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MOISTURE DIFFUSIVITY IN HIGH OLEIC SUNFLOWER SEEDS AND KERNELS

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Moisture diffusivities in high oleic seeds and kernels were obtained from experimental thin layer drying rates in the range of 25–90°C air temperature and 4.2–33.5% initial moisture content (d.b.). Moisture diffusivity back-calculated from Fick´s second law of diffusion varied between 0.85.10^{-10} and 7.26.10^{-10} m^2/s for seeds and between 0.37.10^{-10} and 2.39.10^{-10} m^2/s for kernels. The Arrhenius activation energy for seeds and kernels resulted 31 and 24 kJ/mol, respectively. A new model based on the kinetic parameter of Page equation was proposed as a simple tool to predict water diffusion in high oleic sunflower seeds and kernelss.

Keywords: ***Moisture diffusivity, Sunflower seeds, Kernels.***

INTRODUCTION

Sunflower (*Helianthus annuus* L.) hybrid varieties are almost exclusively used for commercial oilseed production. Native sunflower oil is mainly used for human consumption since it contains a large amount of essential linoleic acid (w6 C18:2) which gives the sunflower seed oil a high nutritional value. In addition, high oleic' varieties have been obtained by chemical mutagenesis of accumulating oleic acid (w9 C18:1) up to 85% in the oil.[1] This oil is nutritionally desired to increase the mono-unsaturated level in the diet. The possibilities of use of this oil are so widespread researchers consider that this differential oil from high oleic sunflower seeds will dominate the type of sunflower to be cultured.[2] This grain is produced at a relative low volume and is still considered a special oilseed. The knowledge of the behavior of these modified grains, especially during post-harvest processing, is not yet available. Drying and storage processes can affect the oil quality of seeds as have been shown previously.[3] The knowledge of drying kinetics contributes to keep the genuine quality of the oil because it is a tool for the proper design and selection of the equipment and operation conditions during post harvest processes. Moreover, diffusivity

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is a transport property which accurate prediction can lead to optimisation of drying processes, especially in highly automated computer aided systems.[4]

Moisture diffusivity in traditional sunflower kernels and hulls were determined at 40 and 50°C,[5] but no references have been found related to the variation of moisture diffusion with temperature and initial moisture content. Based on the above mentioned situation, the objectives of the present work were: to evaluate the moisture diffusivity of water in high oleic sunflower seeds and kernels; to identify the effect of air temperature; to predict activation energy; and to evaluate a new model to estimate the diffusion of water in seeds and kernels of high oleic sunflower based on the kinetic parameter of Page model.

MATERIALS AND METHODS

The evaluation of moisture diffusivity was carried out based on thin-layer drying experiments, as coefficients determined in this way can be used with confidence for scaling up and optimising industrial driers.[4]

Sample Preparation

Trisum 568 (Mycoyen-Morgan), a striated high oleic genotype of sunflower (*Helianthus annuus* L.) was selected to carry out this study. Ten bulk samples, each consisting of 5 kg of seed, were prepared from seeds produced at Oriente, Coronel Dorrego, Argentina, after 80 days of physiological maturity stage. The seeds were manually cleaned for foreign matter, broken and immature seeds. The initial moisture content of the seeds was 14.3% dry basis (d.b., g water/g dry solids). Whole kernels and hulls were both obtained by manual dehulling of the seeds. Seeds and kernels were packed separately in double-layered low-density polyethylene bags sealed and stored at low temperature (5°C) in a refrigerator to reduce the rate of microorganisms growing. For each thin-layer drying test, the required amount of material was taken out and allowed to warm up to room temperature for approximately 2 h.[6]

To evaluate the effect of initial moisture content on diffusion coefficient, samples of seeds and kernels at the desired initial moisture content were prepared by adding calculated amounts of distilled water and sealing in separate polyethylene bags. The drying thin-layer kinetics tests were determined at the following initial moisture contents: 4.2, 14.3, 26.4, and 33.5% d.b. for seeds and at 5.0, 13.2, and 23.8% d.b. for kernels. Moisture content was determined by the oven drying method described in ASAE Standard S352.1[7] at 130°C oven temperature during 3 h. All moisture contents were determined using two replications.

Experimental Tests

A laboratory thin-layer dryer (Fig. 1) was used to evaluate the drying rates of high oleic sunflower seeds and kernels. A fan drove the air through a heating unit towards the drying chamber in which the seeds were spread on a 0.0232 m^2 removable tray. The samples used for the experiments consisted in a single layer of seeds which thickness was less than 0.01 m. The hot air flowed uniformly across the sample at constant velocities in the range of 0.28 to 0.31 m/s, controlled by a damper and measured on a calibrated orifice plate. These air velocities were selected because thin-layer drying of seeds is independent of air

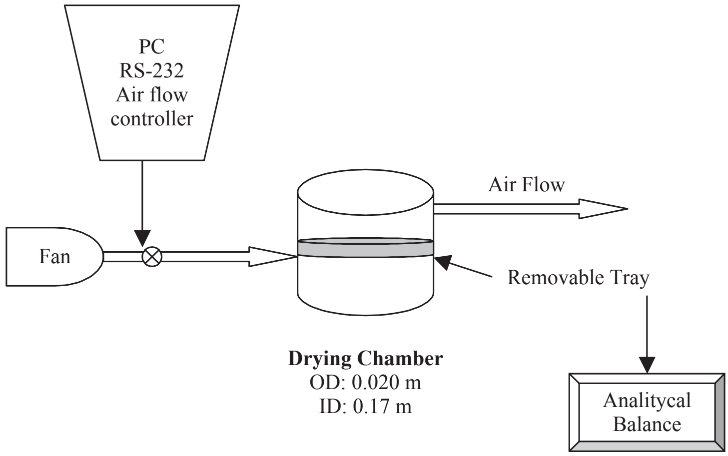

Figure 1 Convective hot air drying apparatus.

velocity when this is higher than 0.2 m/s.[8,9] Before each run, the air was heated at the desired dry bulb temperature through electrical resistances. Relative humidity was measured by using an aspirated psychrometer (Paspst, Type 8550 VW). In order to stabilize the conditions before each test the equipment was previously run for 1 h.

Experimental Design

Drying runs were carried out at five air temperatures (25, 40, 60, 75, and 90°C) and at the initial moisture contents described previously. The moisture loss was registered along time intervals of 2, 4, 6, 10, and 15 min and each test continued during two hours. The equilibrium moisture contents for each temperature and equilibrium relative humidity were obtained from a previous work[10] using the modified GAB model Eq. (1) that includes the dependence of the GAB parameters with temperature:

$$X_e = \frac{A_o.exp(A_1/T).B_G.C_G.ERH}{(1-B_G.ERH).(1-B_G.ERH+B_G.C_G.ERH)}, \quad (1)$$

where X_e is the equilibrium moisture content, A_o, A_1, B_G, and C_G are the estimated GAB coefficients for seeds and kernels and ERH is the equilibrium relative humidity of air into the drying chamber. Table 1 shows the values of Xe used at each experimental condition.

Diffusivity Equations

The equation used to obtain the diffusion coefficient was derived from Fick's second law of diffusion:

$$\frac{\partial X}{\partial t} = D\nabla^2 X, \quad (2)$$

Table 1 Equilibrium moisture content X_e for high oleic sunflower seeds and kernels at the experimental conditions used in the present study.

	Xe [g water/g dry solid]				
T [°C]	25	40	60	75	90
Seed	2.80 (24%)[a]	1.81 (11%)	0.86 (3.6%)	0.52 (1.9%)	0.40 (1.4%)
Kernel	2.45 (24%)	1.94 (11%)	1.49 (4.8%)	1.00 (1.7%)	0.89 (1.6%)

[a]Values between parenthesis represent Equilibrium Relative Humidity (ERH).

where X is the local moisture content (dry basis). This shape of Eq. (2) implies the neglecting of shrinkage during drying, an usual assumption for low moisture content seeds. The analytical solution of Eq. (2) for the case of sphere, assuming unidimensional moisture movement without volume change, constant diffusivity, uniform initial moisture distribution and negligible external resistances results[11]:

$$X' = \frac{X - X_e}{X_o - X_e} = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left[-n^2\pi^2\frac{Dt}{r^2}\right] \tag{3}$$

where X′ is the average moisture ratio; X_o is the initial moisture content; r is the equivalent radius of the seed or kernel; t is time; and D is the diffusion coefficient. For short times, a diffusional equation based on semi-infinite medium concepts and the expansion of Eq. (3) in Mc Laurin series was developed[12]:

$$X' = \frac{X - X_e}{X_o - X_e} = 1 - \frac{2}{\pi}a_V\sqrt{D.t} + \frac{f}{2}a_V{}^2 Dt, \tag{4}$$

where f = 0.661; and $a_v = 3/R$ for spheres. This approximation is valid for $0.2 < X' < 1$ and $0 < z < 1$ with $z = a_v\sqrt{Dt}$ and its accuracy has been tested against experimental data of wheat[13] and quinoa[14] drying. Experimental values of moisture ratio X′ between 0.2 and 1.0 were used to adjust the drying data (X′ versus t) to Eq. 4 so as to find the diffusion coefficient at each temperature.The dependence of moisture diffusivity with temperature was verified using the well known Arrhenius-type relationship:

$$D = D_o e^{\frac{-E_a}{RT}}, \tag{5}$$

where Do is the Arrhenius factor (m^2/s); Ea is the activation energy for moisture diffusion (kJ/kmol); R is the ideal gas constant (kJ/kmol.K); and T is the absolute temperature (K).

A relationship between diffusion coefficient and kinetic parameter k of Page equation was reported for a spherical Al-Ni catalyst.[15] The simplicity of this model will be used to evaluate the moisture diffusion in seeds and kernels of high oleic sunflower taking into account the accuracy of the Page model for the prediction of thin-layer drying rates demonstrated in a previous work.[16] A nonlinear module of Systat Statistical Software [17] was used to calculate the diffusion coefficient from Eq. (4). The statistics used to evaluate the goodness of the adjustments were the standard error of the estimated value (SE) calculated as:

$$SE = \sqrt{\frac{\Sigma(Y - Y\cdot)^2}{df}}, \tag{6}$$

where Y and Y′ are the experimental and predicted values of the variable studied; the mean relative percent deviation (P) calculated as:

$$P = \frac{100}{N}\Sigma\frac{|Y - Y\cdot|}{Y}; \tag{7}$$

and the coefficient of determination (R^2) at a level of 95% of confidence.

RESULTS AND DISCUSSION

To obtain the values of D valid for the initial drying period of interest, in industrial drying, Eq. (4) was fitted to the experimental thin layer drying data, using the equivalent radius of 0.0054 m for seed and 0.0039 m for kernel[18] and assuming that initial moisture content has no effect on moisture diffusivity. These calculated values are shown in Table 2, where D_s and D_k indicate the moisture diffusivities in seed and kernel, respectively. The table also shows the corresponding standard errors for moisture diffusivity at each drying air temperature and the coefficients of determination of the fitting of Eq. (4) by using the non-linear method. Previously determined diffusivities in sunflower kernels, using Eq. (3), were reported[5] with a value of 0.7×10^{-10} m^2/s at 40°C, very close to that reported in this work at the same temperature (0.667×10^{-10} m^2/s).

Analysis of variance was used to estimate the significance of the effect of the initial moisture content on the diffusion coefficient. Results of the ANOVA demonstrated that initial moisture content has no significant effect on water diffusion in high oleic sunflower seeds and kernels at a 95% level of confidence, giving values of Snedecor function F of 11.09 and 14.72 for seeds and kernels respectively, against $F_{0.05,3,4} = 9.12$.

The Arrhenius type-relationship Eq. (5) was proposed to fit the variation with temperature of the experimental values of moisture diffusivity. Figure 2 shows the relationships obtained, where the values of constants and coefficients of determination are presented in Table 3. The activation energy (without taking into account the effect of the

Table 2 Average values (for all runs from different initial moisture contents) of moisture diffusion coefficients in seeds (D_s) and kernels (D_k) at different drying air temperatures, obtained through adjustment of experimental data to Eq. (4).

	D_s (m^2/s)			D_k (m^2/s)		
Temperature(°C)	Value	Std. error	R^2	Value	Std. error	R^2
25	$0.847\ 10^{-10}$	$4.81.10^{-12}$	0.972	$0.370\ 10^{-10}$	$2.12.10^{-12}$	0.913
40	$1.306\ 10^{-10}$	$6.88.10^{-12}$	0.939	$0.667\ 10^{-10}$	$5.03.10^{-12}$	0.970
60	$2.813\ 10^{-10}$	$6.77.10^{-12}$	0.904	$1.055\ 10^{-10}$	$3.45.10^{-12}$	0.989
75	$4.040\ 10^{-10}$	$6.90.10^{-12}$	0.977	$1.333\ 10^{-10}$	$4.17.10^{-12}$	0.986
90	$7.256\ 10^{-10}$	$4.63.10^{-12}$	0.974	$2.431\ 10^{-10}$	$6.60.10^{-12}$	0.967

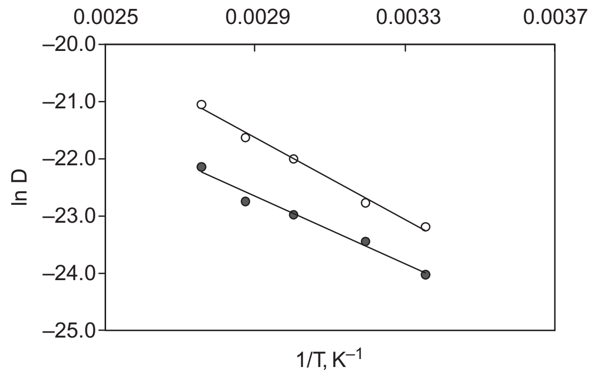

Figure 2 Relationship between diffusion coefficient of seed D_s (white symbols) and kernel D_k (black symbols) and absolute temperature.

Table 3 Constants and correlation coefficients obtained for the parameters of Eq. (5) for whole seed and kernel.

Coefficient	Whole seed	Kernel
D_0 (m^2/s)	1.7859 10^{-4}	6.1848 10^{-7}
E_a (kJ / mol)	30.698	24.009
Correlation (R^2)	0.996	0.980

initial moisture content) in high oleic sunflower seeds resulted 30.7 kJ/mol, 22% higher than in kernel (24.0 kJ/mol). This behavior can be related to previous results[5] that found that moisture diffuses between about two and four times faster through the hull than through the kernel.

A kinetic model based on the Page equation Eq. (8), with the parameters k and n temperature-dependent Eqs. (9) and (10), was proved previously[16] as a good model for thin-layer drying rates for whole sunflower seeds:

$$X\cdot = e^{-kt^n}, \tag{8}$$

where the parameters k and n are temperature dependent according the following relationships:

$$k = AT^B, \text{ and} \tag{9}$$

$$n = E + FT. \tag{10}$$

The values of A, B, E and F and the corresponding statistics are described in Table 4. A first analysis between the values of experimental diffusivities in seeds and kernels and the kinetic parameter of Page equation k showed a non linear dependence of expontential

Table 4 Coefficients of Eq. (8) for the temperature dependence of Page parameters k and n for high oleic sunflower seed and kernel.

	Value	Standard error	R^2
Seed			
A	0.0072525	0.000068	
B	0.6876774	0.008260	>0.99
E	0.5373581	0.006086	
F	0.0027026	0.000136	
Kernel			
A	0.0123133	0.003907	
B	0.5374414	0.060078	>0.98
E	0.5902078	0.040468	
F	0.0023532	0.000647	

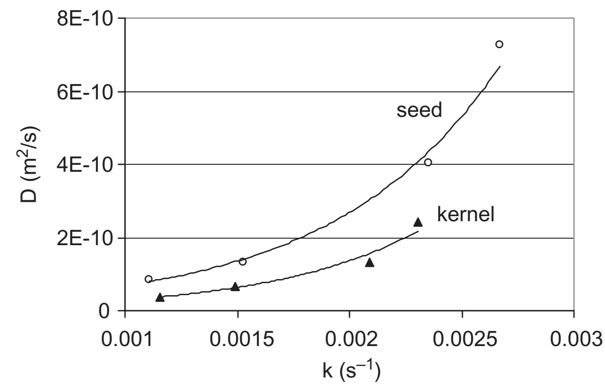

Figure 3 Relationship between moisture diffusivity in seed and kernel obtained from equation 5 and the Page kinetic parameter.

form as can be observed from Fig. 3. The results of the best fit analyzed for four air temperatures tested: 25, 40, 75, and 90°C (the remainder temperature 60°C was used to test the adjustment) are summarized in the following expressions:

$$D_{sk} = 0.1058.10^{-10}.\exp(1576.9.k), \text{ and} \tag{11}$$

$$D_{kk} = 0.3766.10^{-11}.\exp(1786.0.k), \tag{12}$$

where D_{sk} and D_{kk} mean the diffusion coefficient (in m^2/s) in seed and in kernel, respectively, as a function of Page parameter k (with k in s^{-1}). The corresponding standard errors of the estimated parameters and the coefficients of determination R^2 are tabulated in Table 5. Taking into account that the statistics showed a good adjustment, Eqs. (11) and (12) was used to evaluated de diffusion coefficient at 60°C to be compared with the experimental value at this temperature. Diffusion of water in seed, D_{sk} calculated by using

Table 5 Values and statisticals of the coefficients of the Eqs. (11) and (12) at 95% level of confidence.

	Parameter	Standard error	R^2
Seed			
Preexponential factor	$0.1058.10^{-10}$	$0.455.10^{-11}$	0.993
Exponential factor	1576.9	167.6	
Kernel			
Preexponential factor	$0.3766.10^{-11}$	$0.3428.10^{-11}$	0.963
Exponential factor	1786.0	412.67	

Eq. (11) resulted $2.5567.10^{-10}$ m^2/s (absolute error from experimental value resulted 9.1%) and diffusion of water in kernel D_{kk} obtained from Eq. (12) resulted $1.0308.10^{-10}$ m^2/s (absolute error from experimental value resulted 2.3%). This arrangement shows that Eqs. (11) and (12) resulted a good and simple tool to evaluate diffusion of water in high oleic sunflower when kinetic parameter of Page equation is available.

If the diffusion coefficients determined with Eqs. (11) and (12) are plotted against 1/T, the activation energies can be found in a similar way as previouly, by using the Arrhenius model. The activation energy obtained by applying Eq. (5) and using values of D_{sk} calculated from Eq. (11) (with k from Eq. (9)), resulted 29.5 kJ/mol ($R^2 = 0.992$), with an absolute error of 3.9% from the activation energy obtained from D_s values obtained from equation 4 (30.7 kJ/mol). In kernel, the activation energy obtained by applying Eq. (5) and using values of D_{kk} from Eq. (12) resulted 24.2 kJ/mol ($R^2 = 0.979$), with an absolute error of 0.8% compared with the activation energy obtained from D_k values obtained from Eq. (4) (24.0 kJ/mol). These differences can be assumed as negligible and underline the option to use Eqs. (11) and (12) to calculate diffusion coefficients.

Drying kinetics curves (X′vs t) with X′ calculated from Eq. 4 with diffusion coefficient obtained from Eqs. (11) and (12) (for seeds and kernels respectively) were tested against the experimental ones. Figures 4 and 5 show the results obtained for the drying of seeds and kernels, respectively. The goodness of the adjustment was evaluated through the standard error of the estimated value (SE) and the mean relative percent deviation

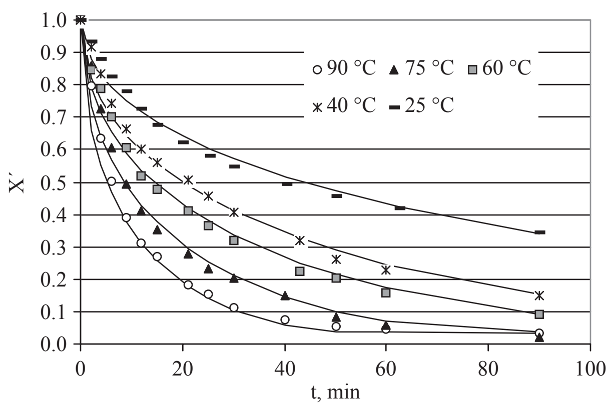

Figure 4 Moisture ratio of high oleic sunflower seeds. Experimental values are represented through symbols while the proposed model based on diffusion coefficient calculated with k parameter of Page model is shown through lines.

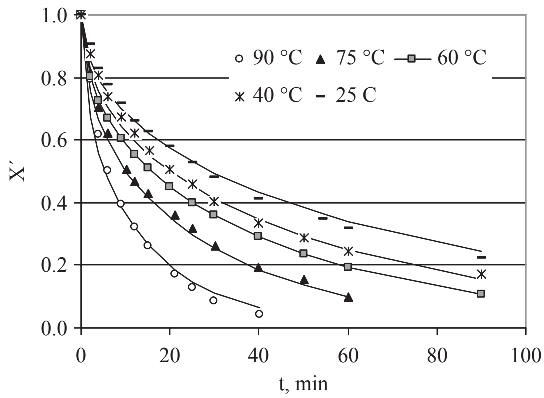

Figure 5 Moisture ratio of high oleic sunflower kernels. Experimental values are represented through symbols while the proposed model based on diffusion coefficient calculated with k parameter of Page model is shown through lines.

Table 6 Evaluation of the goodness of the adjustment of experimental thin-layer drying test (X´vs t) with Equations 11 and 12.

	P		SE	
T (°C)	Seed	Kernel	Seed	Kernel
90	5.551	8.481	0.162	0.141
75	6.322	4.216	0.162	0.086
60	4.956	2.355	0.113	0.068
40	4.151	3.531	0.138	0.093
25	3.140	3.316	0.100	0.081

calculated from Eqs. (6) and (7), respectively. Table 6 summarizes the results obtained. The proposed model showed good agreement with respect to the experimental thin-layer drying tests. The mean relative percent deviation resulted lower than 6.322 for seeds and than 8.481 for kernels. The standard error of the estimated value, that is moisture ratio X', resulted lower than 0.162 for seeds and lower than 0.141 for kernels.

CONCLUSIONS

Equation (4), based on the Becker model, showed adequate for the fitting of experimental data of thin layer drying of high oleic sunflower seeds and kernels in the range of temperature from 25 to 90°C and for different water contents. Highly accurate values for diffusion coefficients were obtained using this method. Page model also fitted adequately experimental data for thin layer drying data for whole seeds and kernels. The kinetic parameters k and n could be satisfactorily related to temperature. Based on these previous results, a new model based on the kinetic parameter of Page equation was proposed as a simple tool to predict the diffusion of water in high oleic sunflower seeds and kernels. The goodness of the adjustment evaluated through the mean relative percent deviation and the standard error of the estimated value demonstrated that the proposed model could be used for prediction of diffusion behavior when kinetics drying has previously studied.

NOMENCLATURE

A, B, E, F	Parameters of the modified Page equation
A_o,A_1, B_G, C_G	Coefficients of GAB equation
D	Diffusion coefficient, m^2/s
D_k	Diffusion coefficient in kernel based on equation 5
D_{kk}	Diffusion coefficient in kernel based on kinetic Page parameter, m^2/s
D_o	Arrhenius factor, m^2/s
D_s	Diffusion coefficient in seed based on equation 5, m^2/s
D_{sk}	Diffusion coefficient in seed based on kinetic Page parameter, m^2/s
d.b.	Dry basis
E_a	Activation energy, kJ/mol
k	Page kinetic parameter, s^{-1}
n	Page parameter, dimensionless
P	Mean relative percent deviation
R	Gas constant, kJ/(mol K)
R^2	Coefficient of determination
RH	Relative humidity of air,% d.b.
r	Equivalent radius, m
SE	Standard error of the estimated value
T	Temperature, K
t	Time, s
X	Moisture content, d.b.
X′	Moisture ratio, dimensionless
X_e	Equilibrium moisture content, d.b.
X_o	Initial moisture content, d.b.
Y	Experimental data
Y′	Predicted values of the variable studied

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