Journal of Newviews in Engineering and Technology (JNET)
Vol 1, Issue 1, December, 2019
Available online at http://www.rsujnet.org/index.php/publications/2019-edition

Texture Change Kinetics of African Breadfruit *(Treculia Africana)* Parboiling.

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ABSTRACT:
Wide application of African breadfruit (Treculia africana) in the food industry is limited by dearth of information on its thermal-strength kinetics when parboiled. The texture parameter behavior of African breadfruit when parboiling was investigated using the fractural force obtained from compression test on the Instron testing machine. Parboiling was done using a thermostat fitted water bath for temperatures ranging from ambient condition through 60°C, 80°C and 100°C, at parboiling times of 10 min, 20 min, 30 min, and 40 min. The fracture forces obtained was imputed into the zero order, first order and second order rate equation models and the curve of best fitted reaction kinetic model was obtained. It was discovered that textural change of African breadfruit parboiling follows second order reaction kinetics model as well as the best regression reliability with a coefficient of determination of 99.540% with a reaction rate constant of 1.416X10^{-9} min^{-1}, and the pre-exponential factor observed to be 1.36X10^{-9}min^{-1}. This work also revealed that the reaction rate of African breadfruit parboiling is dependent on temperature. The activation energy was determined to be117.851 kJ/mol

Keywords: Parboiling, Textural change, Fractural force, kinetics order, activation energy.

Cite This Paper: Wome N. N., Ademiluyi F. T., & Kiin-Kabari, B. D (2019). Texture Change Kinetics of African Breadfruit *(Treculia Africana)* Parboiling. Journal of Newviews in Engineering and Technology. 1(1), 81-90.

1. INTRODUCTION:

African breadfruit (*Treculia africana*) is a leguminous plant belonging to the family of Moraceae, speculated to be of tropical African origin, such as Nigeria, Ghana, Sierra Leone. It can also be found in the West indies and Jamaica (Orwa *et al.,* 2009). Africana breadfruit is a widely grown forest tree for purpose of eating the seeds. It is an important dietary source of protein, calories and other food nutrients for many people in some parts of West Africa. The hard hull and the coat are regarded as chaff when processed.

The cotyledon is good source of food and has a high nutritional status (Orwa, 2009; Nwafor & Mba, 1988). African breadfruit is a good source of vegetable oil (Osabo, et. al. 2009; Onwuka, 1983). It may be eaten roasted, fried or cooked into porridge. The hulls can be fortified with groundnut and maize meal in proper proportion to serve as animal feeds, particularly for snail feed (Ejidike & Ajileye, 2007).

Texture is an important quality parameter which determines the process conditions and acceptability of any food product (Rabeler & Feyissa, 2018). Due to its demand in the industry, the focus in food engineering, science and technology in recent times is to predict the change in the quality of food as a function of both time and environmental conditions. This is necessary in order to generate valuable information for processing, machining, packaging and marketability, and to ensure that the food does not fall below label value. In order to make such useful predictions, substantial information about the kinetics of the reactions leading to loss of quality or nutritional values in the food and the food materials response to external environment are required (Rabeler & Feyissa, 2018; Ling *et al.,* 2015; Labuza, 1984).

Foods are very complex systems and that is why the science of food is sometimes referred to as the study of "messy" chemistry, because it is not always possible to isolate clear-cut chemical reaction mechanisms which lead to the observed changes in the food quality or to have elegant mathematical models that can describe the reaction rate under a variety of conditions, thus compromises some time may be made (Labuza 1984). The important environmental factor in the processing of food materials is temperature, process time and mechanical forces.

Modeling therefore becomes a good tool to justify an optimal process and conditions since most food processing takes place under non-isothermal and non-adiabatic conditions (Onwuka 2005). Kinetic model and fractional conversion are two basic approaches widely used in describing the texture or cellular collapse of biomaterials during thermal processing. The Kinetic model is the measurement of reaction rates for analytical determination of the initial concentration of species of interest taking path in chemical reactions (Onwuka 2005). The kinetic models provide more in-depth understanding of the mechanisms of texture changes during thermal treatment.

In another development, it was reviewed that the core of thermal kinetic studies on food quality changes is all about to quantify a quality attribute using a reaction kinetic model (Rabeler & Feyissa, 2018; Ling *et al.*, 2015). The order of kinetics of quality change can then be determined by plotting the curve of best fit or the goodness of fit of the observations to the reaction order model. According to the report, Kinetics of food quality changes generally follows zero- order, first-order, or second-order reactions kinetics.
This implies that, to accomplish the primary objective of thermal processing (optimise the retention of quality factor while providing a low risk food product), it is necessary to obtain quantitative data on thermal degradation of quality factors (Romaswamy & Marcotte, 2006).
Majority of the reactions occurring in food materials obey well-established kinetics. The thermal destruction of microorganisms, nutrients, quality factors (textures, colour and flavour) and enzymes generally obey first-order reaction kinetics and are temperature dependent (Asmaa *et al.*, 2016; Ansari *et al.*, 2014; Fennema, 1975). According to these authors, real food products do not heat instantaneously but go through a time-dependent temperature treatment, the rate inactivation at several lethal temperatures must be known. He further stated that there are two principal methods of describing the dependence of the reaction rate constant on temperature: The Arrhenius equation (1973) and the thermal death time curve.

When investigating the textural degradation of food material, the concentration term in a chemical reaction model is simply replaced by the textural property measured as firmness. A question may be raised as to the reliability of the kinetic model when concentration terms are replaced with textural properties. This is taken care of by the concept of fractional conversion widely used in chemical engineering to provide an accurate method of correlating the extent of a chemical reaction with the measurement of physical properties (Onwuka, 2005). Most food materials obey a well-defined reaction kinetics model and their reaction rate constant is temperature dependent (Arrhenius temperature dependent). The plot of the reaction rate constant verses the inverse of the absolute temperature would yield a straight line. The activation energy can be deduced from the slope (Ling *et al.*, 2015; Athinoula *et al.*, 2002; Levenspiel, 1973).

Rabeler and Feyissa (2018) studied the kinetic modeling of texture and color Changes during thermal treatment of chicken breast meat. It was discovered that the texture and color showed an increase with increasing with time until they reach an equilibrium point, while the rate of change increased with temperature increase. As a result of this outcome they developed a Kinetic model that take the non-zero equilibrium into account to describe the texture and colure changes of chicken breast meat with temperature and time.

The thermal kinetics of texture variability for raw and roasted hazelnuts was studied by Demir and Cronin (2004) using instrumental analysis. They presented the textural changes in hazelnuts by the fractural force obtained from compression tests. The analysis showed that both time and temperature effects were significant on the textural changes of hazelnuts as represented by the fracture force. The texture response was found to demonstrate the highest sensitivity to temperature change. The goodness-of-fit of zero and first order models to the fractural force was analyzed. It was observed that the overall fit of the zero-order reaction to texture response of force was not as good as for the first-order reaction.

In further study, Xie *et al.* (1998) investigated the textural changes of dry pea in long time cooking and found out that it follows the first-order reaction kinetic. Lau *et al.* (2000) showed that the thermal softening of green asparagus followed first-order reaction kinetics. The textural changes of potatoes during cooking has been describe by Verinden *et al.* (1995) using the first-order reaction kinetics as the best kinetic model.

The kinetics of textural changes of Salmon fish under temperature and time treatments was investigated by kong *et al.* (2007) using shear force as the textural parameter. The First order reaction kinetics were found to give the best curve fit to the model. Arrhenius model (1973) was used to express the temperature dependent on rate constant. A two fractions first order reaction model was found fit with textural change of Portuguese cabbage treated with UV-C and heat blanching. It was also discovered that temperature dependence on firmness followed the Arrhenius behavior (Cruz *et al.,* 2016).

Parboiling otherwise represents a key unit operation in the dehulling or decortications of African breadfruit for human consumption. This is necessary because hull of legumes is known to contain some anti-nutritional factors, such as tannin and some inhibitory enzymes (Banigo et al., 2009). As such, efficient dehulling of legumes is a major problem hindering their wide use as food (Lazaro & Favier, 2002). The essence of putting in place a cost effective and process suitability parboiling process for Africa breadfruit is to eradicate the tediousness inherent in the dehulling process. It is unfortunate to observe that this concept is far away from reality. Though few research works have been done on the bio-chemical and the physical characteristics of African breadfruit, but their findings are not enough to develop and fabricate functional processing method and hardware that takes into consideration the thermal-strength kinetics of African breadfruit parboiling.

This work investigated the reaction kinetics order that best describes the textural change of African breadfruit parboiling. It also established the thermal kinetics parameters of African breadfruit parboiling which can be utilized for design of optimal parboiling process and hardware

2. MATERIALS AND METHODS:

2.1 Sample Preparation

African Breadfruit (Trecilia Africana) seeds used for this experiment were bought from five major markets in south-east and south-south regions of Nigeria. The seeds were sieved and sorted manually for viability of the seeds. Samples were washed with clean running water tap. The washed samples were dried off of water particles by placing them in a big basin with drainers. The samples were then separated into parts and tied with cellophane bags for the different parboiling temperature and time treatments. Eighty (80) g of sample in 30 ml of distilled water were parboiled for each test using a thermostat fitted water bath (Technotest 3539, Italy) model in the Food Science and Technology laboratory, Rivers State University. The Parboiling process was conducted at 60^{o}C, 80^{o}C, and 100^{o}C for parboiling time of 10 min, 20 min, 30 min and 40 min to determine the fractural force used as the textural parameter used for testing the reaction kinetics models.

2.2. Determination of fractural force

The determination of the fracture force requires the product of a complete force-deformation curve using the universal Instron testing machine (Model 440, Instron Limited, England). Compression tests was conducted in conformity with ASAE standard 5368.4 (2000). The test procedures are:

i. The diameters of the specimen were measured and recorded.

ii. A flat plate compression test was selected, and installed in the Instron Universal testing machine.

iii. The specimen was placed in the testing machine under the compression tool, in directions along the longitudinal (split axis).

iv. The machine started and the compression test was run at a slow speed of 2.8mm/min to allow a reasonable period of time of compressive force before failure.

v. The complete force-deformation curve through the point of rupture was recorded. Five (5) replications of the complete test were performed.

vi. Values for force and deformation to bioyield and ruptured point which was indicated by a sudden drop in force were read directly from the curve and recorded.

2.3 Determination of Textural Change Kinetic Order.

The fracture force corresponding to various parboiling temperatures and times were used to substitute for concentration into the equations of zero – order, first – order and second - order reaction kinetic models. The rate constant (K) for all the Kinetic models were determined accordingly and a regression analysis was performed using DataFit software. The best fitted reaction order was determined by comparing the coefficient of determination (R^2) and estimated error (E) for all the temperatures subjected to the 3 reaction kinetics models. The temperature dependence of fractural force was determined using Arrhenius equation model as indicated by (Kong *et al.*, 2007; Athinoula *et al.*, 2002; Cruz *et al.*, 2016). The value of the coefficient of determination (R^2) obtained from the plot of k versus 1/T showed the best degradation rate constant (k) is dependent on Arrhenius temperature. From the straight line of this plot, the pre-exponential factor A_o, Activation energy E_a, the correlation coefficient (R^2) of the texture parameters were obtained in such a way that, E_a and A_o were calculated from the slope and intercept of the regression variable results. (Abdulhameed *et al.*, 2016).

2.4 Reaction Kinetic Analysis

The rate of degradation of the African Breadfruit is assumed to be the same as the rate equation, r, under isothermal condition expressed as;

$$r = -\frac{dC}{dt} = KC^n \qquad (1)$$

Where,

$-\frac{dC}{dt}$ = rate of change of the textural change

K = texture change constant (min^{-1})

C = concentration indicator of the substance reacting (g/dm^3)

t= time of the reaction (min)

n = reaction order

Fractural force is used in quantifying kinetics of textures degradation as fractional conversion (*f*) (Onwuka, 2005). Therefore equation (1) can be expressed as;

$$f = \frac{F_o - F_t}{F_o} \qquad (2)$$

Where,

F_o = fracture force (N) at time, t = 0

F_t = fracture force (N) at time, t = t

For a Zero – Order reaction kinetics, equation (2) becomes;

$$F_o - F_t = K \times t \qquad (3)$$

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For a first – order reaction kinetics, equation (2) becomes;

$$\frac{F_t}{F_o} = \exp^{(-kx\,t)} \quad (4)$$

For a second - Order reaction, equation (2) becomes; equation

$$\frac{1}{F_1} - \frac{1}{F_o} = K_o\,xt \quad (5)$$

Where;
K_o = rate constant and t = time.
From Arrhenius equation,

$$K_o = A_o \exp.\{\frac{-E_a}{RT}\} \quad (6)$$

Taking natural log of both sides we get;

$$\text{Ink} = In\,A_o - \frac{E_a}{RT} \quad (7)$$

Where,
A_o= Pre-exponential factor and has the same dimension as, K_o
E_a= Activation energy (kJ/mol)
R= Universal gas constant = 8.314 (kJ/mol °K)
T= Absolute temperature (°K)

The plot of K against $1/T$ yields a straight line using the model**;**

Y = a exp$^{(-b/x)}$ (form of Arrhenius equation) (8)

Such that;
Y = K_o (9)

a = A_o (10)

$$(-b/x) = \frac{-E_a}{RT}\,S \quad (11)$$

Where; S = Slope of the model.
Therefore, $E_a = SRT_{ref.}$ (12)

2.5 Data Analysis

Data were subjected to one-way analysis of variance (ANOVA) by using the Minitab 16, 2010 software. Observed Mean values were compared for significant difference p ≤ 0.05 by using the Tukey's multiple comparison test. The best fitted reaction model describing the textural degradation behavior of African breadfruit was determined using DataFit version 9.1.32. This was achieved by comparing the regression parameters of the 3 reaction kinetic models. To determine the percentage of texture dependence on rate constant, a form of Arrhenius equation model (1973), Y = a exp$^{(-b/x)}$ was plotted using DatFit version 9.1.32. The regression parameters of the models were also deduced to characterize order of textural change.

Table1. Effect of parboiling temperature and time on th

Temp. (°C)	Parboiling Time (Min) 0	10	20	30	40
28 (Raw)	135.366[a] ± 1.060	-	-	-	-
60	-	54.244[b] ± 1.`059	44.474[c] ± 2.786	37.941[d] ±2.708	32.147[e] ± 2.069
80	-	18.932[gh] ± 2.078	12.173[j] ± 1.336	10.425[kl] ±1.008	10.283[k l] ±2.058
100	-	9.416[lm] ± 3.946	8.996[mm] ± 1.120	5.794[o] ±2.099	4.476[o] ±1.354

*Values are mean of 3 replications ± Standard deviation means that do not share a letter are significantly different.

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3. Results and Discussion

3.1 Effect of parboiling temperature and time on fractural force of ABF.

The effect of parboiling temperature and time on the compressive force of ABF is presented on Table 1. The compressive force required for the raw African breadfruit at ambient condition was 135.366N ± 1.060. At 60^0C, 10 min of heating, the compressive force values reduced to 54.244 N ± 1.059. At 80^0C, 10 min of heating, the compressive force values also reduced from 18.932 N ± 2.078 to 10.283 N ± 2.058 after 40 min parboiling time.

These values reduced as both temperature and retention time increased. Similarly, at 100°C of heating the required compressive force values were 9.416N ± 3.946, 8.996N ± 1.120, 5.794N ± 2.090 and 4.476N ± 1.354 after 10min, 20 min., 30min., and 40min. respectively of hot water retention time. The result presented above clearly shows that there is an inverse relationship between fractural or compressive force of African breadfruit with parboiling temperature and hot water retention time.
This may be due to the fact that molecules of the seeds lose their intercellular adhesion as uptake of moisture, heating time and temperature increases.

This result agrees with the report of Reeve (1977) which states that cell of potatoes generally ruptures during heating process due to failure of the intermolecular adhesion and moisture absorption. Zzaman and Yang (2013) reported that the fractural force of superheated roasted Cocoa seeds reduced with temperature and time. Demir and Cronin (2004) also reported that the compressive load of hazelnuts roasting decreased with increased roasting temperature and time.

Davis *et al.* (2009) concluded that compressive force of both Adikpo and Lafia varieties of groundnut decreased with increasing blenching temperature and time. The effect of temperature and storage time reduced significant the fracture force of Pistachio nuts as reported by Nikzadeh and Sadghat (2008). Burubai *et al.* (2007) concluded that the compressive force necessary to affect the desired seed coat rupture of African nutmeg decreased with increase pre-heating temperature.

3.2. Determination of the Best Fitted Reaction Kinetic order of Textural Change for ABF Parboiling.

The zero, first and second order reaction models were used to test for the best fitted texture change kinetics order of African breadfruit parboiling for 60°C, 80°C and 100°C at parboiling times of 10 min. to 40 min. The information was calculated from equations (1 to 5) as shown on Table 2.

Table 2. Calculation of texture degradation kinetics order of parboiled ABF

(Temp.(°C)	(min.)	Force (F) (N)	0-Order F_o-F_t= kt	1st - order F_t/F_o= exp(-kt)	2nd – order $\{(1/F_t)$-$(1/F_o)\}$=kt
28 (Raw)	0	135.366			
60	0	135.366	0	1	0
	10	54.217	81.149	0.400521549	0.01105702
	20	44.983	90.383	0.332306488	0.014843241
	30	38.232	97.134	0.282434289	0.01876872
	40	32.097	103.269	0.237112717	0.02376818
80	0	135.366	0	1	0
	10	19.014	116.352	0.140463632	0.045205447
	20	12.388	122.978	0.091514856	0.073335901
	30	10.416	124.95	0.076946944	0.088618765
	40	10.319	125.047	0.076230368	0.089521236
100	0	135.366	0	1	0

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10	10.501	124.865	0.077574871	0.087841646
20	9.503	125.863	0.070202266	0.097842548
30	5.699	129.667	0.042100675	0.168082001
40	4.892	130.474	0.03613906	0.197027993

The plot of the kinetics of textural change of African breadfruit parboiling subjected to the 3 reaction models are shown on Fig. 1 to Fig.3.

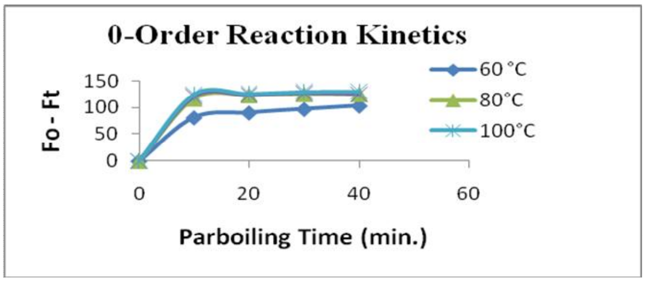

Fig. 1. Kinetics of Texture change of ABF Parboiling using 0 - order Reaction Kinetics.

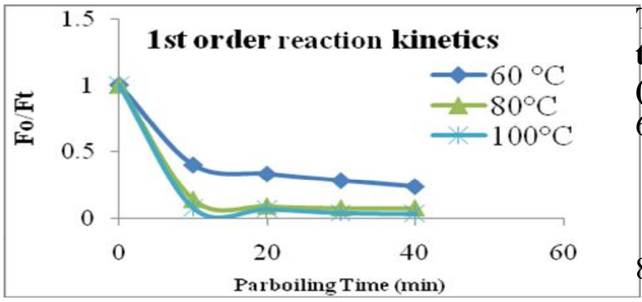

Fig. 2. Kinetics of Texture change of ABF Parboiling using 1st - Order Reaction Kinetics.

Fig. 3. Kinetics of Textural Change of ABF Parboiling using 2nd- order Reaction Kinetics.

The regression parameters such as coefficient of determination, R^2, reaction rate constant, k and standard error, E of Fig. 1 to Fig. 3 were compared to establish the curve of best fitted reaction order using Datafit software to determine the curve of best fit as indicated in Table 3.

It was observed that the second order reaction kinetic model showed a better coefficient of determination values of 0.9080, 0.8059 and 0.9336 and the least standard error values of 0.0027, 0.0166 and 0.0198 for 60°C, 80°C and 100°C respectively. Thus the second order reaction kinetics was the best fitted reaction kinetics order for African bread fruit parboiling. Looking at the second order reaction model from Table 3, the rate constant of textural change of African breadfruit parboiling increased with temperature. The rate constant, K_1 for 60°C was 0.0006 min^{-1} with R_1^2 = 0.9089 and E_1 of 0.0027. For 80°C rate constant, K_2 is 0.0027 min^{-1} with R_2^2 = 0.8059, E_2 of 0.0166. For 100°C K_3 = 0.0052min^{-1} with R_3^2 = 0.9336 with E_3 = 0.0198.

Table 3. Showing the regression parameters of the tested reaction models.

		Kinetic Orders		
Temp t. (°C)	**Kinetic Parameter**	**0**	**1**	**2nd Order**
60	R_1^2	0.4819	0.8592	0.9089
	K_1	3.2213	-0.0544	0.0006
	E_1	30.5091	0.1175	0.0027
80	R_3^2	0.2617	Not Fitted	0.8059
	K_2	4.1245	Not Fitted	0.0027
	E_2	47.1075	Not Fitted	0.0166
100	R_5^2	0.2336	Not Fitted	0.9336
	K_3	4.2916	Not Fitted	0.0052
	E_3	50.0389	Not Fitted	0.0198

This increase in rate constant is in agreement with Peng *et al.* (2014), who reported that the texture kinetics of Carrot cheeps follow second order kinetics model, and the increase in the degradation rate constant of Carrot cheeps texture when treated in varied degree of hot water falls within 0.035min^{-1} and 1.453 min^{-1} for samples immersed in distilled water and 0.018min^{-1} to 0.360min^{-1} for samples immersed in 1.4% $CaCl_2$.

The thiamin degradation in salmon fillets followed second order kinetic model with activation energy of 105.2 kJ/mol when Kong *et al.* (2007) investigated the kinetics of Salmon degradation when heated. However, Lund (1986) concluded that the reaction rate constants of fruits and vegetables are sample specific and are dependent on pH, oxygen, presence of other constituents and environmental factors.

3.3 Determination of the Kinetic Parameters of the texture change of Parboiled ABF

Data obtained with the second order model as shown on Table 4 was used to plot the reaction rate dependence on temperature using equations 8 to 12. The DataFit plot of temperature dependence on rate constant (Arrhenius equation 1973) is shown on Fig. 4. The coefficient of determination $\mathbf{R^2}$ of 0.995 confirms that the rate of change of Texture of African breadfruit parboiling is well described by second order reaction kinetics model and that the reaction rate constant follows Arrhenius equation.

The pre-exponential factor A_o, is the intercept on y-axis of the DataFit regression analysis shown on Fig. 4 as 1.36x10^{-9} min^{-1} using the model Y = a*exp(b/x). (form of Arrhenius equation).The reference temperature is the mean of the three temperatures $\mathbf{T_{ref} = 80^oC}$. The slope of the plot, S =4.05X10^{-2}. The activation energy (E_a) which represents the least amount of energy required for textural change to take place in the cells and tissues of African breadfruit parboiling calculated from equation 12 is **117.851kJ/mol.** The reaction rate constant, $\mathbf{K_o}$ calculated from equation.6 is **1.416x10^{-9}min^{-1}**.

The observed activation energy of 117.851 kJ/mol for African breadfruit parboiling falls within the values of the activation energy reported by Peng *et al.* (2014) for samples of Carrot immersed in distilled water as 138.9 kJ/mol, samples of Carrot treated with 0.1% $CaCl_2$ as 108.0 kJ/mol and for samples of Carrot treated with 1.4% $CaCl_2$ as 108.0 kJ/mol. Lau *et al.* (2000) also reported an activation energy value of 100.6 kJ/mol for green asparagus at temperature treatment range from 70^{o}C to 98^{o}C. This observed activation energy value for African breadfruit parboiling is greater than the value for roasted hazelnut reported by Demir and Cronin (2003) as 39.25 kJ/mol. Huang and Bourne (1983) have reported that the activation energy of vegetables falls within range of 21.35kJ/mol and 146.50 kJ/mol.

4. Conclusion

The fractural force of ABF parboiling reduces as temperature and hot water residence time increases. Using the fractural force as the textural parameter, the textural change kinetics of African breadfruit parboiling follows the second order reaction kinetics model with a reaction rate constant of 1.416x10^{-9}mol^{-1} and pre exponential factor value of 1.36x10^{-9} min$^{\mathbf{-1}}$. The activation energy was determined to be 117.851kJ/mol. The rate of textural change of African breadfruit is Arrhenius temperature dependent. The fractural force and textural change kinetic parameters presented in this work will help in optimizing the texture, temperature and retention time variables during African breadfruit parboiling operation. They are also basic information that can be exploited in the design of dehulling machines and boilers for African breadfruit.

Table 4. Rate constant and absolute temperature

K_x (min^{-1})	Ink_x	T (^oK)	$(\frac{1}{T})$
0.0006	- 7.419	333	0.00300
0.0027	- 5.915	353	0.00283
0.0052	- 5.259	373	0.00267

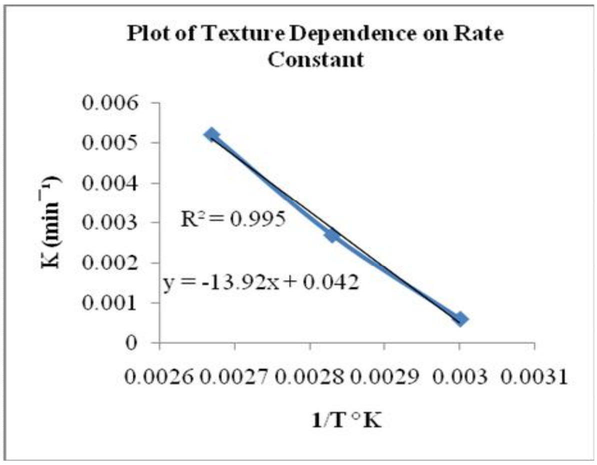

Fig.4. Showing Arrhenius temperature dependence of rate constant.

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