Prediction of Shelf Life of *Dakuwa* (Nigerian cereal/groundnut snack) Using pH as Index of Acceptability

Ocheme, B. Ocheme[1*] Ariahu, C. Chukwuma.[2], Ingbian, E.Kongo.[2] and Igbabul, B.Dooshima[2].
1. Department of Food Science and Technology, Federal University of Technology, Minna, Nigeria
2. Department of Food Science and Technology, University of Agriculture, Makurdi, Nigeria.
*E-mail of the corresponding author: ochemeochemeb@yahoo.com, ochemedo@futminna.edu.ng

Abstract

This study was undertaken to establish the effect of pH on the acceptability of *dakuwa*. *Dakuwa* was prepared by malting and milling maize grains and groundnut. Maize flour and groundnut paste were mixed together in equal ratios with the addition of sugar and red pepper. pH of fresh *dakuwa* was varied using citric acid and subjected to sensory evaluation in order to establish the relationship between pH and acceptability of *dakuwa*. Accelerated storage test was also carried out in order to determine the kinetics of pH change and kinetics of pH change was tested using zero and first order reaction relationships. Linear regression was used to determine Arrhenius equation parameters and the relationship between pH and acceptability. Decreasing pH reduced *dakuwa* acceptability. Order of pH change was adequately described by both zero and first orders of reaction. From the data generated, using first order reaction kinetics, a relationship was derived which can be used to estimate the shelf life of *dakuwa* on the basis of pH.

Keywords: *Dakuwa*, pH, acceptability, kinetics, sensory evaluation, accelerated storage, Arrhenius equation, regression, temperature, shelf-life

1. Introduction

Dakuwa is a cereal and groundnut based snack. It is mainly consumed in the northern parts of Nigeria. *Dakuwa* is prepared from mixtures of cereals, groundnut, ground pepper, ginger, sugar and salt. The ingredients are thoroughly mixed, pounded and moulded into balls that can be eaten without further processing (Abdulrahman and Kolawole, 2003). Nkama and Gbenyi (2001) reported that *dakuwa* is also produced from cereals (maize, millet and sorghum), tiger nuts and groundnuts. These authors also reported that in the traditional method of *dakuwa* processing, the grains are cleaned, toasted and ground together to give a paste.

The changes occurring in foods that can affect the quality of the food may be physical, chemical and biochemical (Robertson, 2006 and Jay *et al*., 2005). Physical changes in foods can manifest in the form of separation due to sedimentation and creaming; agglomeration or caking due to absorption of moisture and gelation due to gel formation and texture changes. Van Boekel (2007) and Robertson (2006) reported that the chemical changes that occur in foods include non-enzymic and enzymic browning resulting in formation of objectionable colours and toxicologically suspect compounds as well as loss of nutritive value; lipid oxidation resulting in loss of essential fatty acids and development of rancid flavour; and hydrolysis leading to changes in flavour and vitamin content. Furthermore, Van Boekel (2005) stated that biochemical changes in foods include lipolysis and proteolysis causing formation of free fatty acids and rancid taste; formation of amino acids and peptides, bitter taste and changes in texture.

Mancebo-Campos *et al*. (2008) stated that stability and quality of food products is a matter of great importance for industrial producers. However, it is complicated and time consuming to monitor the stability of food products under normal storage conditions. Hence, accelerated methods are usually adopted to determine the shelf life of food products. Garcia-Garcia *et. al*. (2008) agreed with this position in their investigation of the shelf life of olives using accelerated test approach. According to Mizrahi (2004) the basic assumption underlying accelerated shelf life testing is that the principles of chemical kinetics can be applied to quantify the effects of extrinsic factors such as temperature, humidity, atmospheric gases and light on the rate of deteriorative reactions By holding a food material in a controlled environment in which one or more of the extrinsic factors is maintained at a higher than normal level, the rate of deterioration will accelerate resulting in a shorter than normal time to product failure. Because of the effect of extrinsic factors, deterioration can be quantified, the magnitude of the acceleration can be calculated and the true shelf life of the product under normal conditions determined.

pH plays an important role in the acceptability and shelf life of food materials. Changes in pH may be indicative of quality changes due to microbial activity or changes in composition. The lower the pH of a food material, the fewer the types of microorganisms that can thrive in that food. Furthermore, the lower the pH of a food material, the more sour the food will taste. Ihekoronye and Ngoddy (1985) reported that sour taste of foods is probably due to the hydrogen ions produced due to dissolution of the food's acid in water. Thus, the pH of a food affects the taste and can cause the food to be accepted or rejected depending on the degree or extent of sourness. The objective of this study was to determine the mechanism of pH change in *dakuwa* and also to determine the effect of pH on the overall acceptability of *dakuwa*.

2. Materials and methods

Maize (*Zea mays*), yellow variety grains and groundnut (*Arachis Hypogeae*) used for preparing *dakuwa* were obtained from local farmers at Gidan Kwano, Chanchaga Local Government, Niger State Nigeria while sugar, salt and granulated red pepper (*Capsicum annum*) were bought from Minna central market, Minna, Niger State, Nigeria.

2.1 Preparation of *dakuwa*

Maize grains and groundnut were manually cleaned. They were then washed in tap water and 400g each were soaked in 2litres of water for 12 hours after which they were germinated for 72 hours. At the end of germination, the maize and groundnut seeds were oven dried at 60^0C for sixty minutes. The groundnut seeds were roasted at 140^0C for thirty minutes while the maize was roasted at 140^0C for sixty minutes. The groundnut was decoated after which both maize and groundnut were milled separately using a local attrition mill. After milling, the maize flour was sieved to obtain a particle size of 0.05mm. The maize flour and groundnut paste were then mixed together in a 1:1 ratio. To 100g of this mixture, 10% and 5% respectively of table sugar and powdered red pepper were added. The mixture was then passed through the attrition mill once and moulded into balls. The *dakuwa* balls were then packaged in low and high density polyethylene while some were left unpackaged. The packaged and unpackaged samples were stored at temperatures of 45, 55, 65 and 75^0C.

2.2 Determination of pH

The pH of *dakuwa* samples were determined by blending 5g of each sample in 50 mL of deionised distilled water. The mixture was filtered and the pH of the filtrate was measured using a pH meter (model CP90: Century Instruments Limited, Mumbai, India) after calibration. Analysis of pH was done every week at 45 and 55^0C, every five days at 65^0C and every three days at 75^0C.

2.3 Sensory evaluation

For the purpose of determining the effect of pH on the overall acceptability, the pH of fresh *dakuwa* was varied from 6 – 4 using citric acid. The samples were then subjected to sensory evaluation to ascertain the pH at, or below which *dakuwa* will no longer be acceptable. A twenty-member, semi-trained panel consisting of students and Staff of Food Science and Nutrition Department, Federal University of Technology, Minna, Nigeria was selected based on their familiarity with *dakuwa* for the sensory evaluation. *Dakuwa* samples were presented in coded white plastic plates. The order of presentation of samples to the panel was randomized. Tap water was provided to rinse the mouth between evaluations. The panellists were instructed to evaluate the overall acceptability of the coded samples on a 7-point scale (1=disliked very much while 7 = liked very much) as described by Iwe (2002).

2.4 Data analysis

The rate of pH change with respect to zero and first order reaction kinetics was analysed using linear regression by means of MINITAB 14 statistical software. The temperature dependence of the rate constant was expressed using Arrhenius equation. The relationship for zero and first order reactions are represented by equations 1 and 2 respectively while Arrhenius relationship is represented by equation 3.

$$c = c_0 - kt \quad (1)$$

$$In\ c = In\ c_0 - kt \quad (2)$$

$$In\ k = In\ A - (E_a / RT) \quad (3)$$

Where:

c and c_0 = final and initial pH; t = time; k = rate constant; A = pre exponential factor or frequency factor; E_a = activation energy; R = universal gas constant; T = absolute temperature.

The relationship between pH and overall acceptability was determined using linear regression. The regression equation was then fitted into Arrhenius equation using first order parameters, to derive a relationship from which shelf life can be estimated on the basis of pH change.

3 Results and Discussion

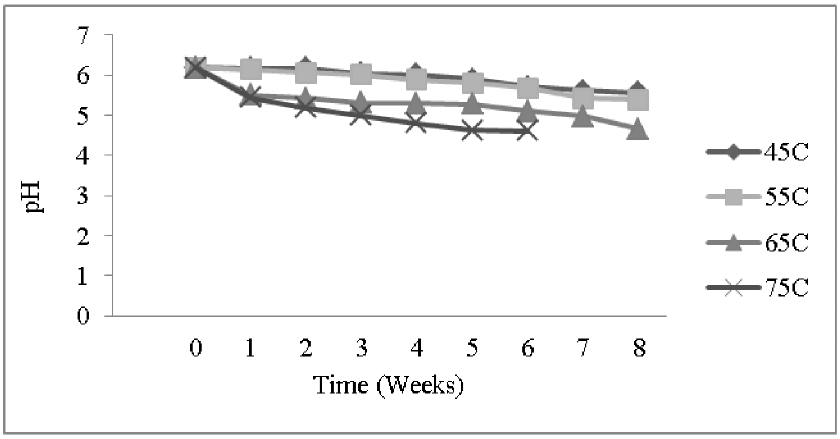

Figure 1. pH of unpackaged *dakuwa* under accelerated storage

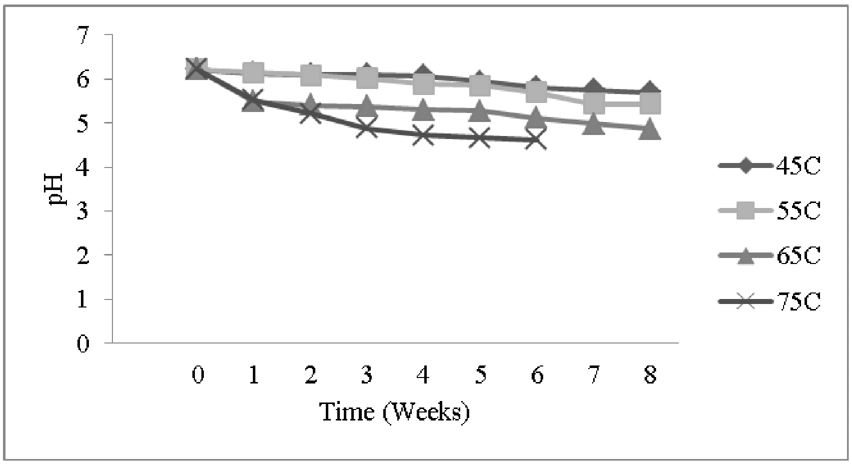

Figure 2. pH of *dakuwa* packaged in LDP under accelerated storage

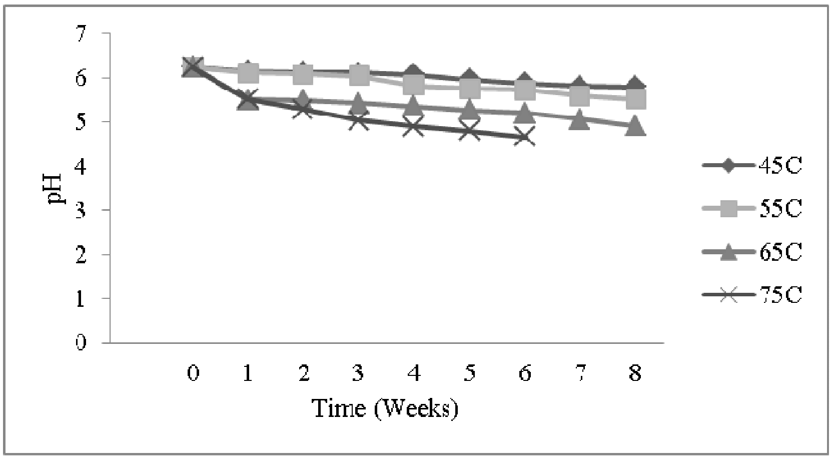

Figure 3. pH of *dakuwa* packaged in HDP under accelerated storage

3.1 pH Changes

The changes in pH of *dakuwa* under storage at different temperatures are shown in figures 1-3. The pH values ranged from 6.19-4.61; 6.22-4.62 and 6.23-4.66 for unpackaged *dakuwa* and *dakuwa* packaged in LDP and HDP respectively. At 45 and 55^{0}C, the pH initially increased before it started decreasing while at 65 and 75^{0}C it decreased continuously. The decrease in pH was more pronounced as the storage temperature was increased: samples stored at higher temperatures had lower ultimate pH. The pH drop observed through the period of storage may be due to the action of microorganisms. It could also be due to an increase in the hydrogen ion (H^+) concentration. Rustom *et al*. (1995) attributed the drop in pH of stored peanut beverage to protein-protein interaction leading to release of hydrogen ion. These authors also reported that increased storage temperature resulted in an increased rate of pH drop. The drop in pH, with respect to keeping quality, will be an advantage as it could limit microbial activity thereby extending the shelf life of the product. Conversely, it may cause the product to taste very sour thereby causing it to be rejected.

3.2 Kinetics of pH changes

Table 1. Regression parameters for first order kinetics of pH change in *dakuwa* under accelerated storage

		Temperature (^{0}C)			
Packaging	**Parameter**	**45**	**55**	**65**	**75**
NP					
	Standard error	0.0054	0.0070	0.0097	0.0130
	Intercept	1.82	1.81	1.73	1.70
	Slope	-0.0169	-0.0212	-0.0201	-0.0312
	K (week^{-1})	0.0169	0.0212	0.0201	0.0312
	r^2	0.963	0.960	0.933	0.937
LDP					
	Standard error	0.0038	0.0078	0.0060	0.0158
	Intercept	1.81	1.81	1.72	1.72
	Slope	-0.0154	-0.0208	-0.0155	-0.0369
	K (week^{-1})	0.0154	0.0208	0.0155	0.0369
	r^2	0.976	0.948	0.956	0.934
HDP					
	Standard error	0.0037	0.0051	0.0062	0.0071
	Intercept	1.82	1.81	1.73	1.73
	Slope	-0.0107	-0.0168	-0.014	-0.0323
	K (week^{-1})	0.0107	0.0168	0.014	0.0323
	r^2	0.957	0.966	0.948	0.982

NP: Unpackaged sample; LDP: low density polyethylene; HDP: high density polyethylene; K: rate constant; r^2: regression coefficient

Table 2. Regression parameters for zero order kinetics of pH change in *dakuwa* under accelerated storage

		Temperature (^{0}C)			
Packaging	**Parameter**	**45**	**55**	**65**	**75**
NP					
	Standard error	0.0289	0.0386	0.0456	0.0472
	Intercept	6.18	6.12	5.62	5.57
	Slope	-0.105	-0.121	-0.103	-0.177
	K (week^{-1})	0.105	0.121	0.103	0.177
	r^2	0.972	0.962	0.943	0.974
LDP					
	Standard error	0.0220	0.0428	0.0352	0.0835
	Intercept	6.13	6.13	5.59	5.59
	Slope	-0.0911	-0.119	-0.0778	-0.187
	K (week^{-1})	0.0911	0.119	0.0778	0.187
	r^2	0.975	0.953	0.940	0.929
HDP					
	Standard error	0.0221	0.0308	0.0310	0.0400
	Intercept	6.15	6.08	5.61	5.61
	Slope	-0.0639	-0.0975	-0.0763	-0.166
	K (week^{-1})	0.0639	0.0975	0.0763	0.166
	r^2	0.956	0.963	0.952	0.978

NP: Unpackaged sample; LDP: low density polyethylene; HDP: high density polyethylene; K: rate constant; r^2: regression coefficient

Table 3. Arrhenius regression parameters for first order pH change in *dakuwa* under accelerated storage

	Packaging Material		
Parameter	**NP**	**LDP**	**HDP**
N	4	4	4
Standard error	1.96	4.46	3.56
Intercept	1.51	3.51	4.54
A (week^{-1})	4.53	33.45	93.69
Slope	-1750	-2420	-2810
E_a (kJ/mol)	14.55	14.55	23.36
r^2	0.987	0.978	0.944

NP: Unpackaged sample; LDP: low density polyethylene; HDP: high density polyethylene N: Number of points; A: frequency factor; E_a: activation energy; r^2: regression coefficient

T he regression parameters for first and zero order kinetics of pH changes in *dakuwa* during storage at different temperatures are shown in tables 1 and 2 respectively while the Arrhenius regression parameters are in Table 3. The standard error and reaction rate constant increased with increasing temperature while the intercept and the coefficient of regression decreased with increasing temperature for both first and zero order kinetics. Standard error values ranged from 0.0037-0.0130 and 0.0221-0.0835 for first and zero order respectively. The reaction rate constants ranged from 0.0107-0.0369 and 0.0639-0.187 for first and zero order respectively while the coefficient of regression fell between 0.933-0.982 and 0.929-0.978 for first and zero order respectively.

The lower standard error and higher coefficient of regression values of first order kinetics of pH changes compared with zero order kinetics indicate that the kinetics of pH changes in *dakuwa* was better described by first order kinetics.

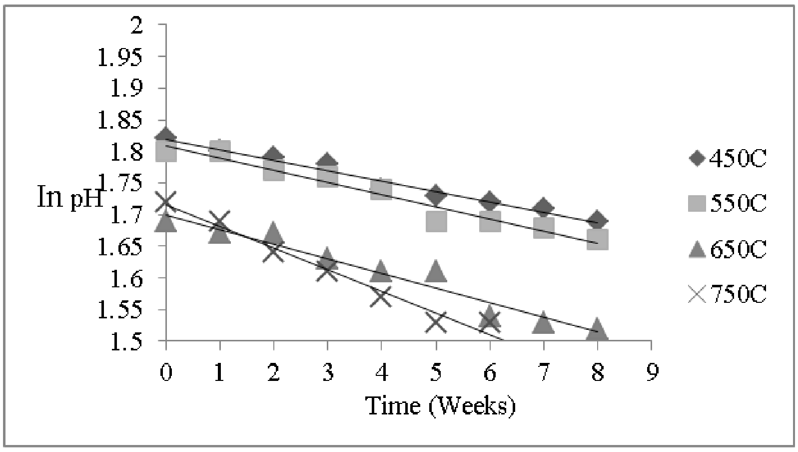

Figure 4. Log-transformed pH of unpackaged *dakuwa* under accelerated storage

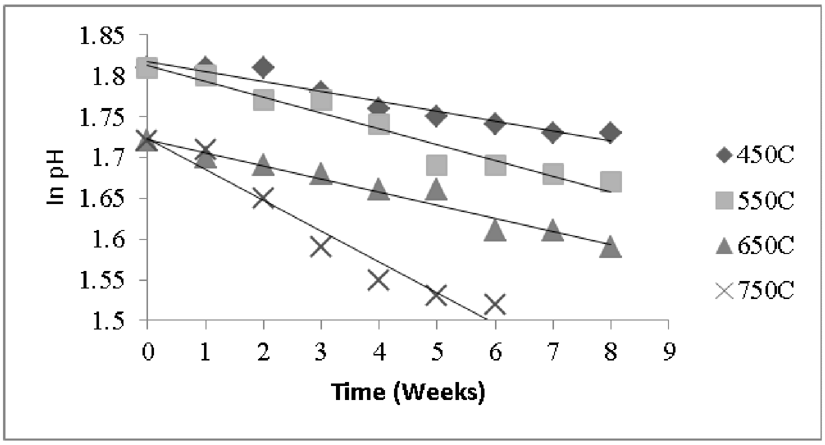

Figure 5. Log-transformed pH of *dakuwa* packaged in LDP under accelerated storage

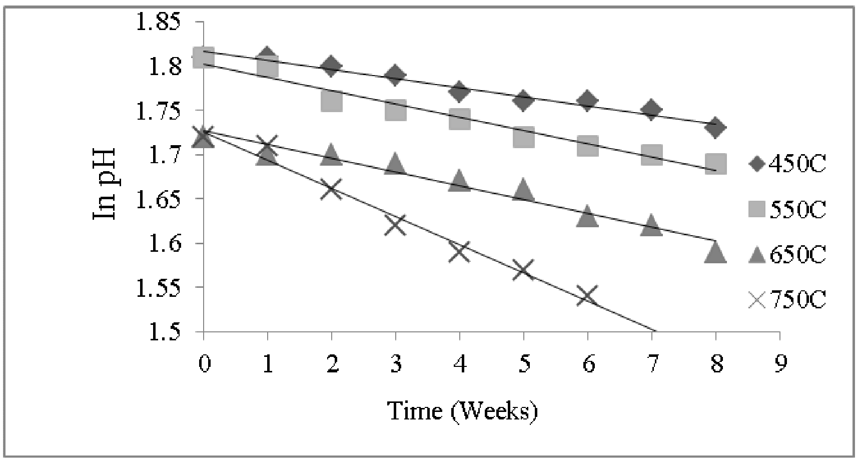

Figure 6. Log-transformed pH of *dakuwa* packaged in HDP under accelerated storage

Figures 4-6 show the plot for the logarithmically transformed data using equation (2). According to Van Boekel (2008) a logarithm plot resulting in a straight line is usually taken as proof of a first order reaction.

The increase in the rate constants with increasing temperature indicates that change in pH will occur faster at higher temperatures. The Arrhenius regression parameters, obtained by linear regression of In K versus 1/T, describe the temperature dependence of pH changes in *dakuwa*. The activation energy, which was obtained from the slope of the plot, is the energy barrier that molecules need to overcome in order to be able to react (Van Boekel, 2007 and Ariahu *et al*., 2010). This means that the higher the activation energy, the slower the change in pH. However, the higher the temperature, the much easier it will be for the molecules to overcome the energy barrier (activation energy) and react and the higher the rate of pH change. Generally, the higher the temperature, the higher the rate of change.

Table 4. Effect of pH on the overall acceptability of *dakuwa*

pH	*Overall acceptability score
6.04	6.72
5.60	6.47
5.20	5.88
4.80	5.11
4.40	4.92
4.00	4.63

*Values are based on a 7 point scale where 7 = like very much; 4 = neither like nor dislike; and 1 = dislike very much.

3.3 pH and overall acceptability

The effect of pH on the overall acceptability of *dakuwa* is shown in Table 4. As the pH decreased, the overall acceptability also decreased. The relationship between pH and overall acceptability as obtained from the linear regression of pH versus overall acceptability was described by the regression equation:

$OA = 0.03 + 1.12pH$ (4)

With respect to pH, equation (4) becomes

$pH = OA - 0.03/1.12$ (5)

For first order kinetics,

$In\ pH = In\ pH_0 - kt$ (6)

relating equation 5 to equation 6 gives

$In\ (OA - 0.03/1.12) = In\ pH_0 - kt$ (7)

with respect to t equation (7) becomes

$t = In\ pH_0 - In\ (OA - 0.03/1.12)/k$ (8)

Where,

OA = the minimum allowable score for overall acceptability below which the product is no longer acceptable.

pH_0 = initial pH of *dakuwa*

pH = final pH of *dakuwa* at which overall acceptability score is just below the minimum

k = rate constant

t = the time it will take for pH_0 to drop to pH

Equation (8) can be used to predict the shelf life of *dakuwa* in different packaging materials at different temperatures. The predicted shelf life will be based on the time it will take for the the pH to drop from an initial value of about 6 (pH_0) to a final value of about 4.8 (pH): the point after which the product will no longer be acceptable going by the result of the sensory evaluation. Furthermore, equation (8) is based on the assumption that other quality indices remain constant (unchanged) throughout the period of storage.

4 Conclusion

pH of *dakuwa* decreased with storage time and the higher the temperature of storage, the higher the rate of decrease. pH change in *dakuwa* was adequately described by first order kinetics. Packaging did not affect the kinetics of pH change in *dakuwa.* A direct relationship exists between the pH and the acceptability of *dakuwa* such that the lower the pH, the less acceptable *dakuwa* becomes. For pH alone to be used in estimating the shelf life of *dakuwa,* other quality indices such as lipid oxidation and microbial activities must be prevented.

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