Grain Sorghum Drying Kinetics Under Isothermal Conditions Using Thermogravimetric Analyzer

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This research aimed to determine the isothermal drying kinetic parameters of grain sorghum using a thermogravimetric analyzer (TGA). The kernels were placed in the TGA under isothermal drying conditions, *i.e.*, 40, 50, 60, 70, 80, 90, and 100 °C. Changes in the sample weight were determined from the TGA and the data were used to determine the moisture ratio and the derivative of the weight loss curves. The moisture ratio data obtained experimentally were fitted to four well-known models, namely Page, Newton, Logarithmic, and Henderson, to determine the best-fit model for the experimental data. The goodness of fit criteria was used to determine the best-fit model. An increased drying temperature from 40 °C to 100 °C accelerated the drying process and decreased the moisture ratio from 0.6091 to 0.2909, after 1 h. The Page model was the best fit for 71.4% of the drying curves, whereas the Logarithmic and Henderson models were the best fit for 28.6% of the studied cases. Increasing the drying temperature from 40 °C to 100 °C increased the effective moisture diffusivity from 0.96 × 10^{-8} m^2/s to 1.73 × 10^{-8} m^2/s. The drying activation energy value reached 9.4 kJ/mol under isothermal drying conditions.

Keywords: Grain sorghum; Moisture content; Drying kinetics; Moisture diffusivity; Activation energy

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INTRODUCTION

Grain sorghum (*Sorghum bicolor* L. Moench) belongs to the Gramineae family and represents the third-largest cereal grain grown in the United States and the fifth-largest grain cultivated in the world. It is known for its drought tolerance and its resistance to other extreme climate conditions, as well as its resistance to fungi and mycotoxins. According to the USDA report (USDA 2016), grain sorghum harvested area for 2015 was estimated at 3.1 million hectares with the average grain yield at 190 bushels per hectare in the United States (1 bushel = 56 pounds or 25.5 kg). Grain sorghum production in 2015 was estimated at 15.2 million tons.

Freshly harvested grain sorghum, with a moisture content of approximately 20% wet basis, has its highest quality at harvest. Grain sorghum usually requires artificial drying to reach the target moisture content for safe storage (Sadaka *et al.* 2015). Drying is one of the important post-harvest processes of agriculture products. This process is typically presented as a drying curve representing the relationship between grain moisture content and drying duration. Drying curves offer valuable information to understand the mechanism of water migration from the product as well as its drying kinetic parameters (Chen *et al.* 2012a). Accordingly, understanding the drying kinetic parameters of a product from its drying curves is necessary to control the overall drying procedure and the quality of the final dried product (Ferrao *et al.* 1998). Quantifying the drying kinetic parameters and the awareness of thermodynamic properties allow researchers to design drying equipment, to calculate the energy required in the process, to study the adsorbed water's properties, and to study the physical phenomena that take place during the drying process. Also, quantifying these parameters provide better understanding of the water transfer mechanisms. The two key kinetic parameters are the effective moisture diffusivity (D_{eff}) and the activation energy (E_a), with the former defined to describe the rate of moisture movement and the latter in quantifying the energy level of water molecules during the drying process. Searching previous literature revealed that some studies stated the value of D_{eff} varies depending on the drying temperature as well as the dried feedstock. This led to a need of quantifying the D_{eff} value for grain sorghum.

Recently, several simulation methods and empirical models have been developed to explore the drying characteristics of agricultural products under isothermal conditions. Chen *et al.* (2012a) reported that several of the existing methods might lack the suitability of determining grain drying kinetic parameters under isothermal conditions. Using traditional methods, *i.e.*, ovens and dryers, to dry grain make it difficult to attain isothermal conditions. It should be mentioned that isothermal conditions not only require that the sample be exposed to constant temperature but also that the temperature must reach the desired drying temperature over a short duration of time. Thus, a fast and straightforward technique for determining the drying kinetics, moisture diffusivity, and activation energy of grain is of pressing importance. Thermogravimetric analysis (TGA) is one of the procedures that precisely measures the rate of change of a sample weight corresponding to temperature or time under controlled conditions (Blaine 1998). Thermogravimetric analysis has been used before for the determination of grain processing kinetic parameters. Its application for grain drying has many advantages, such as simplicity of the process, minimal material requirement, accurate temperature control, and capability of online recording of the experimental data.

Acquistucci *et al.* (1991) used TGA to study the moisture content of the wheat flour during the drying process. The results did not show any difference from those obtained by official methods, demonstrating it to be a reliable technique for future use. Both TGA and derivative thermogravimetric analysis (DTA) were employed to understand the state of moisture within grains (Neher *et al.* 1973). This proved to be a beneficial method for moisture determination over the Karl-Fischer (KF) method, as some of the chemicals are not soluble in KF reagents. Therefore, TGA has found wide application in the pharmaceutical industry (Komatsu *et al.* 1994). Madhava *et al.* (2001) found the drying kinetics of paddy with TGA, and observed that most of the loss occurred between 60 and 100 °C. Fernandez *et al.* (2017) supported the viewpoint that the temperature has the major effect on the activation energy, as the drying rate is dependent on temperature.

Thermogravimetric analysis can also be used to evaluate the moisture diffusivity of solids under isothermal conditions (Li and Kobayashi 2005). Wang (2007) used the TGA technique to study the kinetics of moisture removal from non-food products. Ogawa *et al.* (2012) used TGA for the prediction of the pasta drying process and discovered that the constant rate period of drying should be considered in predicting the drying curves for pasta, which was neglected in the past. Vuataz *et al.* (2010) used TGA and DTA to design reference methods for moisture determination in food powders as they found precise control over the process. Thermogravimetric analysis has also been used to measure the degree of bound water in starch, and the results were comparable with those of differential scanning calorimetry (Tian *et al.* 2011).

The drying kinetics of grains have been studied under thin layer isothermal conditions. Much work has been reported on the kinetic parameters of sorghum under conventional drying methods (Sandeepa *et al.* 2013; Resende *et al.* 2014), but lesser control over the temperature in these methods gives rise to a high level of experimental error. Even though TGA has been employed for diverse applications, there has not been much work reported on this technique to investigate the dehydration behavior of grain sorghum under isothermal conditions.

It was hypothesized that thermogravimetry and derivative thermogravimetric analysis could be used for determination of the moisture ratio and the moisture diffusivity under isothermal conditions. In addition, the four experimental models would establish the best fit with the experimental data. Thus, the objectives of this study were: (a) to explore the effects of drying temperature and drying duration on the grain sorghum drying kinetics under isothermal conditions *via* TGA; (b) to select the best-fit mathematical models for the drying curves; and (c) to determine the moisture diffusivity and activation energy values.

EXPERIMENTAL

Materials

Grain sorghum collection and characterization

Grain sorghum was procured from a local farm, transported to the Rice Research and Extension Center, Stuttgart, AR, USA, and then stored at 4 °C. Approximately 5 kg of sorghum sample was visually examined to remove any damaged kernels. The sample was divided into seven subsamples and stored in polyethylene bags. These subsamples were again stored in the refrigerator at 4 °C. Physical parameters of sorghum, such as moisture content (%), bulk density (kg/m^3), geometric mean diameter (mm), and 1000 kernel mass (g) were investigated. The initial moisture content of sorghum was determined using the standard method ASAE S352.2 (2008). The sorghum bulk density was determined by dividing the mass of grain sorghum by the volume it occupies. The basic dimensions of the sorghum (length, width, and thickness) were measured using a steel digital caliper (General Ultratech, Series – 147, Secaucus, NJ, USA) with 0.02 mm accuracy. The geometric mean diameter was calculated by taking the cube root of the multiplication of the three basic dimensions. A similar method was used by Bande *et al.* (2012) in measuring different seed sizes.

Grain sorghum drying

Grain sorghum samples were dried using a thermogravimetric analyzer (Model TGA 4000, PerkinElmer, Inc. Waltham, MA, USA). The analyzer had a precise temperature control capability that perfectly achieved isothermal drying conditions over a short time. The main technical parameters of the TGA are as follows: top-loading pan balance type; standard furnace that ranged from ambient to 1000 °C; balance precision of 0.01%; and a balance capacity of 1500 mg.

The isothermal kinetics of sorghum drying were studied at different temperature levels including 40, 50, 60, 70, 80, 90, and 100 °C for 4 h. The temperature range, selected for this study, was considerably below that needed for thermal decomposition of the biomass (Sadaka *et al.* 2014). Hence, the mass loss observed was due only to the release of moisture from the grain. Three kernels of grain sorghum were placed in the crucible, heated to the desired temperature level, and then maintained under isothermal conditions for 4 h. The heating rate of 40 °C/min was selected to minimize the time to reach the desired temperatutre. Nitrogen gas was used as a purge gas at a flow rate of 30 mL/min. The crucibles were cleaned and inspected before each run to avoid influence of any remaining residuals.

Methods

Isothermal kinetic analysis of grain sorghum drying

The moisture ratio (*MR*) of grain is considered the proportion of the removed moisture on a dry basis at any time to the overall removed moisture during the drying process. The *MR* values under isothermal conditions was determined by the following equation Eq. 1,

$$MR = \frac{M - M_e}{M_0 - M_e} \quad (1)$$

where *MR* is the moisture ratio, *M* is the moisture content at any time > 0 (%, dry basis), M_o is the initial moisture content (%, dry basis), and M_e is the moisture content at the end of the drying process (%, dry basis).

The drying curves obtained from the TGA data under the isothermal conditions were fitted with four well-known drying models, namely the Page, Newton, Logarithmic, and Henderson models as shown in Table 1.

Table 1. The Isothermal Models Used in this Study (Chen *et al.* 2012a)

Model	Isothermal Models	References	Eq. No.
Page	$MR = \exp(-kt^n)$	Page (1949)	2
Newton	$MR = \exp(-kt)$	Lewis (1921)	3
Logarithmic	$MR = a + b \exp(-kt)$	Akpinar *et al.* (2003)	4
Henderson	$MR = a \exp(-kt)$	Henderson and Pabis (1961)	5

Note: *k* is the drying constant (min^{-1}), *t* is the drying duration (min), *n* is the reaction order, and *a* and *b* are the drying constants

Grain sorghum collection and characterization

To determine the effective moisture diffusivity (D_{eff}) and activation energy (E_a), Fick's second law, shown in Eq. 6, was used as follows,

$$\frac{\partial MR}{\partial t} = \nabla \left[D_{eff} \left(\nabla MR\right)\right] \quad (6)$$

where D_{eff} is the effective moisture diffusivity (m^2/s).

The mathematical solution of Eq. 6 is shown in Eq. 7 (Ashraf *et al.* 2012),

$$MR = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 D_{eff}\, t}{4L^2}\right) \quad (7)$$

where *L* is half of the kernel geometric mean diameter (m).

Equation 7 could be further simplified into a straight-line equation as shown in Eq. 8 (Dadali *et al.* 2007):

$$\text{Ln } MR = \ln\left(\frac{8}{\pi^2}\right) - \left(\frac{\pi^2 D_{eff}}{4L^2} . t\right) \quad (8)$$

A straight line is obtained from Eq. 8 by plotting Ln (MR) *versus* drying duration, and the D_{eff} for each temperature can be calculated from the slope:

$$Slope = \frac{\pi^2 \ D_{eff}}{4L^2} \quad (9)$$

The temperature dependence of D_{eff} is usually expressed by an Arrhenius relationship as in Eq. 10 (Cai and Chen 2008),

$$D_{eff} = D_o \exp\left(- \frac{E_a}{R\ (T+273.15)}\right) \quad (10)$$

where D_0 is the pre-exponential factor (m^2/s), E_a is the activation energy (kJ/mol), T is the drying temperature (°C), and R is the ideal gas constant (8.314, J/K.mol).

The activation energy can be calculated by simplifying Eq. 10 into a straight-line equation as follows in Eq. 11:

$$\text{Ln}\ (D_{eff}) = \ln(D_o) + \frac{E_a}{R}\left(\frac{1}{(T+273.15)}\right) \quad (11)$$

The activation energy could be determined from the slope of the straight line formed from plotting ln(D_{eff}) *versus* [l/ (T + 273.15)].

Model fitting to the experimental data

The experimental data obtained were fitted into the above mentioned four models. The nonlinear regression was performed by using the Solver feature of MS-Excel (Microsoft, version 2013, Chula Vista, CA, USA). To calculate the moisture ratio, initial guesses of the model parameters were made on the basis of values reported in published literature. The minimization technique was used to reduce the sum of the square difference between the experimental moisture ratio values and those obtained by fitting the data to the models. The values of the coefficient of determination (R^2), root mean square error (*RMSE*, Eq. 12), and chi-square (X^2, Eq. 13) have been presented along with kinetic parameters to determine the best-fit scenario. The model with the highest R^2 and least *RMSE* and X^2 was chosen as the best model fitting the experimental data,

$$RMSE = \sqrt{\frac{1}{N}\left(MR_{exp,i} - MR_{pre,i}\right)^2} \quad (12)$$

$$X^2 = \frac{\sum_{i=1}^{N}\left(MR_{exp,i} - MR_{pre,i}\right)^2}{N-z} \quad (13)$$

where $MR_{exp,i}$ is the experimental moisture ratio, $MR_{pre,i}$ is the predicted moisture ratio, N is the number of experimental data points, and z is the number of parameters.

RESULTS AND DISCUSSION

Physical Properties of Grain Sorghum

The results of the physical properties of grain sorghum, including moisture content, bulk density, geometric mean diameter, and the mass of 1000 kernels, are tabulated in Table 2.

Table 2. Physical Properties of Grain Sorghum

No.	Properties and Units	Mean* ± SD Value
1	Moisture content (%, w.b.)	20.51 ± 0.61
2	Bulk density (g/cm^3)	0.81 ± 0.01
3	Geometric mean diameter (mm)	3.34 ± 0.11
4	Mass of 1000 kernels (g)	32.9 ± 0.14

* Values are a mean of five replications ± SD

Effects of Drying Temperature and Drying Duration on Grain Sorghum Moisture Ratio

As mentioned earlier, seven drying temperatures (40, 50, 60, 70, 80, 90, and 100 °C) were tested. Data collected from the TGA revealed that it took 3.72, 6.27, 6.78, 7.90, 9.52, 13.93, and 18.60 min to raise the temperature of grains from room temperature to exact values of 40, 50, 60, 70, 80, 90, and 100 °C, respectively. In other words, it took 1.5% to 7.8% of the drying duration (240 min) to reach the exact desired temperature level or the isothermal conditions. Thereafter, the grain sorghum remained under isothermal conditions as evident by the constant temperature readings from the TGA data. Clearly, this was a shorter time as compared with the remaining time under isothermal conditions.

Figure 1 illustrates the effects of drying temperature and drying duration on the moisture ratio of grain sorghum. The results showed that an increased drying temperature shifted the moisture ratio curves to the left, which translated to a faster decrease in the grain moisture content. In other words, the temperature profoundly and positively affected the drying rate.

At higher drying temperatures, especially greater than 60 °C, each moisture ratio curve showed two distinctive stages including a faster moisture loss stage and a slower moisture loss stage, as shown in Fig. 1.

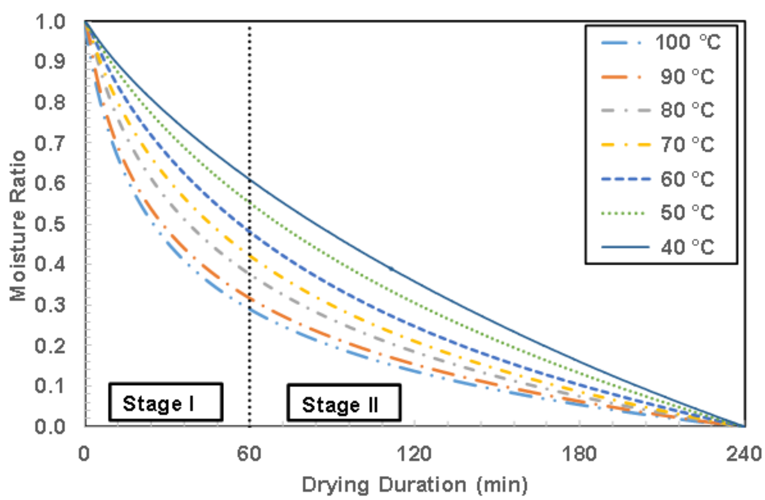

Fig. 1. Effects of drying temperature and drying duration on the moisture ratio of grain sorghum

The faster moisture loss stage took place in the first 60 min depending on the drying temperature, as can be seen by the observable high slope of the tangent lines to the moisture ratio curves. In contrast, the slower moisture loss occurred during the remaining drying duration, as evident by the small slope of the tangent lines to the moisture ratio curves. For comparison, after 60 min (as shown in Table 3), the lowest moisture ratio of 0.2909 was observed at the drying temperature of 100 °C, whereas the highest moisture ratio of 0.6091 was observed with the drying temperature of 40 °C.

The change in moisture loss was directly affected by the binding forces between moisture and grain. Based on the bonding scheme, water in any material is divided into two forms: free water and bound water. Free water is usually present on a surface with weak forces with the material. Free water leaves early by evaporation, whereas the bound water is distributed inside the material and bounded by strong forces, which requires more energy for removal (Chen *et al.* 2012b). At a relatively low drying temperature (below 60 °C), the removed moisture was generally considered to be the free moisture that was weakly bound to the grain.

Table 3. Effects of Drying Temperature on the Moisture Ratio and Drying Rate After 60 min

Temperature (°C)	Moisture Ratio (-)	DTA (mg/min)
40	0.6091	0.0048
50	0.5536	0.0052
60	0.4819	0.0050
70	0.4232	0.0049
80	0.3773	0.0045
90	0.3181	0.0040
100	0.2909	0.0038

Effects of Drying Temperature and Drying Duration on the DTA

Figure 2 shows the derivative of thermogravimetric analysis (DTA) as a function of the drying duration at different drying temperatures. These graphs demonstrated that the peak of the DTA shifted slightly towards the left as the drying temperature was increased. The left shift signified that the maximum, DTA was accelerated with increased drying temperature, as temperature is the factor that expedites the drying process. An interesting representation was found with the maximum peak of the DTA as shown in Fig. 2. The maximum peak of the DTA reached 0.010, 0.011, 0.015, 0.020, 0.024, 0.037, and 0.040 mg/min, which corresponded to the drying temperatures of 40, 50, 60, 70, 80, 90, and 100 °C, respectively. As the drying duration increased, the weight loss derivative decreased for all of the studied temperature levels. This is attributed to the decrease in the available free water, as the majority of the free water evaporated earlier. The weight loss derivative initially increased to the peak and then decreased to a lower level. As the drying process proceeded, less free water on the surface of grain was available. The rate of moisture removal starts to decline and the falling rate begins, which is mostly the case of a later stage of drying of agricultural commodities. Similar results were reported by Cai and Chen (2008).

As mentioned earlier, for comparison, after 60 min (as shown in Table 3), the lowest weight loss of 0.0038 mg/min was observed at the drying temperature of 100 °C, whereas the highest weight loss of 0.0052 mg/min was observed with the drying temperature of 50 °C. This is because at a higher temperature, the migration of moisture from the grain took place earlier, whereas at lower temperature levels, the grains still had more moisture to release. Also at a longer drying duration, after 60 minutes, the migration of moisture from the grain was very small as evident by the near horizontal lines as seen in Fig. 2.

Ogawa *et al.* (2014) also observed higher DTA values during increased temperature rising conditions with durum wheat dough. The trend of moisture loss derivative in this study was similar to that obtained in Chen *et al.* (2012a). They reported that the peak moisture loss was achieved in the temperature range of 60 to 70 °C when they utilized the TGA technique to dry biomass. Madhava *et al.* (2001) investigated the drying kinetics of paddy over a temperature range of 60 to 100 °C. Different peaks of weight losses were observed at different temperatures. It was postulated, from their results, that drying temperature affects the free moisture loss from the grain.

For comparison purposes, accumulated weight loss values were determined for 30 min intervals under all the studied drying temperatures and are presented in Table 4. Increasing the drying temperature increased the weight loss under the studied drying durations. In contrast, increasing the drying duration decreased the weight loss under the studied temperatures. At the highest temperature of 100 °C and the last thirty min of duration, the weight loss was only 4.5% of the weight loss reported at the first thirty min of duration. Increasing the drying temperature from 40 to 100 °C increased the weight loss rate approximately 679% at the first 30 min of drying duration.

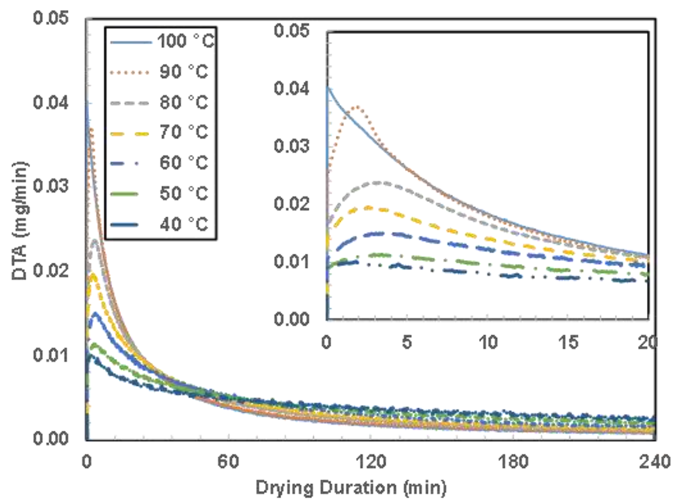

Fig. 2. Effects of drying temperature on the derivative of TGA

Table 4. Effects of Drying Temperature and Drying Duration on DTA (mg/min)

Drying Temp (°C)	Drying Duration (min)							
	0 to 30	30 to 60	60 to 90	90 to 120	120 to 150	150 to 180	180 to 210	210 to 240
40	0.0233	0.0148	0.0123	0.0107	0.0095	0.0086	0.0077	0.0066
50	0.0388	0.0257	0.0197	0.0160	0.0134	0.0116	0.0102	0.0086
60	0.0552	0.0320	0.0224	0.0169	0.0134	0.0109	0.0093	0.0079
70	0.0761	0.0376	0.0243	0.0174	0.0135	0.0110	0.0093	0.0075
80	0.1150	0.0481	0.0294	0.0208	0.0160	0.0129	0.0107	0.0087
90	0.1354	0.0445	0.0255	0.0176	0.0133	0.0108	0.0090	0.0073
100	0.1581	0.0480	0.0266	0.0180	0.0134	0.0106	0.0088	0.0071

Effects of Drying Temperature on the Drying Kinetic Constants

As mentioned earlier, grain sorghum drying was studied under seven drying temperatures. Four models, *i.e.*, Page, Newton, Logarithmic, and Henderson, were fitted to the moisture ratio data for all of the temperature levels. Table 5 shows the drying constants along with the statistical parameters, *i.e.*, R^2, RMSE, and X^2, utilized to govern the best-fit models. All of the models had R^2 values greater than 0.9808, which indicated a sign of good fit. The best combination for each model is presented in bold, as shown in Table 5, which has the highest R^2, and the least RMSE and X^2.

The results revealed that the Page model fitted five cases out of the seven studied cases representing 71.4% of the studied cases. Both the Logarithmic and Henderson models fitted two cases out of the seven studied cases, representing 28.6% of the studied cases. Newton's model did not meet all the criteria of the best-fit models in all the studied cases. Accordingly, it can be suggested that the Page model could be utilized to determine the grain sorghum drying constants under isothermal conditions. These results showed partial agreement with the results reported by Chen *et al.* (2012a). They investigated the drying kinetics of rice straw and found that Henderson's model was the best fit under isothermal conditions. This partial agreement could be postulated to the differences between the two feedstocks. The drying temperature positively affected the drying constant (k_o) for the four studied models, as shown in Fig. 3, and negatively affected the reaction order (n) for the Page model. The drying constant (k_o) values was increased with the increase in the drying temperature signifies that the temperature is the factor that expedites the drying process. The negative effect of the drying temperature on the reaction order is attributed to the mathematical fitting of the data.

Table 5. Effects of Drying Temperature on the Drying Constants for the Studied Models Under Isothermal Conditions*

Model	Temp		Drying Constants					Statistical Parameters		
	°C		k_o	n	a	b		R^2	RMSE	X^2
Page	**40**		**0.0037**	**1.1953**				**0.9884**	**0.0305**	**0.0009**
Newton	40		0.0093					0.9837	0.0423	0.0018
Logarithmic	40		0.0097		0.0000	1.0423		0.9808	0.0400	0.0016
Henderson	40		0.0097		1.0424			0.9808	0.0400	0.0016
Page	**50**		**0.0065**	**1.1018**				**0.9916**	**0.0253**	**0.0006**
Newton	50		0.0105					0.9904	0.0300	0.0009
Logarithmic	50		0.0107		0.0000	1.0199		0.9894	0.0293	0.0009
Henderson	50		0.0107		1.0199			0.9894	0.0293	0.0009
Page	60		0.0124	0.9981				0.9944	0.0199	0.0004
Newton	60		0.0123					0.9944	0.0199	0.0004
Logarithmic	**60**		**0.0121**		**0.0000**	**0.9846**		**0.9949**	**0.0193**	**0.0004**
Henderson	**60**		**0.0121**		**0.9846**			**0.9949**	**0.0193**	**0.0004**
Page	70		0.0209	0.9105				0.9950	0.0178	0.0003
Newton	70		0.0140					0.9937	0.0234	0.0005
Logarithmic	**70**		**0.0132**		**0.0000**	**0.9436**		**0.9950**	**0.0176**	**0.0003**
Henderson	**70**		**0.0132**		**0.9436**			**0.9950**	**0.0176**	**0.0003**
Page	**80**		**0.0314**	**0.8421**				**0.9951**	**0.0168**	**0.0003**
Newton	80		0.0157					0.9909	0.0320	0.0010
Logarithmic	80		0.0142		0.0006	0.9067		0.9919	0.0210	0.0004
Henderson	80		0.0141		0.9069			0.9919	0.0210	0.0004
Page	**90**		**0.0541**	**0.7495**				**0.9950**	**0.0155**	**0.0002**
Newton	90		0.0187					0.9845	0.0464	0.0021
Logarithmic	90		0.0171		0.0235	0.8402		0.9854	0.0259	0.0007
Henderson	90		0.0155		0.8434			0.9843	0.0272	0.0007
Page	**100**		**0.0647**	**0.7237**				**0.9960**	**0.0135**	**0.0002**
Newton	100		0.0206					0.9839	0.0494	0.0024
Logarithmic	100		0.0187		0.0271	0.8198		0.9851	0.0253	0.0006
Henderson	100		0.0165		0.8211			0.9831	0.0274	0.0008

*Note that values in bold font represent the best fit model.

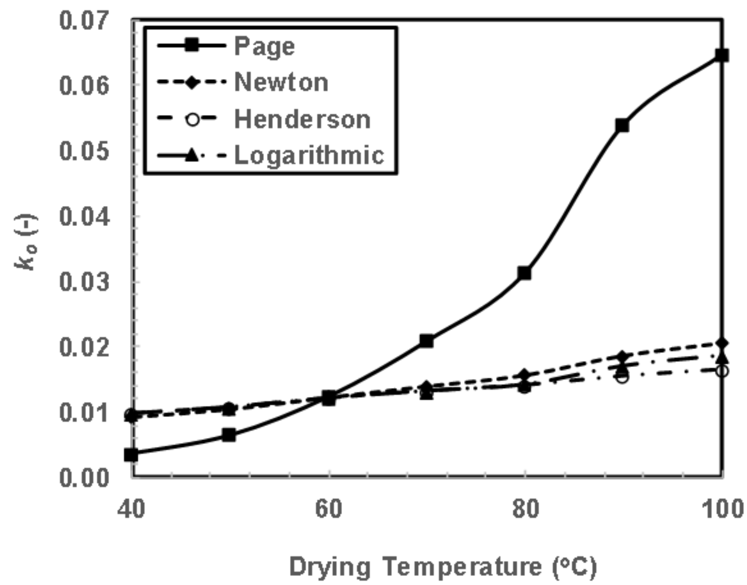

Fig. 3. Effects of drying temperature on the drying constants for the various tested models

Determination of the Effective Moisture Diffusivity and Activation Energy

The D_{eff} values for grain sorghum drying were calculated based on Eq. 9 and are presented in Table 6. Increasing the drying temperature from 40 to 100 °C increased the moisture diffusivity from 0.96×10^{-8} to 1.73×10^{-8} m^2/s. This is attributed to the fact that more moisture is evaporated with a high drying temperature because temperature is the main driving force of moisture evaporation. The values of the D_{eff} obtained from the current study were comparable to those reported in the literature. Correa *et al.* (2011), Chen *et al.* (2012b), and Sandeep *et al.* (2013) evaluated the effective diffusivity coefficient at various temperature levels. They all also concluded that the D_{eff} values increased with increases in the drying temperature.

The effective moisture diffusivity increased with increased drying temperature due to more energy being provided at higher drying temperatures, which increased the activity of water molecules and increased the drying rate. As temperature increased, the bound moisture that is distributed inside the grain with relatively strong bonding began to evaporate in the drying process. Resende *et al.* (2014), also reported that the effective diffusion coefficient of the sorghum grains increased as the temperature and air speed increased. The pattern was described by the Arrhenius equation. The D_{eff} increased linearly with increased drying temperature and air speed, which indicated greater intensity in water transport from the grain's interior to its periphery. Giner and Mascheroni (2002) reported that the values of the diffusion coefficient for the whole kernel ranged from 1.4×10^{-11} $m^{2/}s$ to 7.1×10^{-11} $m^{2/}s$, presenting the classical Arrhenius temperature dependency. This diffusive kinetics is expected to be useful for fast and accurate dryer simulation.

The activation energy was determined by Eq. 11. A linear relationship between *ln* (D_{eff}) and [1 / (T + 273.15)] is presented in Fig. 4 due to the Arrhenius type dependence. The value of the activation energy was obtained from the slope of the line and was 9.4 kJ/mol for grain sorghum under isothermal drying conditions. The activation energy of grain sorghum in this study (9.4 kJ/mol) was higher than that obtained for corn stalk (6.1 kJ/mol) and rice husk (9.2 kJ/mol) by Chen *et al.* (2012b). In contrast, it was lower than those obtained for rice husks (14.1 kJ/mol) by Cai and Chen (2008) and for olive-waste cake (12.3 kJ/mol) by Vega-Galvez *et al.* (2010). Zogzas *et al.* (1996) reported that activation energy generally ranges from 12.7 kJ/mol to 110 kJ/mol for food; therefore, a slightly lower value was observed in the current study. Resende *et al.* (2014) reported that the activation energy values in the sorghum drying process increased with an increase in air velocity. It was also inferior to the value that was established by Correa *et al.* (2011), which verified an activation energy of 10.08 kJ/mol for edible beans, in a temperature range of 25 to 55 °C. The slightly lower value of the activation energy, in the present study, could be attributed to the small flow rate of drying gas or in other words, the small nitrogen velocity utilized in the study. Addtionally, the variation of the drying gas (air or nitrogen) challenging the direct comparison of the activation energy values.

Table 6. Effects of Drying Temperature on the Moisture Diffusivity and Activation Energy

Temperature (°C)	Moisture Diffusivity (m^2/s)	Activation Energy (kJ/mol)
40	0.9665×10^{-08}	9.4
50	1.1178×10^{-08}	
60	1.3158×10^{-08}	
70	1.4438×10^{-08}	
80	1.5370×10^{-08}	
90	1.6418×10^{-08}	
100	1.7349×10^{-08}	

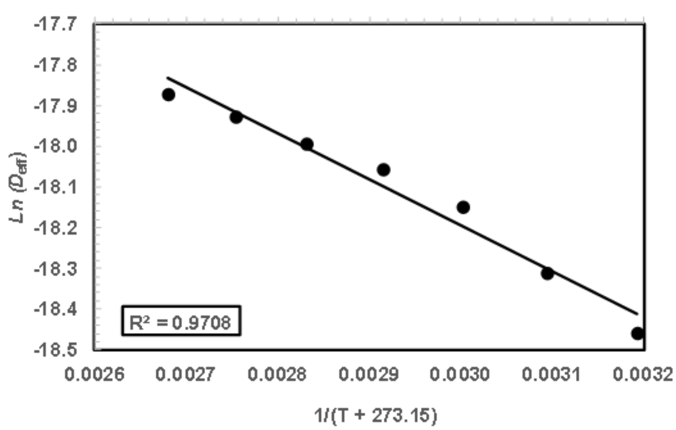

Fig. 4. Arrhenius type relationship between D_{eff} and reverse of absolute drying temperature

CONCLUSIONS

The drying kinetics of grain sorghum under isothermal drying conditions were investigated using TGA. From the experimental work described in this article, several important conclusions can be drawn.

1. Using online weight measurements and precise temperature control, as well as a minimal material requirement, the thermogravimetric approach was suitable for determining the drying kinetics, effective moisture diffusivity, and activation energy of grain sorghum.

2. Both the drying temperature and drying duration affected the moisture ratio values, in which both had a positive effect on the moisture ratio.
3. The Page model was the best fit for describing isothermal drying (71.4% of the studied cases) of grain sorghum.
4. The effective moisture diffusivity ranged from 0.96×10^{-8} m^2/s to 1.73×10^{-8} m^2/s within the given temperature range of 40 to 100 °C. The value of activation energy to dry grain sorghum reached 9.4 kJ/mol for isothermal drying conditions.
5. The moisture ratio results obtained by the TGA needs to be tested experimentaly in grain bin drying.

FUTURE WORK

The drying kinetics, effective moisture diffusivity, and activation energy of other commodities under isothermal conditions will be determined using the thermogravimetric analyzer. It is expected that there will be some variation of the kinetic parameters between grain sorghum and other commodities, depending on the characteristics of these commodities. To fully understand the drying process in grain bins, the TGA data needs to be tested experimentally, since the reaction mechanism may change.

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