

Drying Kinetics of Two Varieties of Bambara Groundnuts (*Vigna subterranea*) Seeds

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Abstract: Bambara groundnuts is an indigenous, underutilized African legume grown primarily for its seeds which are eaten fresh when semi ripe as a pulse when dry and mature or ground into a flour. In this study, the experimental dehydration behavior of two different varieties of bambara groundnuts, Black variety (BB) of moisture content 0.88 g g^{-1} and White variety (WB) of moisture content 0.90 g g^{-1} was investigated and the experiments were carried out under isothermal conditions using convection air-forced dryer at 50, 60 and 70°C . The drying data were fitted to the different mathematical models such as Lewis, Henderson and Pabis, Logarithmic and two-term models. The performance of these models was investigated by comparing the determination of coefficient (R^2), reduced Chi-square (χ^2) and Standard Estimate Error (SEE) between the observed and predicted moisture ratios. The results obtained showed that the logarithmic and the two term models successfully described the drying behaviour of the seeds. Generally, the moisture diffusivity constants derived from the Fick's law of diffusion increased with increase in temperature according to the Arrhenius type equation with BB variety exhibiting low values (5.97×10^{-11} to $8.51 \times 10^{-11} \text{ m}^2 \text{ sec}^{-1}$) and WB high values (1.44×10^{-11} to $2.78 \times 10^{-10} \text{ m}^2 \text{ sec}^{-1}$).

Key words: Bambara groundnuts, seeds, dry kinetic, effective diffusivity, pulse

INTRODUCTION

Bambara groundnuts (*Vigna subterranea*) seeds are important plant food widely produced and consumed in many parts of Africa. They are potentially very rich in proteins and minerals (Minka and Bruneteau, 2000). In Central Africa this legume is commonly cooked and eaten as such or very often is used as a substitute for cowpea (*Vigna unguiculata*) a starting material for the preparation of a widely cherished legume-based food product known as koki (Mbofung *et al.*, 1999). More recently, studies showed that bambara groundnuts milk products are highly acceptable for human consumption and could serve as good weaning foods like Soybean (*Glycine max*) milk (Agunbiade *et al.*, 2011).

Generally, the method of preparing koki is not only laborious, it is equally time consuming and as such not

convenient for individuals living in a busy urban setting. This has a limiting effect on the frequency of preparation and consumption of the product. The successful production of legume-based food flours that can conveniently be used for the preparation of koki could be a way of improving on the availability and consumption of the legume seeds. In fact in the phase of growing urbanisation and increased employment of women in industrial and public sectors, the use of premixes or flours in the preparation of family dishes constitutes a timesaving approach. Such use of flours as ingredients for food processing is dependent on their functional properties which also vary with the drying conditions (Kaptso *et al.*, 2007; Hung *et al.*, 1995).

The major objective of drying is the reduction of the water level of the product for storage during a long time. Drying reduces the water content of food and as such

prolongs the shell life. Drying also has the advantage of reducing the volume and the weight of foods thereby minimizing the cost of packing, storage and transportation (Okos *et al.*, 1992). In this study, drying was exploited in addition as a process of seed shelling. This process is influenced by numerous extrinsic (i.e., temperature) and intrinsic (physical and chemical properties of the seeds) factors. While the effect of extrinsic factors such as temperature on the dehydration kinetic has been extensively explored (Taiwo, 1998) that of intrinsic factors has been limited on the size effect.

Modelling of the drying process of bambara groundnuts is fundamental in determining the optimal time of drying since, varieties of bambara groundnuts have different physical properties (Kaptso *et al.*, 2008). It seems obvious that they could exhibit different behaviours in drying. Many models have been used extensively to follow the drying of fruits as grapes (Doymaz and Pala, 2002), apricots (Togrul and Pehlivan, 2004), figs (Babalís and Belessiotis, 2004), prickly pear (Lahsasni *et al.*, 2004), plum (Doymaz, 2005). Studies on the drying of bambara seeds are very limited, probably because these vegetables are harvested in the dried state.

Therefore, this research was interested in the determination of the drying kinetic as features of two varieties of bambara seeds at three temperatures through some mathematical models available in literature.

MATERIALS AND METHODS

Seed samples: Commonly grown and consumed samples of two varieties of bambara groundnuts (White Bambara coded WB and Black Bambara coded BB) were purchased from a local market in Ngaoundere (Cameroon). Infected seeds and foreign materials were selected from the seeds and they were sealed in polyethylene bags and kept at 4°C in a refrigerator until required for use. The proximate composition of the seeds samples analyzed according to AOAC (1998) and mineral composition by Atomic Absorption Spectroscopy AAS 1100 (Perkin-Elmer, USA) are summarized in Table 1.

Determination of the physical characteristics of seeds:

The physical characteristics of the legumes seeds were evaluated essentially according to Baryeh (2001) with minor modifications where necessary. For each grain sample, 100 grains were selected at random and their individual Length (L), Width (W) and Thickness (T) were measured from the 3 principal dimensions which are in three mutually perpendicular directions using a micrometer gauge reading to 0.01 mm. It was defined as the distance from the eye's seed to the opposite end while W

Table 1: Proximate composition of bambara groundnuts seeds on dry weight basis

Parameters	Varieties	
	White Bambara (WB)	Black Bambara (BB)
Moisture content (%)	11.30±0.24	11.6±0.29
Ash (g/100 g)	3.80±0.07	3.61±0.06
Proteins (g/100 g)	17.80±0.23	19.70±0.17
Available carbohydrate (g/100 g)	61.70±0.44	57.9±1.00
Fat (g/100 g)	6.12±0.02	5.90±0.18
Ca (mg/100 g)	41.56±1.57	3.24±0.05
Na (mg/100 g)	1.11±0.19	1.17±0.61
Al (mg/100 g)	0.52±0.06	0.49±0.01
Mn (mg/100 g)	ND	ND
Fe (mg/100 g)	5.40±0.07	3.21±0.05
Mg (mg/100 g)	248.91±1.25	246.82±2.28
Zn (mg/100 g)	0.53±0.05	1.15±0.01
Cu (mg/100 g)	0.45±0.02	0.47±0.02

ND: Not Detected

and T taking in the two opposite perpendicular direction of eye seed represented the major and the minor seed diameters. Using the different readings, the geometric mean diameter, degree of sphericity, surface area and volume were calculated according to Mohsenin (1970), Baryeh (2001) and Unal *et al.* (2006).

The seed mean mass was determined on 100 seeds using an electronic balance (Sartorius®) with a precision of 0.001. The mean true volume of the seed was determined according to the water displacement method of Karababa (2006). The seed true density (ρ_s), expressed as g/mL was calculated as the ratio of weight of seeds to the true volume while the bulk density (ρ_b), also expressed as g/mL was determined according to Okezie and Bello (1988). Following this the porosity ϵ of the seeds which is the fraction of the space in the bulk seed which is not occupied by the grain was computed from the values of seed true density and bulk density according to Baryeh (2001).

Kinetics of water dehydration: Wholesome seeds of similar sizes of each variety were selected and soaked at room temperature in distilled water (1:3; w/v) for 12 h time from which the saturation moisture was enough to facilitate the removal of seed coat after the drying. In these conditions, the water contents of seeds were 0.88 and 0.90 g g⁻¹ dry seeds for the varieties BB and WB, respectively. After soaking, seeds were equilibrated to room temperature for 5 min after which they were displayed on clays and allowed to dry in a convection air-forced dryer (Riviera and Bar, France) at different temperatures (50, 60 and 70°C). During 780 min of drying, samples were weighed on a balance (Sartorius®) with a precision of 0.001 every 10 min and the changes in mass of the seeds with time were used to plot the kinetic curve of water loss.

Mathematical modelling: In general, drying models can be categorized as theoretical, semi-theoretical and empirical models. Some semi-theoretical drying models that have been widely used in the literature include Lewis Model, the Henderson and Pabis Model, the Logarithmic Model and the two-term model. These models are generally obtained by simplifying the general series solution of Fick's second law. The Henderson and Pabis Model is the first term of the general series solution of Fick's second law. This model used to follow the drying of black tea (Panchariya *et al.*, 2002) is given by the Eq. 1:

$$MR = a.exp(-k.t) \quad (1)$$

The Lewis Model shown in Eq. 2 is a special case of the Henderson and Pabis Model where intercept is unity. It was used to describe the drying of barley (Bruce, 1985; Ayensu, 1997):

$$MR = exp(-k.t) \quad (2)$$

To overcome the shortcomings of the Lewis Model, Yaldiz *et al.* (2001) suggested Eq. 3 as a drying model. This was successfully used to describe the drying characteristics of many agricultural products:

$$MR = a.exp(-k.t)+c \quad (3)$$

The two-term model shown in Eq. 4 is the first two terms of the general series solution to the analytical solution of Fick's second law which has also been used to describe the drying of agricultural products (Togrul and Pehlivan, 2004):

$$MR = a.exp(-k_0.t)+b.exp(-k_1.t) \quad (4)$$

In all these relations, MR is given by the relation:

$$MR = \frac{(Mt-M_e)}{M_0-M_e} \quad (5)$$

where, Mt, M₀ and M_e are moisture contents (expressed in g/g dry matter of seeds) at times t (min), time 0 and to equilibrium, respectively; k, k₀ and k₁ are the kinetic constants of drying expressed in sec⁻¹.

Determination of the effective diffusivity (D_{eff}) and energy of activation (E_a): The effective diffusivity of the seeds was estimated by using the mathematical Fick's Second Model. With assumptions of moisture migrating only by diffusion, negligible shrinkage, constant temperature and diffusivity coefficients and long drying times are given (Crank, 1975):

$$MR = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_{eff} t}{r^2}\right) \quad (6)$$

Where:

D_{eff} = The effective diffusivity (m² sec⁻¹)

r = The radius of the seeds (m)

For long drying times (setting n = 1), Eq. 6 can be further simplified to a straight-line equation as (Riva and Peri, 1986):

$$MR = \ln\left(\frac{6}{\pi^2}\right) - \left(\frac{\pi^2 D_{eff} t}{r^2}\right) \quad (7)$$

The effective diffusivity was determined according to Lomauro *et al.* (1985) by plotting ln(MR) versus time. The slope, k of the straight line obtained was used to calculate the effective diffusivity, D_{eff} as followed:

$$k = \frac{\pi^2 D_{eff}}{r^2} \quad (8)$$

The diffusion coefficients reported were correlated with the reciprocal of the absolute temperature, according to the Arrhenius type equation:

$$D_{eff} = D_0 \exp\left[\frac{E_a}{R(T+273.15)}\right] \quad (9)$$

Where:

D₀ = The diffusivity for an infinite temperature

E_a = The activation energy for moisture diffusion

R = The gas constant (8.31451 J/mol/K)

T = The absolute drying temperature (expressed in °C)

The value of E_a was calculated by linear regression of Log (D_{eff}) versus 1/T.

Statistical analysis: The non-linear regression analysis was performed using the Sigma Plot Computer Program to determine the constant of the models while the linear regression was used to determine the effective diffusion and the activation energy. The coefficient of determination (R²) and the Standard Estimate Error (SEE) generated by the software were used as the criteria for selecting the best model. The higher R²-values and the lower SEE values showed the best fitting parameters (Akpınar *et al.*, 2003). Means and standard deviations were computed from data. Duncan multiple comparison procedure were used to classify the mean when ever there was a significant difference. The statistical analyses and the surface plots were done using Statgraphics 5.0 and Statistica Softwares for Windows, respectively.

RESULTS AND DISCUSSION

Physical properties: The physical properties of the different seed varieties are presented in Table 2. The seeds weight was similar for the two varieties of bambara. The seed weight obtained in the present study (0.62-0.72 g) are in agreement with that obtained (0.50-0.80 g) by Baryeh (2001) for a moisture content of seeds between 5 and 35% who found that seed mass increases linearly with seed moisture content.

The seed weight obtained was higher than those reported by Dje for four varieties of Ivorian Coast bambara seeds (0.48-0.55 g) and Olapade *et al.* (2002) for eight varieties of Nigerian cowpeas. No significant difference was observed among the weight and size (L, W and T) of bambara seeds varieties. In fact Olapade *et al.* (2002) and Taiwo (1998) reported on cowpea seeds the range values of L, W and T to be 0.73-1.00, 0.49-0.73 cm and 0.33-0.57 cm, respectively while the corresponding range values reported by Baryeh (2001) on bambara seeds were 1.01-1.52, 0.95-1.15 and 0.82-1.10 cm, respectively.

In relation to L, W and T, the values of Dg obtained are in conformity with those obtained by Baryeh (2001) on bambara grains. In addition it was observed that bambara has a more rounded shape as referred to the degree of sphericity. Similar elliptical shapes of bambara seeds had been reported by Baryeh (2001). The true volume of the seeds also showed significant variation with black bambara exhibiting the lowest value and the white bambara seeds the highest.

It was observed that the calculated volumes (Vg) were systematically lower than the true volume. Consequently and in conformity with studies by Baryeh (2001), the grain density, ρ_g was systematically higher than the bulk density. While the range of values for grain density in the present study is higher than that reported by Olapade *et al.* (2002) for nine Nigerian cowpea varieties. The bulk density (0.88-0.91 g mL⁻¹) was much higher than that reported by the same researchers (0.61-0.72 g mL⁻¹). The differences could be due to the water content of the seeds. In fact, Baryeh (2001) had shown that the specific and the bulk density of bambara seeds decrease with increase in water content; the bulk density being most affected by the variation in water content between 5 and 15%.

Mathematical constants of models: The drying rate curves of the WB and BB seed varieties at the temperatures of 50, 60 and 70°C are shown in Fig. 1. It is clear from these curves that temperature and time have significant effect on moisture loss in both WB and BB

Table 2: Some physical characteristics of bambara groundnuts seeds

Parameters	Bambara groundnuts	
	WB	BB
Width (cm)	0.99±0.09	0.94±0.08
Thickness T (cm)	0.99±0.09	0.94±0.08
Length L (cm)	1.18±0.08	1.19±0.10
Weight (g)	0.72±0.08	0.62±0.035
Dg (cm)	1.05±0.07	1.02±0.07
True volume (mL)	0.54±0.07	0.49±0.03
Degree of sphericity	0.89±0.06	0.85±0.06
Volume Vg (cm ³)	0.53±0.13	0.47±0.12
Porosity ε (%)	32.53±2.14	29.92±1.63
Surface S (cm ²)	3.48±0.44	3.26±0.45
Bulk density ρ_b (g mL ⁻¹)	0.91±0.03	0.88±0.02
True density ρ_g (g mL ⁻¹)	1.33±0.06	1.26±0.02
Surface colour	Cream	Black

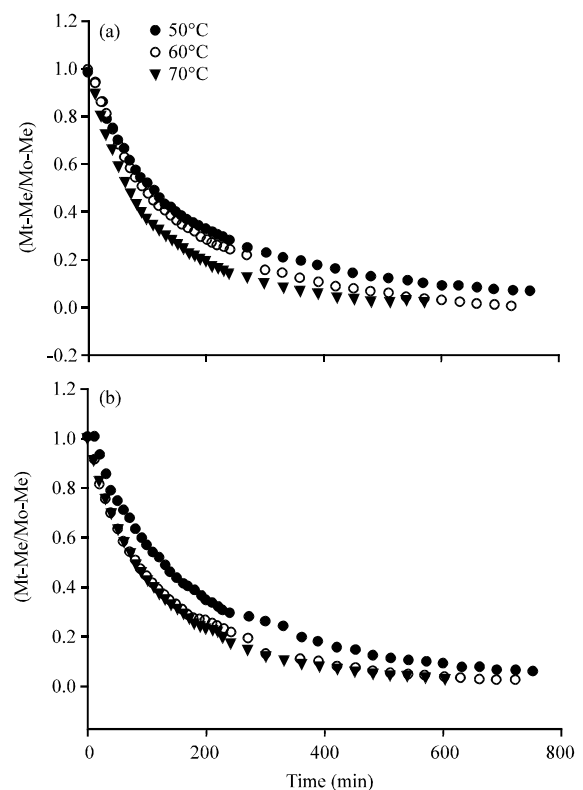


Fig. 1: Varietal and temperature differences in drying pattern content of; a) white and b) black bambara groundnuts

varieties. In fact, moisture loss is the major mass transport phenomenon that takes place during dehydration of food products. It is also visible as expected that the equilibrium moisture content decrease with increasing temperature. The equilibrium moisture contents for WB variety were 0.18, 0.11 and 0.10 g kg⁻¹ dry solid, respectively for 50, 60 and 70°C while the corresponding values for BB variety were 0.12, 0.12 and 0.11 g kg⁻¹ dry solids. The application of the models to the drying of bambara seeds revealed

Table 3: Curve fitting criteria for various models and for drying of characteristics of legume following the different models

Models	White Bambara (WB)			Black bambara (BB)		
	50°C	60°C	70°C	50°C	60°C	70°C
Lewis						
k (10^{-2})	0.56±0.02 ^a	0.66±0.03 ^b	0.91±0.01 ^d	0.56±0.00 ^a	0.74±0.02 ^c	0.78±0.02 ^c
r ²	0.96	0.99	0.98	0.98	0.98	0.98
SEE	0.05	0.02	0.03	0.04	0.04	0.03
Henderson and Pabis						
a (10^{-2})	91.2±1.10 ^a	95.7±0.7 ^c	94.3±0.6 ^{bc}	92.3±0.3 ^{ab}	92.3±0.70 ^{ab}	94.6±0.30 ^{bc}
k (10^{-2})	0.49±0.01 ^a	0.63±0.03 ^b	0.85±0.07 ^c	0.56±0.02 ^a	0.67±0.01 ^b	0.73±0.02 ^b
r ²	0.98	0.99	0.99	0.99	0.99	0.99
SEE	0.04	0.02	0.02	0.03	0.03	0.02
Logarithmic						
a (10^{-2})	87.5±1.40 ^a	94.6±1.6 ^{ab}	92.5±1.20 ^b	89.3±1.2 ^{ab}	90.5±1.90 ^{ab}	92.36±1.7 ^{ab}
k (10^{-2})	0.67±0.02 ^{ab}	0.67±0.05 ^{ab}	0.97±0.08 ^d	0.61±0.05 ^a	0.77±0.04 ^{bc}	0.84±0.03 ^{cd}
c (10^{-2})	8.73±0.14 ^a	2.27±0.12 ^a	3.92±0.12 ^b	6.11±0.15 ^d	4.02±0.17 ^b	4.64±0.18 ^c
r ²	0.99	0.99	0.99	0.99	0.99	0.99
SEE	0.02	0.02	0.02	0.01	0.02	0.01
Two-term						
a (10^{-2})	49.2±1.20 ^d	24.4±1.80 ^a	39.1±0.90 ^c	38.4±1.10 ^{bc}	33.2±2.50 ^b	40.4±2.10 ^c
k ₁ (10^{-2})	1.31±0.03 ^c	2.23±0.06 ^d	2.17±0.05 ^c	1.32±0.07 ^a	2.32±0.06 ^c	1.74±0.05 ^b
b (10^{-2})	51.0±1.70 ^a	77.5±2.50 ^d	61.6±1.30 ^{bc}	60.4±1.60 ^b	67.4±3.50 ^c	60.0±3.00 ^b
k ₂ (10^{-2})	0.28±0.03 ^{ab}	0.52±0.04 ^{ab}	0.61±0.01 ^{ab}	0.35±0.03 ^{ab}	0.58±0.04 ^{ab}	0.51±0.03 ^{ab}
r ²	0.99	0.99	0.99	0.99	0.99	0.99
SEE	0.01	0.01	0.01	0.01	0.01	0.01

*Means with the same superscript along the lines are not significantly different at $p < 0.05$. SEE is the Standard Estimate Error, R² is the coefficient of determination of the model, k, k₁ and k₂ are the constant rate of dehydration

that the respective equations generally had high R² and low SEE (Table 3). In fact, R² and SEE range values were respectively 0.96-0.99 and 0.0049-0.046 indicating a good fit (Madamba *et al.*, 1996).

As expected, the Lewis Model for both WB and BB seed varieties dried at 50°C exhibited the highest SEE (0.05) and the lowest R²-value (0.96). For this model, it was observed that drying temperature have a significant effect on the rate constant of dehydration, k. The constant rate varied between 0.56×10^{-2} and $0.91 \times 10^{-2} \text{ min}^{-1}$ values which were lower than that ($3.04 \times 10^{-2} \text{ min}^{-1}$) found by Doymaz (2005) for drying of figs. The low values of the rate constant of diffusion of bambara seeds may be attributed to low diffusivity of water through the shell membrane. Comparatively the Henderson and Pabis Model exhibited higher R²-values and lower SEE with the rate constant of dehydration, k, varying from 0.49×10^{-2} to $0.85 \times 10^{-2} \text{ min}^{-1}$ not significantly different to that from the Lewis Model. The logarithmic and the two terms models exhibited the highest values of R² and the lowest SEE suggesting that they can be successfully applied to the dehydration kinetic of Bambara seeds.

Effective diffusivity and energy of activation: According to Eq. 7, the plot of MR versus time yielded two straight lines between times 0 and 40 min and from 40-780 min, corresponding to two falling rate periods. The values of the effective diffusivity were calculated for the second falling rate period for each variety and temperature separately (Fig. 2 and 3). The results of effective diffusivity (D_{eff}) are presented in Table 4. D_{eff} of the WB

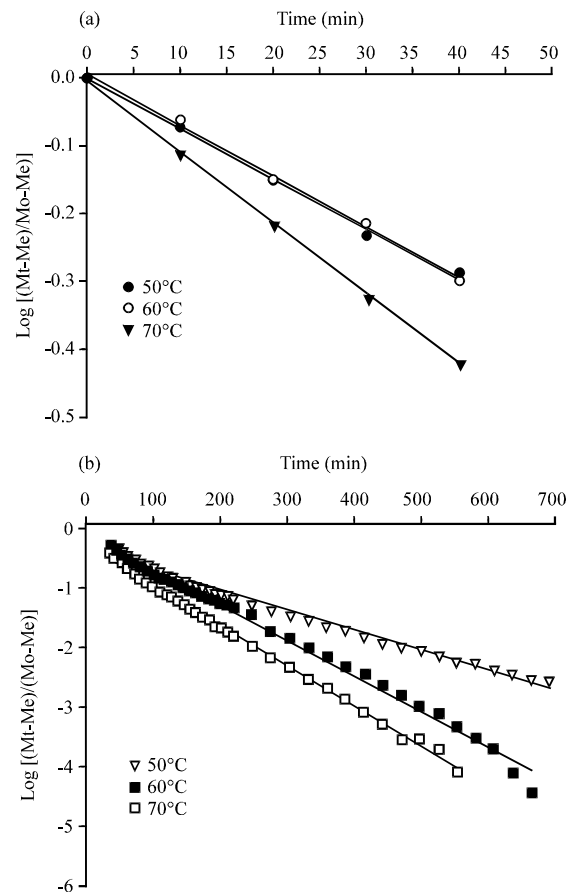


Fig. 2: Logarithmic variation in dry matter of white bambara; a) 1st falling rate, b) 2nd falling rate

Table 4: Diffusion coefficients and energy of activation for the two varieties of Bambara

Materials	Temperature	Time (min) to reach M_e	D_{eff} ($m^2 sec^{-1}$)	Activation energy E_a ($kJ mol^{-1}$)	Relationship	R^2
WB	50°C	690±30	1.44×10^{-10}	31.90	$D_{eff} = 2.14 \times 10^{-05} \exp(-31.90.10^3/RT)$	0.89
	60°C	480±30	2.48×10^{-10}			
	70°C	310±20	2.78×10^{-10}			
BB	50°C	>780	5.97×10^{-11}	16.43	$D_{eff} = 2.79 \times 10^{-08} \exp(-16.43.10^3/RT)$	0.92
	60°C	540±20	7.90×10^{-11}			
	70°C	480±20	8.51×10^{-11}			

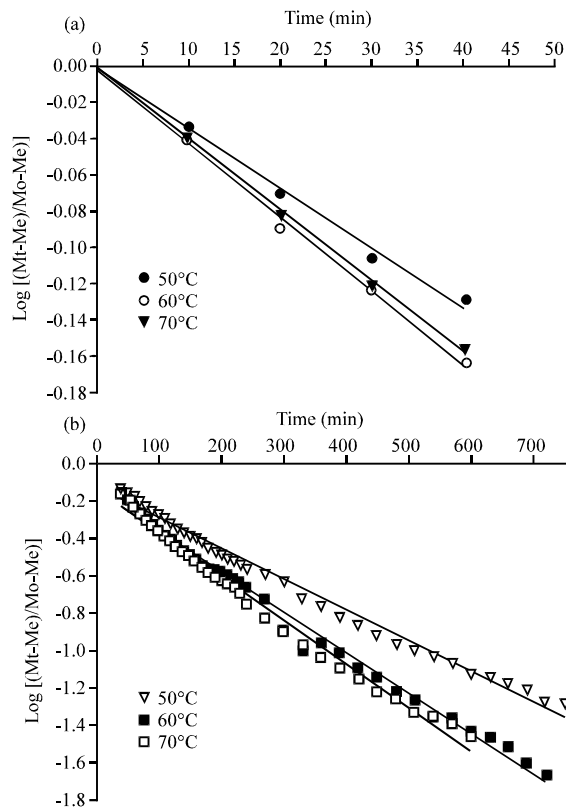


Fig. 3: Logarithmic variation in dry matter of black bambara; a) 1st falling rate and b) 2nd falling rate

variety were systematically higher than that of the BB variety. D_{eff} of WB variety varied from 1.44×10^{-10} to $2.78 \times 10^{-10} m^2 sec^{-1}$ as the drying temperature increased from 50-70°C. For the same range of temperature, D_{eff} of BB variety varied from 5.97×10^{-11} to $8.51 \times 10^{-11} m^2 sec^{-1}$. In recent studies, Kaptso *et al.* (2008) revealed a high diffusivity of moisture in WB variety during hydration. The results so obtained confirmed the high diffusivity of moisture in WB seeds, suggesting a difference in the physicochemical characteristics of these food materials. Comparatively to other foodstuffs, D_{eff} obtained for bambara groundnuts were lower than $1.3 \times 10^{-9} m^2 sec^{-1}$ reported for apricots (Mahmutoglu *et al.*, 1995) but within the general range of 10^{-9} to $10^{-11} m^2 sec^{-1}$ reported for food materials (Madamba *et al.*, 1996; Doymaz, 2005). At the best of the knowledge, the present values of effective

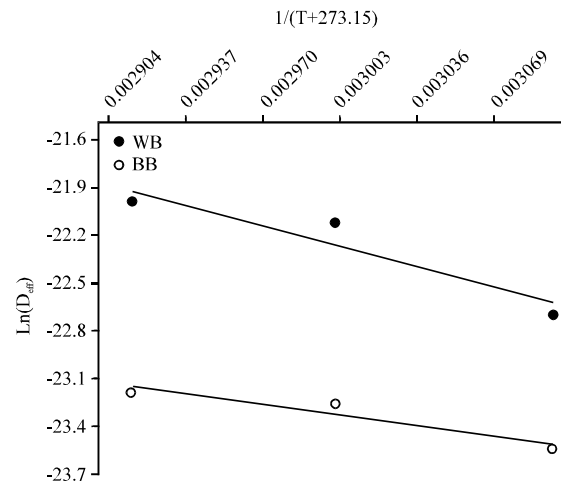


Fig. 4: Logarithmic variation of the effective diffusivity with temperature for the two varieties of bambara

diffusivity are the first in the literature for bambara groundnuts. The results so obtained are of great interest in the control of moisture during drying of bambara seeds.

From the graphs of Fig. 4, it is possible to verify the increase in diffusivity when the temperature is raised. The slope of the Arrhenius curve for the BB seeds appeared to be slightly flatter than that for WB seeds. This indicated that changing the drying temperature has a greater effect on water dehydration kinetics for BB seeds than for WB seeds. From the slope of the straight line, the activation energy E_a of 31.90 and 16.43 $kJ mol^{-1}$ were obtained for WB and BB varieties, respectively (Table 4) while the corresponding Arrhenius factors (D_0) were 67.99×10^{-3} and 10.04×10^{-5} . The values of E_a obtained in this research are in the range of 15 and 95 $kJ mol^{-1}$ reported for other food products (Ramallo *et al.*, 2001; Konishi *et al.*, 2001; Park *et al.*, 2003). The lower value of the activation energy found for BB seeds compared to WB seeds was not expected since recent studies by Kaptso *et al.* (2008) on hydration kinetic of these seeds revealed higher activation energy for BB seeds. The difference on the activation energy of dehydration and hydration highlighted modifications that could have taken place during the hydration process prior to dehydration. In fact, it has been shown that compared to WB variety, the seed coat by BB variety provided a primary barrier to rapid absorption of moisture (Kaptso *et al.*, 2008). This

suggested that during dehydration the seed coat do not longer constituted a barrier and in this respect, the diffusion totally depended on the physicochemical characteristics of the cotyledons such as their capacity to interact with water, the porosity of the grain, etc. Findings by Abu-Ghannam and McKenna (1997) on hydration kinetic of beans have shown that the role of the barrier induced by seed coat to moisture exchanges is lower at high moisture contents and temperatures due to plasticizing effect of water. Evaluating the properties of the cotyledons then appeared more important to help in understanding the difference in the diffusivity of the two seeds varieties.

CONCLUSION

The present study revealed that the two varieties of bambara seeds have different physical properties. The white bambara are bigger in size while black bambara are smaller in size. The empirical models used in this research adequately describe the drying behaviour of white and black bambara groundnuts seeds for the range of temperatures 50-70°C. The moisture diffusivity constants of the two varieties increase with increase in temperature according to the arrhenius equation with BB variety exhibiting low values and WB high values. The moisture diffusivity constant through seeds during drying is related to the ability of seed constituents to absorb water and to some extent to the porosity of flour. The influence of temperature on the drying process is an important aspect to take into consideration when choosing the operation conditions. The results obtained in the present work show that it was possible to infer that the choice of higher temperatures allows faster drying rates resulting in faster dehydration processes with important economical aspect.

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