Brazilian Journal
of Chemical
Engineering

ISSN 0104-6632
Printed in Brazil
www.abeq.org.br/bjche

Vol. 22, No. 02, pp. 303 - 309, April - June, 2005

THE DRYING OF AMARANTH GRAIN: MATHEMATICAL MODELING AND SIMULATION

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(Received: October 20, 2004 ; Accepted: March 4, 2005)

Abstract - A model for isothermal diffusion of bound water was used to simulate the thin-layer drying kinetics of amaranth grain. The model assumes that the driving force for the transport of bound water is the gradient of spreading pressure. The gradient of spreading pressure was related to the moisture gradient using the GAB isotherm. This variation shows a relative maximum moisture content about 8% (d.b), after which the diffusion coefficient falls sharply as the moisture content is further reduced. To verify the model, drying tests of amaranth grain were conducted at 40 to 70ºC in a laboratory drier from 32.5 to 6% moisture (d.b.). Equilibrium moisture contents were also determined using an electronic hygrometer at temperatures and relative humidities corresponding to drying conditions. The applicability of the model to simulation of drying curves was satisfactory in the full range of moisture.

Keywords: Amaranth grain; Moisture diffusivity; Thin layer drying; Variable diffusivity.

INTRODUCTION

In the literature it is possible to find many mathematical models for describing the drying process. Isothermal models based on Fick's law for moisture diffusion were used to simulate the drying kinetics of cereal grains and starchy materials (Steffe & Singh, 1980; Walton et al., 1988; Tolaba et al., 1990; Leslie et al., 1991).

It is generally accepted that moisture diffusion controls the drying of moist solids and Fick's law has been used to describe changes moisture concentration, simulating drying curves with moderate success. Some researchers have observed unexpected behavior for experimentally determined diffusion coefficients, not only in magnitude but also in functional form. Fish (1958) reported increasing moisture diffusivities in potato starch gels with an increase in moisture, reaching a maximum at moisture levels of about 0.3 kg water/kg of dry solid. Similarly, Saravacos and Raouzeos (1984) found that for corn starch gels, water diffusivity reached a maximum value at a moisture of about 15%, dry basis, decreasing significantly at lower and higher moistures.

Becker and Sallans (1957) postulated two mechanisms of moisture migration during the dehydration of wheat kernels. For moisture levels above 14% (dry basis) water migrates through the porous structure of wheat kernels as a viscous flow with the pressure gradient as the driving force for diffusion. As moisture decreases, water does not totally fill the pores but forms a film that coats the internal surfaces.

In addition to moisture concentration gradient and vapor pressure gradient, other gradients such as

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*To whom correspondence should be addressed spreading pressure gradient, have been postulated as to be the driving force of the drying process (Babbitt, 1950). The choice of driving force is of importance from a physical point of view because the careful consideration of the physical aspects may contribute to development of more accurate relationships between diffusion coefficient and moisture content.

The aim of the present study is to apply a model for isothermal amaranth grain drying based on Babbitt's (1950) analysis and verify it experimentally.

MATHEMATICAL MODEL

Assuming that the driving force for the diffusion of bound water is the spreading pressure, π, for isothermal conditions, it can be related to the surface free energy by the following expression (Smith et al., 1997):

$$d\pi = \sigma RT\, d\left(\ln a_w\right) \tag{1}$$

where σ is the surface concentration of water, R the gas constant, T the absolute temperature and a_w the water activity.

Water surface concentration and moisture content are related by

$$\sigma = m/M\gamma \tag{2}$$

where m is the moisture content, M the molecular weight of water and γ the specific surface area of the solid. Substituting equation (2) into equation (1) and integrating results in

$$\pi = \frac{RT}{M\gamma}\int_0^{a_w} m\, d\left(\ln a_w\right) \tag{3}$$

The mass flow rate of water due to the spreading pressure is defined as (Babbitt, 1950)

$$J = -\eta \rho m \frac{d\pi}{dr} \tag{4}$$

where η is a resistance coefficient, ρ the solid density, m the moisture content and $d\pi/dr$ the spreading pressure gradient.

Differentiating equation (3) and replacing the result in equation (4) gives

$$J = -\eta p \frac{RT}{M\gamma}\frac{m^2}{a_w}\frac{da_w}{dm}\frac{dm}{dr} \tag{5}$$

The differential continuity equation for the migration of water in a porous solid of spherical shape is

$$\frac{\partial \rho_A}{\partial t} + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 J\right) = 0 \tag{6}$$

where ρ_A is the concentration of water per unit volume of solid. If the expression of J given by equation (5) is substituted into equation (6), taking into account that $\rho_A = m\rho$, the following equation results

$$\frac{\partial m}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left\{r^2 D\left(m\right)\frac{\partial m}{\partial r}\right\} \tag{7}$$

where D(m) represents the dependence of the diffusion coefficient on moisture, given by the expression

$$D\left(m\right) = \frac{\eta R\, T}{M\gamma}\frac{m^2}{a_w}\frac{da_w}{dm} \tag{8}$$

From this equation, the diffusion coefficient can be obtained by evaluating a_w and da_w/dm from the GAB isotherm equation. The three-parameter GAB model can be written as (Schär & Ruëgg, 1985):

$$\frac{m}{m_m} = \frac{C k a_w}{\left(1 - k a_w\right)\left(1 - k a_w + C k a_w\right)} \tag{9}$$

where m_m is the monolayer moisture content and C and k are the GAB parameters. Operating with equation (9) and substituting the results into equation (8), the following expression results

$$D\left(m\right) = \frac{\eta R T}{M\gamma}\left(\frac{C m_m k a_w}{1 + \left(C - 1\right)k^2 a_w{}^2}\right) \tag{10}$$

To solve equation (7) and equation (10) the following initial and boundary conditions are assumed:

$$m = m_0 \quad \text{at} \quad t=0 \quad \text{and} \quad 0 \le r \le r_0 \tag{11a}$$

$$m = m_e \quad \text{at} \quad t>0 \quad \text{and} \quad r=r_0 \tag{11b}$$

$$\frac{\partial m}{\partial r} = 0 \quad \text{at} \quad t>0 \quad \text{and} \quad r=0 \tag{11c}$$

where m_0 and m_e are the initial and surface moisture contents. Equations (7) and (10) together with the initial and boundary conditions (11a,b,c) were solved numerically in order to simulate the drying behavior of cereal grains.

MATERIALS AND METHODS

Amaranth grain (Amaranthus cruentus) was provided by the Facultad de Agronomía, Universidad Nacional de La Pampa, Argentina. Prior to drying, the grains were screened to assess the average diameter. The weighed average diameter was calculated from $d = \left(\sum d_i\, w_i\right)/w$ where d_i is the average screen opening, w_i is the weight between the (i -1)th and the ith sieves starting from the smallest number and w is the total sample weight $\left(\sum w_i\right)$. The average diameter for amaranth grain was 0.90 mm.

DRYING EXPERIMENTS

The drying equipment consists of a centrifugal fan blowing air over six 2 kW electric bar elements into the base of a chamber and then upwards through a vertical duct. The vertical duct has a flow-homogenizing section containing a bed of glass spheres to assure a uniform velocity and temperature profile for the air entering the drying chamber. A plastic cup (diameter 85mm, height 25 mm) with a mesh base and lid served as the drying chamber and was placed at the outlet of the duct. All temperatures were measured using copper-costantan thermocouples. The inlet air dry bulb temperature was controlled to within ±0.2°C by an electronic proportional controller. Wet and dry bulb temperature measurements were made to determine the relative humidity of the drying air. Drying temperatures studied were 40, 50, 60 and 70°C. A thin layer of amaranth grains, weighing about 20g, was used for each drying experiment, the progress of which was followed by weighing the sample periodically on a precision balance (±0.1 mg). For this purpose, the drying cup was removed, rapidly weighed and placed back in the drier at specific time intervals. An air velocity of 3 m s^{-1} was used in all experiments. Drying experiments were conducted in a moisture range of approximately 32.5 to 6.0%, dry basis. Moisture content of the grains was determined by placing samples of about 2g in a vacuum oven at 130°C for 1 hour (AOAC METHODS 943.01, 1995).

EQUILIBRIUM MOISTURE CONTENTS

The equilibrium moisture contents of amaranth grain corresponding to the desorption branch of sorption isotherms at temperatures between 40 and 60ºC were taken from the literature (Pollio et al., 1998). The desorption isotherm at 70ºC, covering a water activity range between 0.10 and 0.90, was measured with a Novasina Thermoconstanter Humidat TH2 meter, following the procedure described by Falabella et al., (1992). The water activity measurements below 0.11 were found by placing the samples in a vacuum desiccator with a saturated solution of NaOH.

RESULTS AND DISCUSSION

Estimation of Diffusion Coefficient

The main difficulty in evaluating the variation in the diffusion coefficient with moisture applying equation (10) is to estimate the resistance coefficient, η. Becker and Sallans (1957) used a single value of $\eta = 1.67\text{x}\ 10^{-12} m^2\ s\ kg^{-1}$ to simulate the drying of wheat kernels at various temperatures. In this study the analytical expression derived by Skaar and Babiak (1982) was used:

$$\eta = \frac{\delta}{u_w} \exp\left[-\frac{E_D - E_W}{R\,T}\right] \tag{12}$$

where μ_w is the water viscosity of adsorbed water, δ is the mean spacing between water adsorbed molecules and E_D is the activation energy for the variation in the diffusion coefficient with temperature and E_W that corresponding to the variation in water viscosity with temperature. The problem is now reduces to evaluating the parameters of equation (12). For δ the value $3.0\text{x}10^{-10}$m, which corresponds to the thickness of a monomolecular layer of water, was used (Aguerreet al., 1989). The viscosity μ_w was assumed to be equal to the viscosity of liquid water. Based on the Arrhenius equation, E_W obtained from the rate of change in μ_w with T is 16.7 kJ mol^{-1}. The activation energy E_D for the diffusion of adsorbed water was calculated from the following relationship (Aguerre et al, 1989):

$$E_D = 0.5E_H \; E_D = 0.5\,E_H \qquad (13)$$

Where E_H is the energy of desorption of the monolayer. This magnitude was calculated within the framework of the BET theory, following the procedure described by Aguerre et al. (1984). Behavior of the theoretically predicted diffusion coefficient at low moisture contents, obtained from equation (10), is illustrated in Figure 1 for amaranth at two temperatures.

The C, k and m_m constants of the GAB equation were calculated from the experimental isotherms, using a nonlinear analysis to fit equation (9) to the corresponding equilibrium data of the starches tested. These are given in Table 1 together with the resistance coefficients calculated from equation (12).

Table 1: Amaranth grain parameter values for equation (10) at different temperatures.

Temperature (°C)	m_m(dry basis)	C	k	h ($m^2\,s\,kg^{-1}$)
40	0.0631	11.34	0.82	1.29×10^{-9}
50	0.0580	9.89	0.80	1.36×10^{-9}
60	0.0553	8.35	0.78	1.49×10^{-9}
70	0.0492	6.81	0.75	1.78×10^{-9}

The curves show a relative maximum in moisture content dependence of the diffusion coefficient at a moisture value of about 0.08 kg water/kg dry solid. It can be seen that the maximum of the curves shifted slightly to lower moisture contents as temperature was increased. After the maximum was passed the diffusion coefficient fell sharply as the moisture content of the samples was further reduced. Few studies have been done on the variation inof diffusion coefficients with moisture concentration in the range of low moisture contents.

The experimental data from Fish (1958) show that the maximum of the diffusion coefficient in starch gels occurs at moisture contents of about 0.30 kg water/kg dry solid and decreases for lower moisture levels. Leslie et al. (1991) had found a maximum value for the diffusion moisture coefficient at contents 0.10 – 0.15 kg water/kg dry solid during water desorption of various corn starches. For moisture contents lower and higher than the maximum they observed that the diffusion coefficient decreases monotonically. The Maximum values for D reported by Leslie et al. (1991) for native corn starch varied from 6.5 to 9.8×10^{-10} m^2 s^{-1} for a temperature range of 7 to 60ºC; the values predicted by the present model are almost one order of magnitude smaller than the values given above, as can be seen in Figure 1.

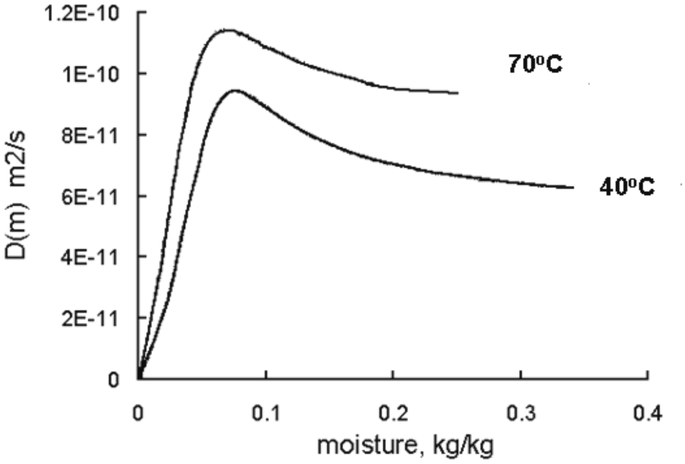

Figure 1: Diffusion coefficient variation for amaranth grain with moisture at 40 and 70°C

DRYING SIMULATION

To predict the drying behavior of amaranth grains, equation (7), equation (9) and equation (10) together with the boundary and initial conditions given by equations (11,a,b,c) were numerically solved. The GAB equation parameters were calculated from the corresponding equilibrium data. The respective values are given in Table 1 together with the resistance coefficients calculated from equation (12). The surface moisture content, m_e, was calculated from the corresponding desorption isotherms under the drying conditions.

The comparison between predicted drying curves and the experimental ones are shown in Figure 2. It can be observed that for moisture contents less than that corresponding to the maximum of the diffusion coefficient (about 0.08 kg water/kg dry solid) the fall in D is sharp, while for the higher ones the diffusion coefficient seems to approach a constant value. Becker and Sallans (1957) have also reported a relatively complex dependence of the diffusion coefficient on moisture content during the drying of wheat kernels. They observed that as moisture was removed, the diffusion coefficient increased monotonally to reach a nearly constant value in the moisture range of 0.07 to 0.10 kg water/kg dry solid; when the moisture content of the grain was < 0.07 kg water/kg dry solid the diffusion coefficient fell again.

According to the present model the properties of moisture diffusion in amaranth are directly related to moisture desorption isotherms. As can be seen from equation (8) the values of D(m) depend on the m/a_w ratio and on da_w/dm, the so-called isotherm factor (Viollaz et al., 1978). It is interesting to point out that Becker and Sallans (1957) needed three isotherm equations to describe the entire drying range of wheat grains.

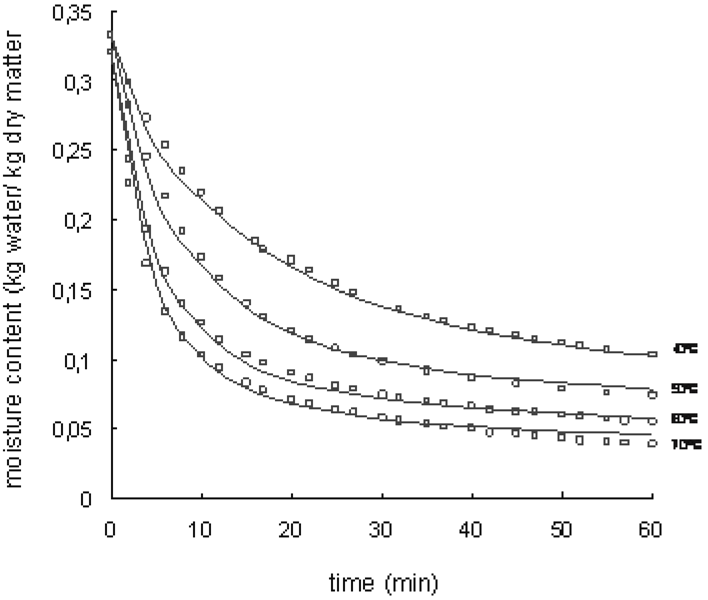

Figure 2: Comparison of experimental (symbols) and predicted (line) drying curves for amaranth grain

CONCLUSIONS

The present study on the drying of amaranth grain reveals the following points:

1) The model for the dependence of diffusivity on moisture and temperature assumes that the driving force for the transport of bound water is the spreading pressure gradient and is related to the moisture gradient driving force through the desorption isotherm.

2) The moisture content of the grain had a pronounced effect on the effective diffusivity. At moisture levels above 30% the interaction between water and polymer chains in the amarath grain did not seem to affect the diffusive process, as the constancy of the effective diffusivity with moisture reveals. As moisture was removed, the diffusion coefficient increased gradually to reach a maximum. After the maximum was reached, the diffusion coefficient fell sharply, as the water content decreased.

3) The match between simulated and experimental drying curves was satisfactory in the full range of moisture.

Given that the diffusion coefficient is related to sorptional characteristics of the product, it would be of interest to know how the shape of the sorption isotherm influences the variation in the diffusion coefficient with moisture. The model can be employed with other crops, provided that the physical properties and equilibrium vapor pressure versus moisture content relationships are known.

NOMENCLATURE

a_w	water activity	dimensionless
C	GAB constant in equation (9)	dimensionless
d	diameter	m
D	diffusion coefficient	m^2/s
E_D	activation energy for water diffusion	J/mol
E_H	energy of water desorption	J/mol
E_W	activation energy for viscosity	J/mol
J	flow rate of water	kg/m^2 s
k	GAB constant in equation (9)	dimensionless
m	moisture content	kg/kg
m_0	initial moisture content	kg/kg
m_e	surface moisture content	kg/kg
m_m	monolayer moisture content	kg/kg
M	molecular weight of water	kg/kmol
r	radius	m
R	universal gas constant	J/K kmol
t	time	s
T	temperature	K
w	weight	kg

Greek Symbols

d	thickness of water monolayer	m
σ	surface concentration of water	kmol/m^2
π	spreading pressure	N/m^1
ρ	solid density	kg/m^3
ρ_A	moisture concentration	kg/m^3
γ	specific surface area of solid	m^2/kg^1
η	resistance coefficient	m^2 s/kg^1
μ_w	water viscosity	Pa s

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