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Experimental investigation and mathematical modeling of the unsteady drying kinetics of durum wheat grains

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Abstract

Dehydration of durum wheat often occurs under conditions where the effects the drying temperature, the water activity and the elasticity of the grains are significant to influence the drying kinetics. We here investigate the unsteady isothermal desorption process of a moisture from durum wheat grains by employing the static gravimetric method conducted at 30°C and 40°C and at controlled relative humidity values of 6.26% and 74.7%. Moreover, to explain our measured data, we have derived a new elastic diffusion model that extends Fick's laws by taking into account the effect of the elasticity of the deformable grains. To consider the grain shrinkage during dehydration, we express the diffusion governing equation into the "grain material" coordinates system. We discuss in more detail the unidirectional radial mass transfer via scaling analysis and numerical solutions followed by a successful comparison between the model predictions and our measured data. A diffusion-elasticity coupling constant ψ_0 emerges naturally in the diffusion equation and its effects on the drying kinetics as well as on the grain radius retraction are examined. We found out that the elasticity enhances mass transport within the investigated grains and thus decreases the drying time.

Keywords: *Elasticity, Durum Wheat, isothermal drying, spherical grains, gravimetric data.*

1. Introduction

Even though the dehydration of agro-food products is a well-known process employed since millennia, it remains nonetheless an active research field of interest not only to food-related industrial sectors but also to applied sciences as well. Indeed, in order to dry out efficiently a moistened product to ensure for instance its proper shelf preservation, it is necessary to optimize several processing key parameters such as the drying time and temperature, the water activity and the physical and mechanical properties of the material structure [1]. This appears to be of particular importance for durum wheat grains due to their strong sensitivity to the abovementioned key parameters. Besides, during the drying process, the grains shrink and thus deform; and as such, the drying kinetics might become strongly influenced both qualitatively and quantitatively. The deswelling-induced deformation and thus the emergence of elasticity are often accompanied by stresses development within the medium, which may lead in some circumstances to crazing or cracking [2-5]. Note that most of the past studies have exclusively investigated the effects of the temperature and water activity on the drying of food products [6-10]. Only a few have examined the effects of the elasticity on the drying of pasta [2-5]. Durum wheat grains and in fact most agro-food products are, from a mechanical point of view, complex structured media; that is, when undergoing mass transport, their molecular internal structure deforms and may hence actively participates to the diffusion process. Consequently, diffusion into such media does not generally obey Fick's laws within some well-defined ranges of characteristic time scales [11]. Note that Fick's first law simply states that the diffusion mass flux is linearly proportional to the gradient of penetrants' concentration while the second law is the continuity equation [12]. The deviations from the Fickean predictions are termed non-Fickean, anomalous or viscoelastic [13-26], and their description requires, a more generalized mathematical model that comprehensively considers the elastic contribution of the medium and it coupling with the molecular process of diffusion. The goal of this contribution is twofold. First, we carry out, using the static gravimetric method several isothermal desorption experiments first at 30°C and 40°C and second for two relative humidity values equal to 6.26% and 74.7%. Second, we derive a model, using Linear Irreversible Thermodynamics (LIT) and Continuum Mechanics (CM) approaches, which explicitly takes into account the elastic deformation of the grains. To consider the grains volume change, we have expressed the modified diffusion equation into the Lagrangean spherical coordinates and have limited the investigation to the linear regime corresponding to small isotropic deformations. Then, we thoroughly investigate the 1D drying process via scaling analysis, numerical solutions and comparison with our measured desorption data. A new parameter, ψ_0, emerging naturally in the derived diffusion equation, expresses the relative importance of the elasticity of the medium to mixing/demixing processes. Moreover, we have also examined the dynamics of the boundaries by introducing a time evolution equation for the moisture content at the surface of the grain. Throughout this investigation, we have examined the influence of the temperature, relative humidity and the grain elasticity on the drying kinetics. Moreover, the model has the advantage of being easily solved numerically.

2. Model derivation

The system under consideration is a two-component mixture composed of small molecules of moisture and solid grains. When subjected to the unsteady isothermal drying, the grains deform because of the transient deswelling process. The coupling arising between the deformation of the grains and the diffusion process of the moisture influences, in some ranges of characteristic time scales, the behavior of mass transport that deviates from the classical Fickean predictions. A more extended model is required to predict these deviations. Our starting point is the well-known two-fluid approach [27], where each component of the binary mixture is described by its own set of the independent state variables. Thus, the mass conservation equations for the two components are given by

$$\frac{\partial \rho_g}{\partial t} = -\nabla \cdot \left(\rho_g v_g\right) \tag{1}$$

for the grain, and

$$\frac{\partial \rho_w}{\partial t} = -\nabla \cdot (\rho_w v_w) \tag{2}$$

for water (moisture). The quantities ρ_g and ρ_w stand for the apparent mass densities of a solid grain and water respectively while v_g and v_w refer to their respective velocity vectors. Therefore, we define the relative momentum density vector of the moisture (water) relative to the grain (i.e. diffusion mass flux vector) as

$$J = \rho_w (v_w - v_g) \tag{3}$$

Moreover, by introducing the water content state variable

$$w = \frac{\rho_w}{\rho_g} \tag{4}$$

And using the equations (1) to (3), we easily arrive at the following time evolution equation expressing the water mass conservation into the grain

$$\rho_g \frac{\partial w}{\partial t} = -\nabla \cdot J - \rho_g v_g \cdot \nabla w \tag{5}$$

Now, using the fact that

$$\rho_g = \frac{\rho_w^*}{\alpha + w} \tag{6}$$

involving the materials constant $\alpha = \rho_w^* / \rho_g^*$, which stands for the ratio of water to the grain material densities respectively, we can easily show that the water diffusion equation within the grain reads as

$$\rho_w^* \frac{dw}{dt} = -(\alpha + w) \nabla \cdot J \tag{7}$$

Where, $d/dt = \partial/\partial t + v_g \cdot \nabla$, is the material derivative. Applying the thermodynamics of linear and irreversible processes, we write down the water diffusion mass flux J as a linear function of the gradient of the water chemical potential μ_w

$$J = -\frac{L(w)}{T} \nabla \mu_w \tag{8}$$

Where L is the Onsager coefficient and T is the constant absolute temperature (in Kelvin). Following past studies, we here assume that L is dependent on the water content state variable w and express it into the following simple form [12, 14-17, 19, 21-23]

$$L(w) = L_0 exp(k_D w) \tag{9}$$

Where k_D is a material parameter and L_0 is the value of L at the dry state ($w = 0$). The concentration dependency of L expresses the plasticization and the changes induced by diffusion that are occurring within the volume of the grain. The water chemical potential μ_w is a sum of two contributions; one arises from the mixing/demixing processes and can be determined using the Flory-Huggins free energy [28] and the other stems from the elastic contribution of the grains originating from its elastic deformation. Thus, we have

$$\mu_w = \mu_w^{mix} + \mu_w^{elas} \tag{10}$$

In the linear elastic regime, both quantities are uniquely dependent on the water content, w. Thus, using the chain differentiation rule, we have

$$\nabla \mu_w = \left(\frac{\partial \mu_w^{mix}}{\partial w} \right) \left(1 + \frac{\partial \mu_w^{elas} / \partial w}{\partial \mu_w^{mix} / \partial w} \right) \nabla w \tag{11}$$

Inserting Equation (11) into the diffusion mass flux expression (8), we express the latter into the following condensed form

$$J = -\rho_w^* D(w)(1 + \psi(w)) \nabla w \tag{12}$$

Where ρ_w^* is the already defined water material density. This equation involves two concentration–dependent quantities; $D(w)$ and $\psi(w)$. The first is the diffusivity of the water molecules in the grain and is given by [12, 14-17, 19, 21-23]

$$D(w) = D_0 exp(k_D w) \tag{13}$$

Where the exponential prefactor D_0 defined as

$$D_0 = \frac{L_0}{\rho_w^* T}\left(\frac{\partial \mu_w^{mix}}{\partial w}\right) \tag{14}$$

stands for the diffusivity coefficient in the absence of plasticization or volume change. The second functional $\psi(w)$ given by

$$\psi(w) = \left(\frac{\partial \mu_w^{elas}}{\partial w}\right) \Big/ \left(\frac{\partial \mu_w^{mix}}{\partial w}\right) \tag{15}$$

stands for the elastic-diffusion coupling functional assessing the relative importance of the elasticity of the medium to mixing (e.g. sorption) or demixing (e.g. desorption). In the case of an integral desorption process, ψ depends strongly on the water content w. However, in the case of a differential desorption corresponding to small deformations, it can be approximated, without any loss of generality, by a constant ψ_0. In that case, as we shall show in the forthcoming section, ψ_0 can be determined from fit to experimental data or assessed through scaling analysis. Finally, we write down the new diffusion mass flux expression into a more conventional condensed form as

$$J = -\rho_w^* \mathfrak{D}^*(w) \nabla \mathrm{w} \tag{16}$$

Where, for the sake of clarity, we have introduced the apparent moisture diffusivity as

$$\mathfrak{D}^*(w) = D_0 exp(k_D w)(1 + \psi(w)) \tag{17}$$

Obviously, the equation (17) shows that the apparent diffusivity is enhanced by the elasticity of the grain and thus is diffusion. Finally, the water continuity equation in the gains is

$$\frac{dw}{dt} = (\alpha + w)\, \nabla \cdot (\mathfrak{D}^*(w)\, \nabla w) \tag{18}$$

If $\psi = 0$ and $k_D = 0$, one recovers the classical Fickean parabolic diffusion equation. To take into account the shrinkage of the grain during the drying process, we transform the equation from the Eulerean coordinates r into the Lagrangean (i.e. grain material) coordinates R using the following usual transformation [18]

$$dr = F \cdot dR \tag{19}$$

Where the second-order tensor F stands for the deformation gradient second-rank tensor. Thus, we have

$$detF = \frac{V_{deformed}}{V_{undeformed}} = \frac{1}{1 - \emptyset} \tag{20}$$

Where the quantity $\emptyset$ refers the volume fraction of the moisture (water) present in the binary mixture. Therefore, the diffusion equation in the grain material coordinates reads as

$$\frac{dw}{dt} = (\alpha + w)\, F^{-1} \cdot \nabla_R \cdot (\mathfrak{D}^*(w)\, F^{-1} \cdot \nabla_R w) \tag{21}$$

Where the quantity, ∇_R , refers to the spatial gradient expressed in the Lagrangean coordinates system.

3. Unidirectional diffusion process and scaling analysis

3.1. Unidirectional formulation

In the case of transport of moisture in spherical grains subjected to small and isotropic deformations provoked by the grain shrinkage, the diffusion process occurs mainly in the radial direction, to be denoted in the following by the scalar R. Thereby, the diffusion equation (21) in the radial Lagrangean coordinate is

$$\frac{dw}{dt} = (\alpha + w)\left[\frac{1}{F}\frac{\partial}{\partial R}\left(\frac{\mathfrak{D}^*(w)}{F}\frac{\partial w}{\partial R}\right) + \frac{2\mathfrak{D}^*(w)}{R\,F^2}\frac{\partial w}{\partial R}\right] \quad (22)$$

Where F is the first component of the deformation gradient tensor, which becomes in the *1-D* process as

$$\det F = F = \frac{1}{1-\emptyset} = \frac{\alpha + w}{\alpha} \quad (23)$$

Seeking solutions to Equation (22) requires the knowledge of the initial and boundary conditions. As our investigated medium is complex, the surface boundary relaxes in a characteristic time scale comparable to that of diffusion. Thus, the fixed water content w_{eq} traditionally assigned in the Fickean regime as a boundary condition can no longer be used for such a time-dependent boundary problem. Therefore, we introduce the state variable $w_b(t) = w(t, R = R_0)$ (R_0 being the radius of the dry grain) that describes the water content at the surface boundary and whose time evolution equation has the following classical form [21, 24-25]

$$\frac{\partial w_b}{\partial t} = -K_s\left(w_b - w_{eq}\right), \quad (24)$$

where K_s is a material parameter that depends on the rate of sorption-desorption processes occurring at the surface boundary and w_{eq} is the water content at the final equilibrium state. Thus, the ordinary differential equation (24) becomes the time-dependent boundary condition at the surface of the grain for the partial differential equation (22). Moreover, at the center of the spherical grain, we have a null mass flux

$$\left.\frac{\partial w}{\partial R}\right|_{R=0} = 0 \quad (25)$$

3.2. Scaling analysis

To scale the whole model equations, we introduce the dimensionless water content state variable

$$\widehat{w} = \frac{w}{w_0} \quad (26)$$

Where the normalization constant $w_0 = w(t = 0, R)$ stands for the water content at the swollen initial equilibrium state of the wet grain. We also introduce the dimensionless time and the dimensionless space coordinate as

$$\hat{R} = \frac{R}{R_d} \qquad \theta = \frac{t}{\tau_{d0}} \quad (27)$$

Here, we have scaled the radial Lagrangean coordinate R by the diffusion characteristic length scale R_d which refers to the radius of the grain at the completely dry state ($w = 0$). On the other hand, the time variable t, is normalized by the diffusion characteristic time scale, $\tau_{d0} = R_d^2/D_0$, which is expressed in terms of the diffusivity $D_0 = D(w = w_0)$ assessed at the initial swollen state. Therefore, the normalized diffusion equation for the water content in the non-dimensional Lagrangean coordinate becomes

$$\frac{\partial\widehat{w}}{\partial\theta} = \frac{\partial}{\partial\hat{R}}\left(f(\widehat{w})\frac{\partial\widehat{w}}{\partial\hat{R}}\right) + \frac{2f(\widehat{w})}{\hat{R}}\frac{\partial\widehat{w}}{\partial\hat{R}} \quad (28)$$

In which we have used, for the sake of clarity the following quantity

$$f(\widehat{w}) = \frac{\alpha^2(1+\psi)exp\left(k_D w_0(\widehat{w}-1)\right)}{(\alpha + w_0\widehat{w})} \quad (29)$$

Moreover, the normalized initial condition is

$$\theta = 0 \quad and \quad 0 \leq \widehat{R} \leq 1; \qquad \widehat{w} = 1 \quad (30)$$

The boundary condition at the surface of the grain, $\widehat{R} = 1$, is

$$\frac{\partial \widehat{w}_b}{\partial \theta} = -\frac{(\widehat{w}_b - \widehat{w}_{eq})}{D_e} \quad (31)$$

Which involves the normalized final equilibrium water content in the grain $\widehat{w}_{eq} = w_{eq}/w_0$ and the new dimensionless parameter

$$D_e = \frac{1}{K_s \tau_{d0}} \quad (32)$$

Finally, at the center of the spherical grain, $\widehat{\boldsymbol{R}} = \mathbf{0}$, we have

$$\left.\frac{\partial \widehat{w}}{\partial \widehat{R}}\right|_{\widehat{R}=0} = 0 \quad (33)$$

4. Experimental

We have used the static gravimetric method to determine, during the isothermal drying process, the weight loss of durum wheat spherical grains whose average diameter in the dry equilibrium state is of the order of 1.25 mm. Each wet sample has an initial mass equals to 4 g. In all the experiments, the initial water content, in the wet regime, is set, as in the pasta industry [4**]**, to $w_0 = 42\ \%$. With a smaller value, the grain disaggregates, while at a larger value, the grains tend to cluster. First, we have examined the effect of the relative humidity (HR) for a fixed temperature. To do so, the wet samples are introduced inside an airtight jar containing an appropriately selected saturated salt solution to regulate the HR. We have used two salt solutions; KOH and NaCl to set HR respectively to 6.26% and 74.7%. The jars are then placed in a laboratory oven set to a constant temperature of 40°C in order to achieve an isothermal drying of the product (Fig. 1). Second, we have examined the effects of the drying temperature for a fixed HR. The wet samples, put in an open container at equilibrium with the room's relative humidity HR, are placed inside the oven where the experiments are first conducted at 30°C and then at 40°C. For each experiment, two series of measurements are carried out, each consisting of five runs and each run with sixty measuring points. At regular time intervals, the weight of the sample is measured with a precision balance ($\pm\ 0.1\ mg$) until the final desorption equilibrium state is reached. At the end of each experiment, we dry out the samples at 120°C for a period of 24 hours and then weigh them once again to determine the water-free dried out mass m_g (i.e. $w = 0$). At each time step, we have determined the weight loss percentage of the grains $W(t) = m_w(t)/m_g$ by assessing the ratio of the weight of the water content $m_w(t) = m(t) - m_g$ ($m(t)$ being the weight of the wet sample at time t) present in the wet sample to that of the dry sample m_g.

(a) : Temperature scale
(b) : Hermetic jar
(c) : Sample holder
(d) : Durum wheat grains
(e) : Support
(f) : Saturated salt

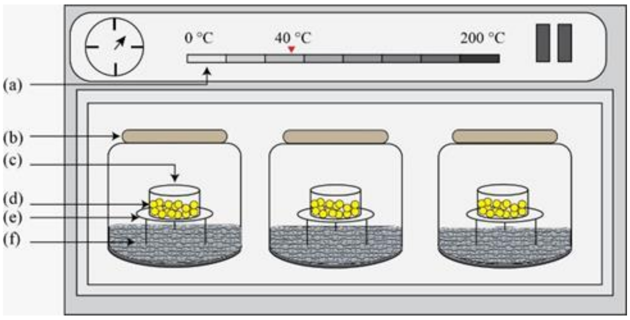

Figure 1. The experimental set up used for the isothermal drying of durum wheat grains

5. Results and discussion

In the following, we shall discuss the behavior of the unsteady isothermal drying of the grains based on our collected gravimetric data and on the numerical predictions obtained using the model equations Eqs. 22 and 24 derived above. Mathematically, one can calculate the weight loss using the following integral

$$\frac{W(t)}{W_0} = 3\int_0^1 \hat{w}\,\hat{R}^2 d\hat{R} \qquad (34)$$

Where $W_0 = W(t=0)$ is the total amount (weight) of moisture per m_g present in the grain at the initial wet state, which is evaluated at the initial moisture content w_0. The time-dependency of the weigth loss $W(t)$ provides a good indication of the behavior of mass transport either Fickean or non-Fickean. In the Fickean regime, the weight loss varies as a linear function of the square root of the time while in the non-Fickean regime, it shows a panoply of time-dependent functions that can be approximated by a polynomial function of the time variable [11]. Any deviation from the square root kinetics leads to a new behavior that can no longer be described by Fick's laws. These are termed in the litterature as anomalous, viscoelastic or non-Fickean behaviors [13-26]. The time-dependent weight loss $W(t)$ is calculated using Eq. 34 once the water content $\hat{w}$ is determined at each time step by solving numerically the discretized governing equations of the proposed model. Another global quantity of interest that can be determined is the time dependent radius of a grain. During the drying process, the grain shrinks, and we can calculate the transient changes of the grain radius using the following integral

$$\frac{r(t)}{r_{max}} = \left[3\int_0^1 \left(\frac{\alpha + w_0\hat{w}}{\alpha + w_0}\right)\hat{R}^2 d\hat{R}\right]^{1/3} \qquad (35)$$

Where $r_{max} = r(w = w_0) = R_d\left[1 + \frac{w_0}{\alpha}\right]^{1/3}$ is the grain radius at the initial wet state and R_d is the already defined radius of the grain at the completely dry state $(w = 0)$. In all our simulations, the functional ψ is assumed to be a constant equals to ψ_0. This justified by the fact that the desoprtion is a differential process and the deformations resulting form the deswelling process are small, linear and isotropic. Scaling analysis shows that this parameter can be expressed as $\psi_0 = 3K\,\Omega_w/2\Re T$, where $\Re$ is the gas constant, T the absolute temperature(in Kelvin), K is the compressibility coefficient (i.e. $3K = E/(1-2\upsilon)$, E being the Young's modulus and υ is the Poisson ratio) and Ω_w is the moisture molar volume. The fact that we have taken into account the time-dependency of the surface boundary expressed by Eq.(24) or it normalized form Eq.(28) has allowed us to appropriately describe, as will be shown in the follwing, the unsteady desorption process at the early stages of the drying process of the grains. The boundary equation is time irrversible and thus the behavior of diffusion is viscoelastic as the surface dynamics is

controlled by the magnitude of De. As a summary, the model involves three dimensionless groups of physical parameters: the elastic-diffusion coupling ψ_0, the boundary number D_e and the material parameter k_D.

5.1. *Effect of the drying temperature*

We firstly set the relative humidity HR to 50% and conduct the experimental and numerical investigations at two drying temperature values set to 30 °C and 40°C.

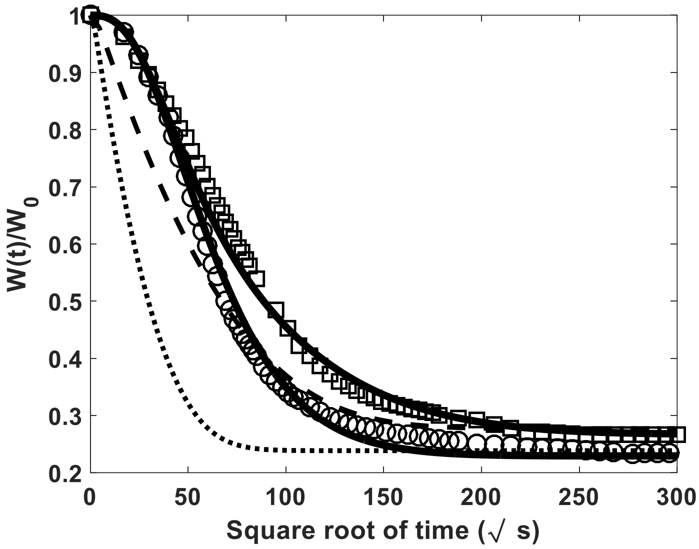

Figure ***2.*** Measured and predicted normalized weight loss $W(t)/W_0$ versus square root of real time, $\sqrt{t}$ ($in\ \sqrt{s}$) at 30 °C and 40 °C.

The discontinuous curves drawn in symbols correspond to our experimental data ('□' at 30°C and 'o' at 40°C). The continuous lines are predictions of our model and the dashed lines are predictions by Fick's laws at the same temperatures. HR is hold constant at 50%. Figure 2 shows both the measured and predicted transient weight loss profiles $W(t)/W_0$ versus the square root of time $\sqrt{t}$ (time in seconds) during the drying process of durum wheat grains at 30°C and 40°C for fixed HR at 50%. The samples were dried from an initial wet state with $w_0 = 0.42$ to a final equilibrium state w_{eq} equals to 0.112 at 30°C and w_{eq} equals to 0.0963 at 40 °C. The radius of the dry grain (i.e. $w = 0$) is $R_d = 1.25\ 10^{-3}\ m$ and the parameter α is calculated and found out to be equal to 0.607. The water molar volume is $\Omega_w = 18\ \ 10^{-3}\ kg\ mol^{-1}$. The experimentally determined diffusivity coefficients are shown in Table 1. In Figure 2, we also show two curves drawn in discrete symbols (□) and (o) which correspond to the experimental data of the weight loss collected at 30°C and 40°C respectively. The continuous curves are predicted using the model equations (22-32) while the dashed lines correspond to predictions using Fick's laws obtained at the same temperatures. It is quite clear that the Fickean model is completely unable to predict the experimental drying data of the couscous grains. The non-Fickean model derived herein provides a much better description for the drying process than the former. As explained earlier, one main reason for such a deviation is due to the fact that diffusion in complex media is strongly influenced, in certain ranges of characteristic time scales, by the active participation of the internal structure and its elastic deformation. As shown in Figure 2, increasing the drying temperature reduces, as expected, the drying time; which is in conformity with previous investigations [9-10]. The latter is completely underestimated by the Fickean model. Thus, decreasing the temperature has protacted the time to attain the final equilibrium dry state and hence increased the drying time for the grains. The best fit scenario is obtained for values of

the three fitting model parameters ψ_0, D_e and k_D shown in Table 1. The diffusion-elastic constant ψ_0 decreases with temperature T since they are inversely proportional as shown by the scaling analysis. The predicted value of ψ_0, obtained through the best fit of the model to experimental data, allows us to determine the yet unavailable experimental values of the physical parameters of the material such as the compressibility modulus K of the grain and thus the Young modulus E provided the Poisson ratio ν is given, since $E = 3K(1-2\upsilon)$. We found out that at $T = 30°C$, $K = 56\ MPa$ and at $T = 40°C$, $K = 77.1\ MPa$. This leads to $E = 3.35\ MPa$ for $\nu = 0.49$ and $E = 33.5\ MPa$ for $\nu = 0.4$ for the former temperature and to $E = 4.62\ MPa$ for $\nu = 0.49$ and $E = 46.2\ MPa$ for $\nu = 0.4$ for the latter if one assumes that the Poisson ratio for such materials is in the range intervalle lying between 0.4 and 0.49. The measured drying time at 30°C is $827\ min$ which is that predicted by the model while at $40°C$ it is found out to be equal to $653\ min$ (the predicted value is around 648 min). Therefore, increasing the temperature by $10°C$ at the same HR decreases the drying time by 21% in this case. More dataset is needed to find out the accurate relationship between the drying time and the temperature changes.

Table1. ***Parameters used in the model equations***

T (°C)	w_{eq}	$\hat{w}_{eq} = w_{eq}/w_0$	$D_0(m^2/s)$	ψ_0	D_e	k_D
30	0.112	0.2666	$4.6\ 10^{-11}$	0.6	0.04	4.5
40	0.0963	0.2292	$2.03\ 10^{-10}$	0.8	0.4	7

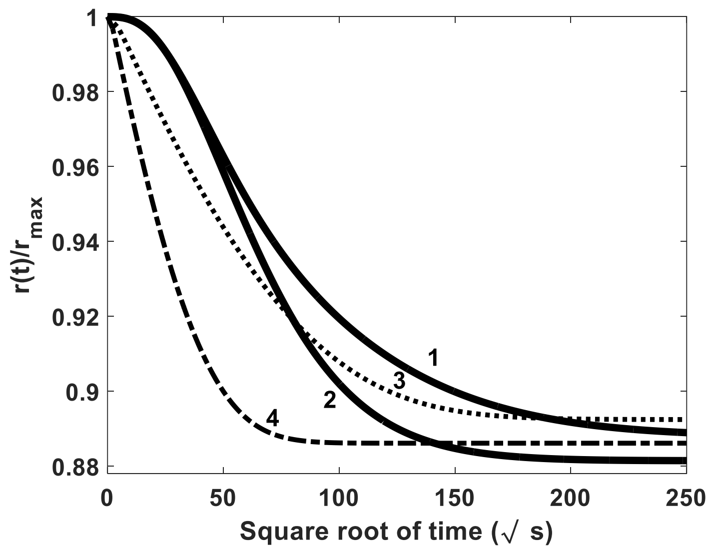

Figure 3. Predicted profiles of the radius of the grain $r(t)/r_{max}$ versus the square root of time.

The continuous curves '1' and '2' correspond to our model predictions at 30°C and 40°C respectively while the dashed curves '3' and '4' are those obtained using the Fickean model respectively at the same temperatures. HR is held constant at 50%. The shrinkage kinetics of the grain is shown in Figure 3. As exhibited, the elastic deformation clearly influences the kinetics of the shrinkage of the grain. In the Fickean regime, the final equilibrium values of the grain radius, displayed by the profiles 3 ($T = 30°C$) and 4 ($T = 40°C$), are reached faster than in the case of the non-Fickean profiles 1 ($T = 30°C$) and 2 ($T = 40°C$). Note that the latter correspond to the best fit obtained between the measured data and the predictions from the non-Fickean model derived above. This actually provides the drying kinetics scenario that best matches the experimental observations. Both models predict, for a given temperature T and a given HR, the same final shrunk radius obtained at the final equilibrium water content, w_{eq}. As shown in

Figure 3, the Fickean theory underestimates the time to reach the final deswelling extent, in particular when increasing the drying temperature. Note that the profiles are all normalized by r_{max} which stands for the radius of the swollen grain at the initial water content w_0. Here, in all our experiments, we have $w_0 = 0.42$ which corresponds to an initial swollen grain radius r_{max}= $1.489\ 10^{-3}m$. Thus, the swelling extent $\Delta V/V = (r_{max}/R_d)^3 - 1$ of the grain at the initial state is of the order of 69 % and thus our linear model appears to be suitable and appropriate for describing the process of diffusion in the case of small deformations. At $T = 30°C$, the radius of the grain at the final state $w_{eq} = 0.112$ is $r_{eq} = 1.323\ 10^{-3}m$ and at $T = 40°C$ and $w_{eq} = 0.0963$, we have $r_{eq} = 1.313\ 10^{-3}m$; which correspond to swelling extents of the order of 18.5 % and 16% respectively. For very small values of w_{eq} say less than 10%, we can approximate, at the first order, the radius retraction, r_{eq}/R_d by the following simple relationships, $w_{eq}/3\alpha$, which is verified for the two values, calculated above. Figure 4 exhibits the profiles of the normalized water content versus the normalized radius of the grain based on the Lagrangean undeformed radial coordinate, $\hat{R}$. The time step between two successive curves in the LHS figure (30°C) is 48.12 min while in the RHS figure (40°C), it is 53.07 min. Note that the effect of the time-boundary condition on the surface of the grain ($\hat{R} = 1$) is visible. We observe that the drying of the surface boundary of the wheat grains occurs in a certain finite time but not as instantaneously as assumed in most previous investigations [2-5] where the surface moisture content is assumed to reach the dry state in a null time; that is as soon as the drying process is launched.

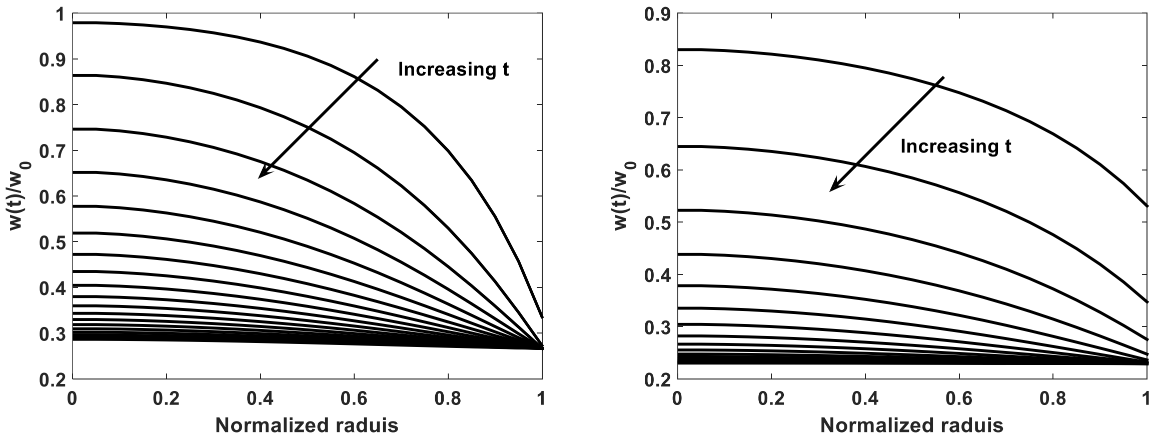

Figure 4. Predicted profiles of the normalized water content $w(t)/w_0$ versus the normalised radius $\hat{R}$ for fixed $HR = 50\%$. LHS: $T = 30°C$ $w_{eq} = 0.112$, $D_\varepsilon = 0.04$, $k_D = 4.5$, $\psi_0 = 0.6$ and $D_0 = 4.6\ 10^{-11}$ (m^2/s). RHS: $T = 40°C$ $w_{eq} = 0.0963$, $D_\varepsilon = 0.4$, $k_D = 7$, $\psi_0 = 0.8$ and $D_0 = 2.03\ 10^{-10}$ (m^2/s).

5.2. Effect of the relative humidity HR

Now we hold constant the drying temperature at 40°C and conduct the dehydration process for values of HR set to 6.26% and 74.7%. Increasing HR increases ψ_0. This is due to the fact that the compressibility modulus K decreases with the amount of the water content.

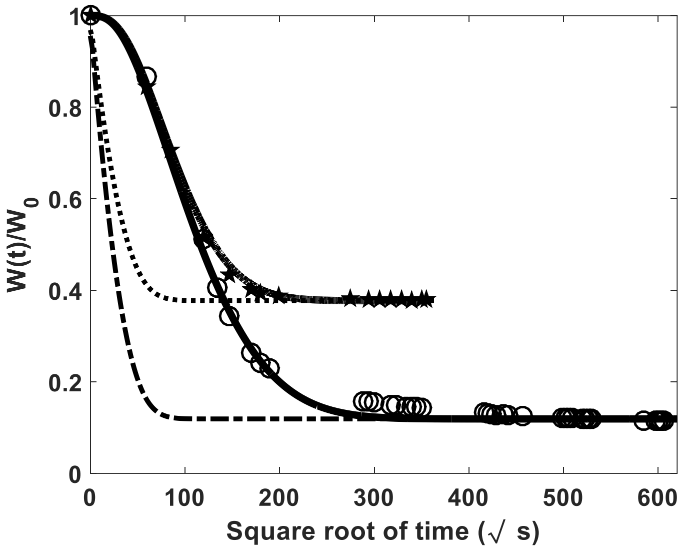

Figure 5. Measured and predicted normalized weight loss $W(t)/W_0$ versus square root of real time, $\sqrt{t}$ ($in \sqrt{s}$) at 30 °C and 40 °C.

The discontinuous curves drwan in symbols correspond to our experimental data ('*' for HR=74.7% and 'o' for $HR = 6.26\%$). The continuous lines are predictions of our model and the dashed lines are predictions by Fick's laws. The drying temperature is held constant at 40°C; Figure 5 shows the influence of the relative humidity on the kinetics of the desorption process while holding constant the drying temperature to 40°C. The measured drying time at $HR = 6.26\%$ is found out to be of the order of $1369\ min$ while at $HR = 74\%$ it is equal to, $827\ min$. Moreover, the experimental values coincide quite well with the predicted values. Therefore, increasing HR ten times tremendously decreases the drying time since the final water content at the final equilibrium state is also enhanced by the increase of HR, which plays a key role in the drying process. As we have previously discussed and illustrate it now in Figure 5, the Fickean model fails completely to predict the dehydration of the durum wheat grains. The Fickean predicted drying times are underestimated for both measured data. Obviously, only the non-Fickean elastic model appears to be faithful to the physics behind the desorption process as is shown by the best fit obtained between the model predictions and the experimental data. The relative humidity influences, not only as expected, the magnitude of the desorbed amount of water but also the kinetics of the drying process in particular at the final stages. The slow kinetics of the surface boundary essentially captures the physics at the early stages of the drying process, which is revealed to be out of the scope of the parabolic Fickean predictions. Table 2 shows all the model parameters used in the calculations as well as those predicted such as the compressibility and Young moduli. The effect of HR on the shrinking extent of the grain is visible as illustrated in Figure 6. For a fixed drying temperature $T = 40°C$, at $HR = 6.26\%$, the radius of the grain at the final state $w_{eq} = 0.049$ is $r_{eq} = 1.283\ 10^{-3}m$ and at $HR = 74\%$ $w_{eq} = 0.1584$, we have $r_{eq} = 1.35\ 10^{-3}m$; which correspond to swelling extents of the order of 8% and 26% respectively which can be regarded as within the range of the linear elastic deformation. Thus at the same temperature, increasing HR increases the deswelling extent from the initial wet state of the grain.

Table 2. ***Physical parameters***

HR	w_{eq}	$\hat{w}_{eq} = w_{eq}/w_0$	D_0 $x10^{10}m^2/s$	ψ_0	D_e	k_D	**K (MPa)**	ν	E **(MPa)**
6.26%	0.049	0.1190	2.03	0.9	1.7	8	86.7	0.4 - 0.49	52 - 5.20
74%	0.1584	0.3772	2.03	0.2	1.2	3.8	19.3	0.4 - 0.49	11.56 - 1.15

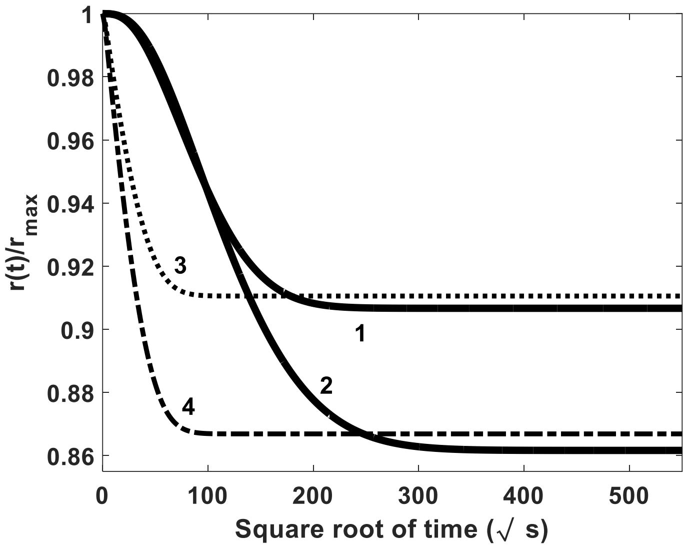

Figure 6. Predicted profiles of the radius of the grain $r(t)/r_{max}$ versus the square root of time at 40°C.

The continuous curves '1' and '2' correspond to our model predictions at $HR = 74\%$ and for $HR = 6.62\%$ respectively while the dashed lines '3' and '4' are obtained using the classical Fickean model respectively at the same HR. The temperature is held constant at 40°C.

5.3. *Effect of the elasticity-diffusion coupling constant* ψ_0

Figure 7 shows on the other hand the effects of the elastic-diffusion coupling constant ψ_0 on the kinetics of the weight loss as well as on the shrinkage of the grain. The physical parameters used as input in the model equations and those predicted for calculating $W(t)/W_0$ and $r(t)/r_{max}$ are: $w_{eq} = 0.112, D_e = 0.04$, $k_D = 4.5$ and $D_0 = 4.6\ 10^{-11}$ (m^2/s). For such a particular thermodynamic state, Figure 7 shows that increasing ψ_0 from zero to three decreases the drying time by 27%. As expected, decreasing ψ_0 by decreasing the compressibility modulus K, delays the time to reach the final equilibrium state and therefore increases the drying time. The latter becomes maximum when ψ_0 completely vanishes. Thus, the deviations from the predictions of Fick's laws are mostly detected when enhancing the elasticity of the medium.

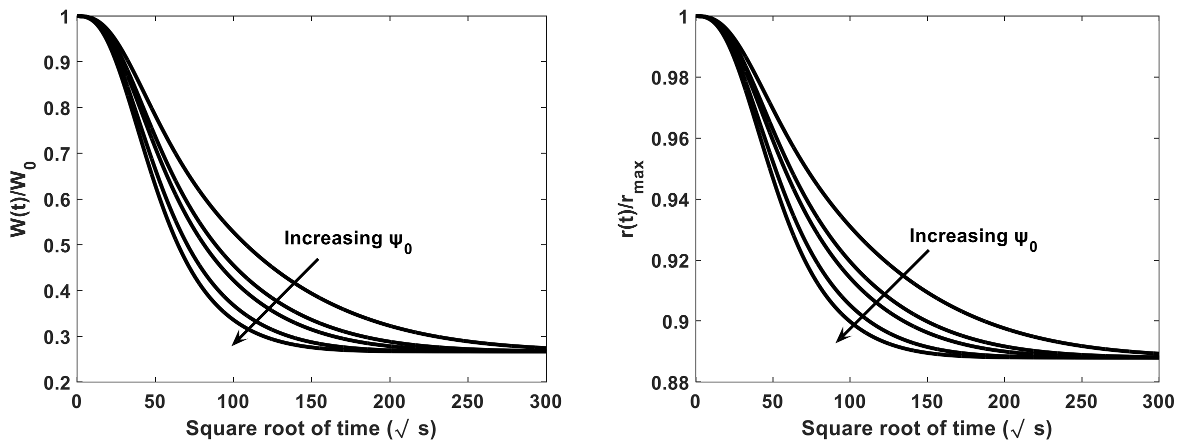

Figure 7. Effects of ψ_0 on the predicted weight loss $W(t)/W_0$ and radius retraction $r(t)/r_{max}$ versus $\sqrt{t}$ ($in\ \sqrt{s}$); $\psi_0 =\ 0, 0.6, 1, 2\ and\ 3$.

6. Conclusion

In this paper, we have used the static gravimetric method to experimentally determine the isothermal drying kinetics of durum wheat grains put into a humidity-controlled environment (with relative humidity values of 6.26% and 74.7%) and at two constant drying temperatures (i.e. 30°C and 40 °C). In addition to that, we have derived an elastic non-Fickean model that implicitly takes into account the influence of the elasticity of the internal structure on the diffusion process. In the particular case of unidirectional diffusion, we have expressed the diffusion equation in the Lagrangean radial coordinate in order to consider the shrinkage of the grains. We have then scaled the governing equations and solved them numerically using the finite difference method. As the couscous grains are assumed to constitute an elastic and deformable medium, the drying kinetics is found out to be influenced by an elasticity-diffusion coupling constant ψ_0, which depends on the compressibility modulus K of the grains, the experimental temperature and the water molar volume. Throughout this systematic study, we have examined the influence of the elasticity of the grain, the drying temperature and the relative humidity on the kinetics of the desorption process. Predictions from both the classical Fickean and our non-Fickean elastic diffusion equations are confronted to experimental data and their limitations are emphasized. The Fickean model is shown to clearly fail for explaining the observed behaviors. Therefore, the behavior of the drying kinetics of the durum wheat grains is essentially non-Fickean. The dynamics of the surface boundary of the grain is examined and we have demonstrated that it controls the early stages of the drying process. Moreover, the experimental and predicted weight loss profiles reveal the obvious influence of the elastic-diffusion coupling constant ψ_0 which enhances the desorption process and thus reduces the drying time. The model proposed here does not however take into account the porosity of the grain and its consideration is postponed to a future investigation.

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Conflict of Interest: The authors declare they have no conflict of interest

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