

Modeling Cereal Grain Drying with Variable Diffusivity

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ABSTRACT

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The thin-layer drying of rough rice, maize and sorghum at several temperatures was investigated. Simulation of the experimental data was performed by solving numerically the diffusion equation with variable diffusion coefficient for spherical-shaped grain. To account for this variation, an analytical expression for the dependence of the diffusion

coefficient with moisture content was obtained based on considerations of the energy needed to dissociate water molecules from their sites and of resistance to diffusion. When the expression for diffusivity was used for predicting drying behavior of the grains, a good agreement was obtained between experimental data and the theoretical prediction.

The thin-layer drying of grains has received different treatments in literature. Many authors have accepted that moisture diffusion controls the drying of grain, at least at moderate kernel temperatures (Becker and Sallans 1955, Thompson et al 1968, Handy and Barrer 1969, Whitaker et al 1969). Assuming that the seed is a spherical body with uniform diffusivity, various investigators found that the analytical solution to the diffusion equation reproduce the general form of the experimental drying curves of various cereal grains (Bakker-Arkema and Hall 1965, Suárez et al 1980, Steffe and Singh 1980, Tolaba and Suárez 1988, Ece and Cihan 1993). While excellent fits of experimental data have been obtained using the diffusion equation, it is unlikely that the assumptions made in solving the diffusion equation are valid. Most researchers agree that the diffusivity is moisture-dependent. Chu and Hustrulid (1968) postulated a model with concentration-dependent diffusivity, where solution by numerical means is normally necessary. A similar approach was used by Aguerre et al (1985) and Dutta et al (1988) to model drying kinetics of some cereal grains.

Until now, it seems that no theoretical form of the dependence of the diffusion coefficient on moisture content has been presented for seeds. This is not surprising given the differences in experimentally determined diffusion coefficients reported by many investigators (differences in magnitude as well as functional form) for some starchy materials. Thus, Fish (1958) found that the water diffusivity in potato starch gels increases as the moisture content increases, reaching a maximum at moisture level of 0.3 kg water/kg of dry solid. On the other hand, Saravacos and Raouzeos (1984) determined that for corn starch gels, water diffusivity reached a maximum value at moisture content of ≈12–15% (dry basis) and decreases significantly at lower and higher moisture. A similar variation of the water diffusivity was observed by Leslie et al (1991) in several starch-based systems with differing amylase to amylopectin ratios.

It is inferred from the foregoing review that although the diffusivity varies with moisture during the drying process of grains, very few studies have been conducted to support this point of view. Therefore, there is a need to investigate on this aspect and to establish an approach that can be used for predicting the drying behavior of grains under determined working conditions.

Based on thermodynamics approach, an attempt is made here to formulate a mathematical expression for the diffusion coefficient

variation with moisture content. The resulting expression was used to describe the isothermal drying of various cereal grains.

Formulation of the Model

The diffusion equation representing the isothermal drying process can be expressed in spherical coordinates as:

$$\frac{\partial m}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D(m) \frac{\partial m}{\partial r} \right] \quad (1)$$

Note that the temperature gradients have negligible effect on the moisture movement in drying of most cereal grains (Fortes et al 1981, Parti 1993). Equation 1 is subjected to the following initial and boundary conditions:

$$\begin{aligned} m &= m_0 & \text{at } t = 0 \text{ and } 0 \leq r \leq R \\ m &= m_e & \text{at } t > 0 \text{ and } r = R \\ \partial m / \partial t &= 0 & \text{at } t > 0 \text{ and } r = 0 \end{aligned}$$

It has been assumed that at $r = R$, the surface resistance to vapor diffusion is negligible and, therefore, the moisture concentration on the grain surface falls to the equilibrium value immediately at the start of the falling rate period of drying. Introducing the following dimensionless variables:

$$m^* = \frac{m - m_e}{m_0 - m_e}; \quad r^* = \frac{r}{R_0}; \quad D^* = \frac{D(m)}{D_0}; \quad \text{and } Fo = \frac{D_0 t}{R_0^2}$$

Equation 1 can be transformed as follows:

$$\frac{\partial m^*}{\partial Fo} = \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^{*2} D^* \frac{\partial m^*}{\partial r^*} \right) \quad (2)$$

The initial and the boundary conditions are:

$$m^* = 1 \quad \text{at } Fo = 0 \text{ and } 0 \leq r^* \leq 1 \quad (2a)$$

$$m^* = 0 \quad \text{at } Fo > 0 \text{ and } r^* = 1 \quad (2b)$$

$$(\partial m^* / \partial r^*) = 0 \quad \text{at } Fo > 0 \text{ and } r^* = 0 \quad (2c)$$

It must be noticed that $D^* = D(m)/D_0$ varies during the drying process. To estimate this variation, we will make use of the diffusion model for adsorbing solids formulated by Nelson (1986). From that model, the energy required for sorbed water molecules to become dissociated from their sites is calculated on the basis of equilibrium among the sorbed, dissociated and vapor phases of water in the adsorbed solid. Nelson (1986) assumed at first stage a passage of sorbed water to liquid water, requiring an energy equivalent to isosteric heat, Q_{sr} . In a second step, liquid water becomes dissociated and surface diffusion takes place. Molecules of dissociated water can move from one adsorption site to another due to E_D , the necessary energy to separate water molecules from their sites. Finally, water molecules change to activated state and are capable to overcome barriers due to intermolecular frictional

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forces; the energy of the activated state is indicated here as E_A . If E is the energy of water molecules in the sorbed, dissociated, and fully activated states, we can write for $D(m)$ the following expression (Nelson 1986):

$$D(m) = D_1 \exp(-E/RT) = D_1 \exp[-(Q_{st} + E_D + E_A)/RT] \quad (3)$$

where D_1 is a parameter of the model to be determined from experimental data. Methodology to estimate Q_{st} , E_D , and E_A , is given later.

MATERIALS AND METHODS

Literature values of hygroscopic equilibrium data corresponding to the desorption branch of sorption isotherm were used: rough rice at 40, 50, and 60°C (Zuritz et al 1979); sorghum at 30, 38, and 50°C (Falabella et al 1989); and maize at 40, 50, and 70°C (Tolaba and Suárez 1988).

Selected drying kinetics curves of rice, sorghum and maize were also taken from the literature: rough rice at 30, 50, and 60°C (Aguerre 1984); sorghum at 30, 38, and 50°C (Suárez et al 1980); and maize at 40, 50, and 70°C (Tolaba and Suárez 1988).

Calculation of Isosteric Heat

The commonly used method to calculate the isosteric heat is based on the Clausius-Clapeyron equation:

$$\left[\frac{\partial \ln a_w}{\partial (1/T)} \right]_m = -\frac{Q_{st}}{R} \quad (4)$$

The left term of Eq. 4 was estimated numerically, approximating the derivative by a finite difference. For this purpose the equilibrium data of the materials investigated were modeled by means of the GAB equation. The variation of isosteric heat with moisture content was fitted by means of an empirical equation:

$$Q_{st} = Q_0 e^{-am} \quad (5)$$

where Q_0 and a are constants. For each cereal grain these constants were calculated using a nonlinear regression procedure and the resulting values are given in Table I.

An alternative equation to calculate Q_{st} and its variation with moisture content was used. The equation was derived by Aguerre et al (1986) based on the experimental verification of the differential entropy of adsorption as a linear function of the differential enthalpy of adsorption (thermodynamic compensation effect) for water sorption by biological materials:

$$Q_{st} = RK_1 K_2^{m/m_0} \quad (6)$$

The parameters K_1 and K_2 are empirical constants to be determined, while m_0 is an arbitrary moisture value which was as-

TABLE I

Parameter Values of Equations 5 and 6 for Various Cereal Grains					
Grain	Q_0 (kJ/mol)	a	K_1 (K)	K_2 (K)	m_0 db
Rice	140.212	19.802	12,920	0.2751	0.0712
Maize	104.743	21.600	19,462	0.2740	0.0586
Sorghum	142.685	12.764	19,000	0.2560	0.0809

TABLE II

Parameter Values of Equation 11 for Various Cereal Grains			
Grain	T (°C)	n	$D_1 \times 10^6$ (m ² /s)
Rice	40	0.696	3.80
	50	0.754	1.45
	60	0.804	1.70
Maize	40	0.596	1.70
	50	0.688	2.28
	70	0.782	1.90
Sorghum	30	0.650	2.15
	38	0.616	5.00
	50	0.612	8.20

sumed equal to monolayer moisture defined in BET. theory. For each cereal grain, the calculated values of Q_{st} versus m were fitted to Eq. 6, and the constants K_1 and K_2 were determined by regression analysis. The corresponding values of K_1 , K_2 , and m_0 are also given in Table I.

RESULTS AND DISCUSSION

Estimation of E_D and E_A

From thermodynamics consideration, Nelson (1986) obtained an expression for the enthalpy change from the vapor state to the dissociated state, $H_V - H_D$, which is:

$$H_V - H_D = \lambda - RT/n \quad (7)$$

where RT/n is the work done by a mole of water in expanding from the activated state to the vapor state. The parameter n can be obtained from spreading pressure–water activity relationship, and their values were recently reported by Tolaba et al (1995) for the three grains under consideration. The enthalpy change from the vapor state to the sorbed state, $H_V - H_S$, is known to be:

$$H_V - H_S = Q_{st} + \lambda \quad (8)$$

Subtracting Eq. 7 from Eq. 8 results in:

$$H_D - H_S = Q_{st} + RT/n \quad (9)$$

From this expression, the energy required to change from the liquid state to the dissociated state (E_D) is:

$$E_D = RT/n \quad (10)$$

The values of n for the products and temperatures investigated are given in Table II.

Finally, the energy associated to the activate state (E_A) was considered equivalent to the activation energy for self-diffusion of liquid water. This assumption seems to be valid for the diffusion of small size water molecules through biopolymers, as indicated by Mark (1942). For self-diffusion of liquid water $E_A = 22.175$ kJ/mol.

From the previous considerations it results for $D(m)$ the following expression:

$$D(m) = D_1 \exp \left[- \left(Q_{st} + \frac{RT}{n} + 22.175 \right) / RT \right] \quad (11)$$

From this equation, all quantities except Q_{st} are constants when T is constant and Q_{st} accounts for the dependence of D on moisture content. It also results from Eq. 11 that the activation energy is:

$$E(\text{kJ/mol}) = Q_{st} + RT/n + 22.175 \quad (12)$$

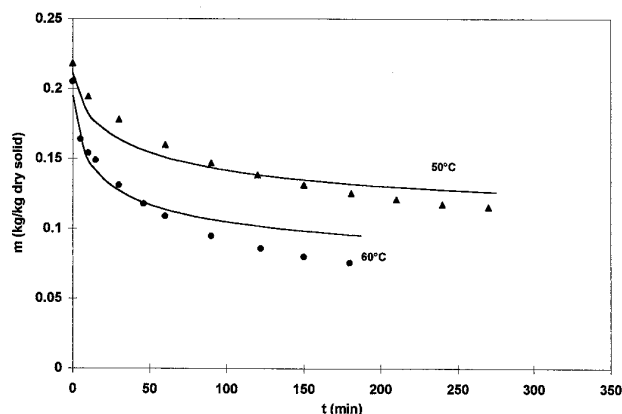


Fig. 1. Comparison of experimental (symbols) and predicted (line) drying curves for rough rice. Dependence of isosteric heat on moisture was calculated by Eq. 5.

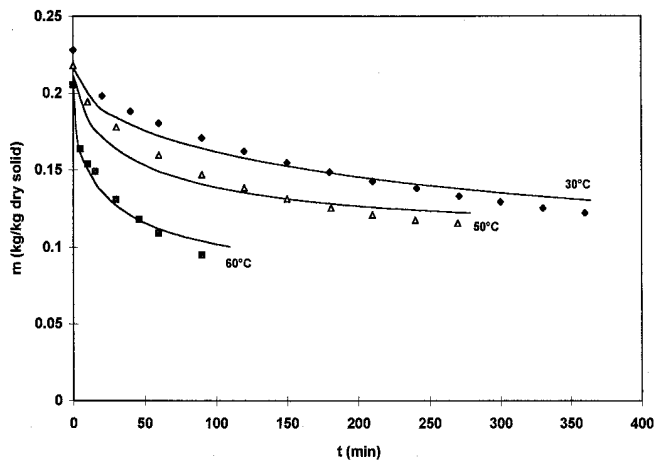


Fig. 2. Comparison of experimental (symbols) and predicted (line) drying curves for rough rice. Dependence of isosteric heat on moisture was calculated by Eq. 6.

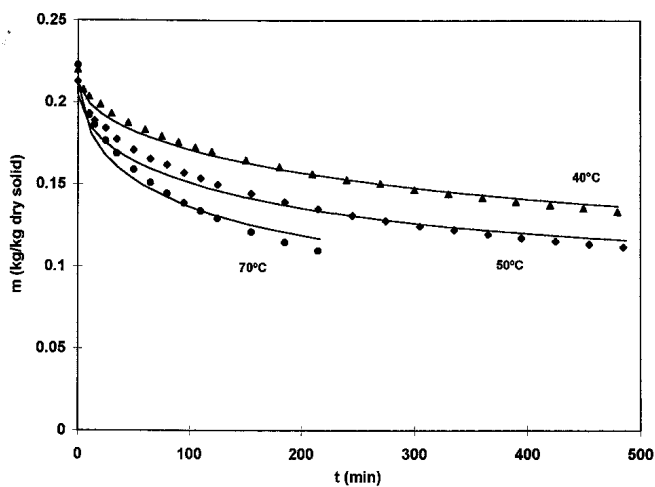


Fig. 3. Comparison of experimental (symbols) and predicted (line) drying curves for maize. Dependence of isosteric heat on moisture was calculated by Eq. 6.

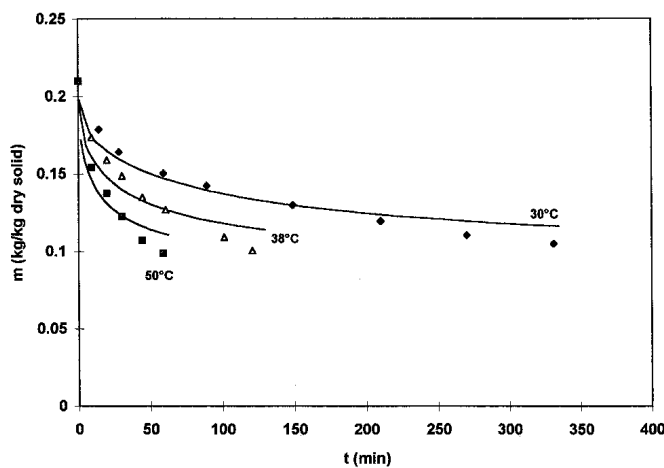


Fig. 4. Comparison of experimental (symbols) and predicted (line) drying curves for sorghum. Dependence of isosteric heat on moisture was calculated by Eq. 6.

Comparison of Model Predictions and Experimental Data

Equation 2, boundary conditions (Eq. 2a-c) and Eq. 11 were integrated numerically using a Crank-Nicholson implicit finite-difference method. As the parameter D_1 in Eq. 11 is unknown, this

must be determined for each drying condition. This was done by trial and error, comparing predicted and experimental drying curves.

For rice, drying kinetic curves were calculated with the two mathematical expressions given by Eq. 5 and 6 to estimate the isosteric heat variation with moisture content. The results of the simulation are shown in Figs. 1 and 2, plotted using the mean moisture content of the grain and drying time. A better agreement between experimental and predicted drying curves can be observed when Eq. 6 is used to estimate the variation of Q_{st} with moisture content. The comparison between experimental and predicted drying curves for maize and sorghum are shown in Figs. 3 and 4, respectively. It must be mentioned that those predicted drying curves were obtained using Eq. 6 for the estimation of Q_{st} . The corresponding values of D_1 are given in Table II. For the convenience of the reader, the values of the parameter n calculated by Tolaba et al (1995) are also reported in Table II for the drying temperature and material investigated.

To evaluate moisture dependence of the diffusion coefficients, moisture profiles predicted by the model were used to calculate mean diffusion coefficients (\bar{D}^*) as follows:

$$\bar{D}^* = \frac{\int_0^1 D^*(m)mr^{*2} dr^*}{\int_0^1 mr^{*2} dr^*} \quad (13)$$

This equation was used to evaluate integral diffusion coefficients for maize and its variation with the mean moisture content of the grain (Fig. 5). It is clearly noted that the diffusion coefficients corresponding to the different drying temperatures decrease as the mean moisture content of the grain decreases. This is due to an increase of the energy requirements as drying progresses because at low moisture contents water molecules are tightly bound to the adsorbed sites. For the purposes of comparison, the values of diffusion coefficients reported by Tolaba (1989) and calculated from the analytical solution of Fick's second law for constant moisture diffusivity were also plotted in Fig. 5, as shown by the dotted lines.

A similar variation of the diffusion coefficient with moisture to that obtained here, was reported by Fish (1958) during water desorption in starch gels. According to that author, the diffusion coefficient begin to fall when the moisture content of the gel is <30% (db). For higher moisture contents, the diffusion coefficient remained constant, probably due to the fact that the interaction between water and starch ceases to affect the diffusion process. For saturated gel >30% moisture content, Fish (1958) found that the activation energy for diffusion was similar to self-diffusion of liquid water. This agreed with results found here as derived from Eq. 12. As at high moisture content Q_{st} tends to 0, the activation energy of the diffusion process becomes practically equal to the self-diffusion of liquid water. It must be noticed that the term RT/n is relatively small (for the drying conditions used in this work values were ≈ 3.2 kJ/mol).

On the other hand, Leslie et al (1991) reported a relatively more complex dependence of the diffusion coefficient with moisture content during the water desorption in corn starches. As moisture was removed, the effective diffusivity increases gradually to reach a maximum at a water content of $\approx 10-15\%$. After the maximum was reached, the effective diffusivity fell sharply as the water content decreased. According to Leslie et al (1991), such complex dependence is the result of two effects, the increase of porosity as well as the physicochemical interactions water-substrate, as drying proceeds.

Variations of the activation energy (E) with moisture content calculated from Eq. 12 are represented in Fig. 6. In all cases, the activation energy approaches to the activation energy of self-diffusion and increases considerably as the moisture content tends to 0. This is so because the energy $E_D = H_D - H_S$ needed by sorbed molecules to achieve the dissociate state increases with the reduction of moisture.

LITERATURE CITED

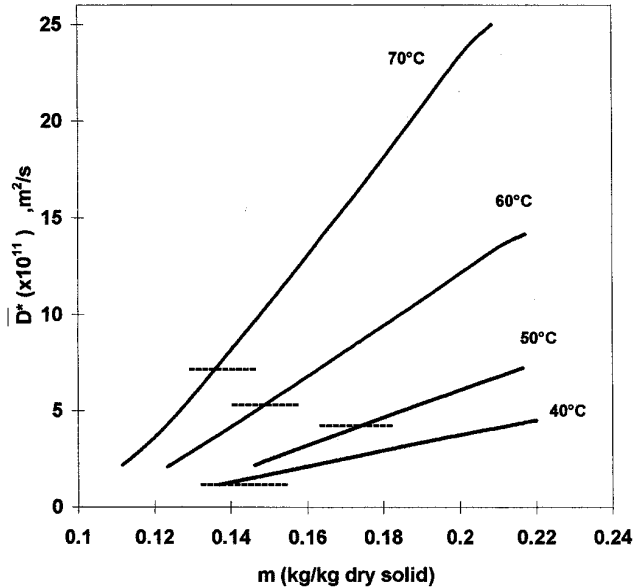


Fig. 5. Integral diffusion of coefficient \bar{D}^* as a function of mean moisture content for maize at different temperatures. Comparison with literature data indicated by dotted line (Tolaba and Suárez 1988).

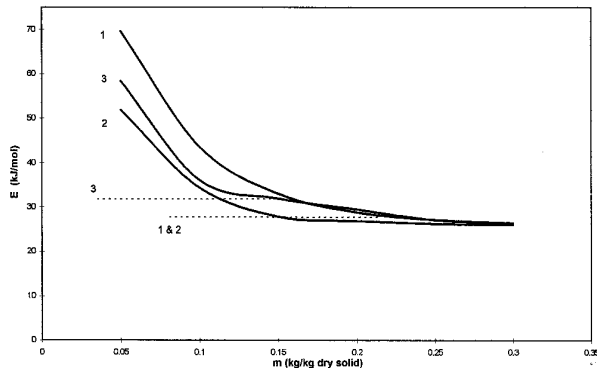


Fig. 6. Activation energy as a function of moisture content for rice (1), corn (2), and sorghum (3). Dotted line indicates comparison with literature data: 1 (Steffe and Singh 1980), 2 (Tolaba 1989), and 3 (Suárez et al 1980).

In Fig. 6 are shown the variations of E with moisture content for rice, sorghum, and maize (the temperature adopted for that calculation was 40°C). In the same figure, dotted lines also represent the corresponding activation energies reported in the literature for the mentioned materials. It is interesting to point out that the literature values indicated in Fig. 6 were obtained from Fick's second law assuming constant moisture diffusivity.

CONCLUSIONS

Considering the energy required to free water molecules from sorption sites in a solid adsorbent, an analytical expression was derived for moisture content dependence into moisture diffusivity. The resulting expression together with the Fick's second law were integrated numerically to simulate drying behavior of some cereal grains.

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