when the drying curves are processed. It can be also used successfully for describing many other processes the plots of which have the form of S-shaped curves. The increasing S-shaped curves are described by functions of the form $y = A\,\text{erf}(p(\tau - \tau_0)) + B$, which, just like function (3), is a general solution of differential equation (2).

(3) Equation (8) and its analogues were used by the present authors when studying sorption and desorption [11], decrease in concentration of culture substrate and growth of biomass in microbiological apparatus [12], variation of temperature in the central portion of bread items in baking [13], etc. This equation can also be applied to the study of many other phenomena and processes—for example, adhesion, processes of growth and intensity of breaking in biology [14], thermal and biochemical inactivation in microbiology [15], crystallization and diffusion [16], some phenomena of chemical kinetics [17] and immunology [18]. The great diversity of processes that can be described by equation (2) is attributed to the fact

that these processes are represented by the diffusion equation

$$\frac{\partial U}{\partial \tau} = \operatorname{div}(D \operatorname{grad} U).$$

Equation (2) results from the diffusion equation, the use of a number of specifying assumptions and the introduction of generalized variables. The explanation for the wide applicability of this equation can be found in ref. [19], which summarizes the postulates of generality in the theories of the growth of biological, crystalline, plasma and other structures with preservation of similarity. These structures are characterized by self-sustained growth or decay, occurring spontaneously without the participation of external forces and when certain conditions prevail in the surrounding medium.

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EQUATIONS DES COURBES DE SECHAGE

Résumé—On suggère une nouvelle méthode pour obtenir, à partir de données expérimentales, une équation approchée de la courbe de séchage en forme de fonction d'erreur qui satisfait une équation différentielle du second ordre associée à une équation de diffusion. Des exemples de calcul sont donnés qui partent de données sur le séchage de grains de polyéthylène à basse pression.

GLEICHUNGEN FÜR DEN TROCKNUNGSVERLAUF

Zusammenfassung—Zur Ermittlung einer Näherungsgleichung für den Trocknungsverlauf feuchter Stoffe aus Meßdaten wird ein neues Verfahren vorgestellt. Die ermittelten Fehlerfunktionsgleichungen befriedigen eine gewöhnliche Differentialgleichung 2. Ordnung mit angepaßtem Diffusionsterm. Berechnungsbeispiele zeigen, wie aus den Meßdaten für das Trocknungsverhalten von Getreidekörnern oder Niederdruck-Polyethylen die Gleichungen ermittelt werden können.

УРАВНЕНИЯ КРИВЫХ СУШКИ

Аннотация—В статье предложен новый метод получения на основе экспериментальных данных приближенного уравнения кривой сушки в виде функции, удовлетворяющей обыкновенному дифференциальному уравнению второго порядка, связанному с уравнением диффузии. Приводятся примеры расчетов, выполненных на основе данных о сушке зерна и полиэтилена низкого давления.