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Kinetic modeling of ascorbic acid loss in baobab drink at pasteurization and storage temperatures.

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***Abstract**: The degradation kinetics of ascorbic acid was determined in baobab drink during pasteurization and storage temperatures at 60-90°C for 3 hours and 0 – 40 °C for 5 weeks respectively. The loss of ascorbic acid at all temperatures followed the first order kinetic model as the coefficient of determination (i.e. R^2-value) ≥ 0.953. Rate constants of ascorbic acid degradation ranged from 9.72 – 26.31 x10^{-3} /minute and 5.266 – 29.95x10^{-3} /day during pasteurization and storage respectively. Decimal reduction time (D-value) and half-life ranged between 87.52 – 236.87 and 26.35 – 71.30 minutes and 76.89 – 437.78 and 23.15 – 131.78 days for pasteurization and storage temperatures respectively The temperature dependence of degradation reaction was well described by the Arrhenius relationship. The activation energy, Q_{10} factor, and Z-value obtained ranged from 24.24 – 58.66 kJ/mol, 1.06 - 1.58 and 4.74 – 7.96 °C for the temperature range within which experiments were carried out. The values were similar to many others reported for food systems in literatures.*
***Keywords:** Baobab drink, ascorbic acid, , rate constants, Arrhenius plot, activation energy.*

I. Introduction

The African baobab belongs to the family Bombaceae and the genus *Adansonia.* It is a tree often associated with dry savannah and occurs naturally in most countries of the south of Sahara [1]. It possesses a unique fruit type with woody pericarp surrounding a whitish powdery appearance, slightly sour taste and spongy pulp with manifold seeds [2]. Leaves, bark and fruits of this tree are traditionally employed in several African regions as foodstuffs and for medicinal purposes, and for that reason baobab is also named "the small pharmacy" or "chemist tree" [3,4]. The native African populations commonly use the baobab fruit as famine food to prepare decoctions, sauces, ice-creams, jams and natural refreshing drink, due to its nutritional properties [5,6,7,8,9,10]. The pulp is therapeutically employed as febrifuge, analgesic, anti-diarrhea / anti-dysentery and for treatment of smallpox and measles [4].

Nutritional analysis of baobab fruit pulp has shown that the fruit is an excellent source of pectins, calcium, ascorbic acid and iron [11]. ascorbic acid content of baobab fruit pulp compared with oranges by Manfredini *et al*, [12] and was shown to be at least three times higher (150-499 mg/100g vs 46mg/100g). Nour *et al*, [13] reported that the ascorbic acid content of baobab fruit pulp was 300 mg/100g whereas data from Wilkinson [14] shows that the vitamin levels ranges from 74 to 163 mg/100g. The recommended daily allowance (RDA) for ascorbic acid is 75 mg for women and 90 mg for men, and so 40g of fruit pulp would give at least recommended daily amount of ascorbic acid.

Ascorbic acid is an important component of our nutrition and used as additive in many foods because of its antioxidant capacity. Thus, it increases quality and technological properties of food as well as nutritional value [15,16]. However, ascorbic acid is known to be a vitamin sensitive to a number of factors, including pH, moisture content, oxygen, temperature and light [17]. Degradation of ascorbic acid proceeds both aerobic and anaerobic pathways [18,19] and depends upon many factors such as oxygen, heat, light [20), storage temperature and storage time [21,22]. Oxidation of ascorbic acid occurs mainly during the processing of juices [18], whereas, anaerobic degradation of ascorbic acid mainly appears during storage [16,19,23] which is especially observed in thermally preserved juices. Due to these afore-mentioned reasons, it is generally observed that, if ascorbic acid is well retained, the other nutrients are also well retained [24]. Hence, ascorbic acid is usually considered as an index of nutrient quality during processing and storage of foods [25].

In modern food technology, the trend is to maximize the nutrients retention in both processing and storage. Kinetic studies help engineers and scientists to optimize processing systems and design processes, to improve or optimize existing processes and develop control systems for processing operations by finding rates of reaction that occur during heat processing operations [26]. Knowledge of the rates of various reactions helps to predict how quick the reaction mixture is able to move to its equilibrium condition and its mechanism [27].The kinetic modeling has been widely used to evaluate thermal stability of ascorbic acid in different food systems such as orange serum [9]; orange juice [17,28]; orange-carrot juice [29]; lemon juice [20,30]; citrus

juice concentrates [31,32]; pumpkin [33]; potato [34] and guava juice [35]. The dearth of information on degradation of ascorbic acid in baobab drink and associated products indicates the need for studies along that line.

Therefore, this study was undertaken to determine the kinetic parameters for ascorbic acid degradation in baobab drink at processing (pasteurization) (60 – 90 ^{o}C) and storage (0 – 40 ^{o}C) temperatures.

II. Materials And Methods

2.1 Materials

Baobab fruits were harvested at maturity from parent trees found around LAUTECH, Ogbomoso, Nigeria. All chemicals/reagents used were of analytical grade

2.2 Preparation of Baobab Drink

Ripe Baobab fruits were manually broken and pulp was manually separated from the seeds. Thereafter, the fiber in the pulp was reduce by passing it through 250μm British standard sieve and packed in low-density polyethylene bag until further use. Baobab drink was prepared by mixing 200 g pulp with 1000 ml distill water so that more than daily recommended dose of ascorbic acid can be adequately provided for in approximately 200 ml of the drink [1,12]. The mixture was homogenized using a kitchen blender (Binatone model BLG - 401) for 5 minutes and pasteurized at 80^{o}C for 15 min. The drink was aseptically packaged in plastic bottles and stored in freezer until further use.

2.3 Thermal treatments

Stability of ascorbic acid at different temperatures was determined with little modifications according to Mok & Hettiarachchy [36]. In this method, 5 ml of baobab drink was poured into screw capped test tube and were heated in a thermostatically controlled water bath with an accuracy of ±2 ^{o}C at 60, 70, 80 and 90 ^{o}C for processing temperatures while samples for storage temperatures were kept at freezing temperature (-5 ^{o}C), refrigeration temperature (5^{o}C), on laboratory table (25^{o}C) and at 40^{o}C in a thermostatically controlled incubator. Samples in test tubes were taken for analysis at 30 minutes interval for 180 minutes and every week for 5 weeks for processing and storage temperatures respectively. Each sample temperature was quickly brought to room temperature either by cooling in an ice bath or warming in a water bath in order not to interfere the course of determination of ascorbic acid content.

2.4 Ascorbic acid determination

Determination of ascorbic acid was done using 2 -6- Dicholoro-phenol Indophenol dye reagent according to the method described by Ruucke [37]. The dye was standardized so that one gram of ascorbic acid is equivalent to one ml of the dye used. About 5 ml of sample was blended with about 20 ml of 0.4% oxalic acid for two minutes in a blender and then filtered through Whatman filter paper (No. 1). The filtrate was made up to 50 ml with 0.4% oxalic acid. Ascorbic acid in 4 ml filtrate was titrated against standard 2-6-Dichlorophenol Indophenol. The experimental results are shown in TABLE 1.

2.5 Kinetic modeling

Degradation of ascorbic acid is described using the process reaction rate and the influence of temperature on the reaction rate. The kinetic parameters used are reaction rate constant (k) and the Arrhenius activation energy (E_a) which were analyzed as described by van Boekel [38]. A first order degradation was presumed in order to arrive at the reaction rate constant as:

$$-dC/dt = kC \quad (1)$$

where C is the instantaneous concentration of ascorbic acid, t is time and k is the reaction rate constant (time^{-1}),. By separation of variable, integration of Eq.(1) yields:

$$C = C_o \exp(-kt) \quad (2)$$

Linearization of equation 2 by taking natural logarithm of both sides yields;

$$Ln(C/C_o) = -kt \quad (3)$$

For first order reaction, a plot of '$Ln(C/C_o)$' against process time 't' will be a straight line as shown in Fig. 1 & 2, and the rate constant is represented by the slope which are reported with their respective correlation coefficients (R^2value) in TABLE 1.

Decimal reduction time (or D_{value}) is defined as the time required for ascorbic acid to reduce by one log-cycle at a particular temperature and it is calculated from the rate constant as;

$$D_{value} = Ln(10)/k \quad (4)$$

Half-life, the time required for ascorbic acid to degrade to 50% of its original value and was calculated from the rate constant as:

$$t_{1/2} = Ln(0.5)/k \quad (5)$$

Influence of temperature on ascorbic acid degradation was determined using the Arrhenius equation:

$$k = k_o \exp(-E_a/RT) \quad (6)$$

where, k_o is frequency factor or pre-exponential constant; E_a (kJ/mol) is the activation energy of the reaction; T is the absolute temperature of the medium; and R is the universal gas constant (8.314kJ/mol.K).
Linearization of Eq. (6) by taking natural logarithm of both sides yields;

$$Lnk = Lnk_o - E_a/RT \quad (7)$$

The parameters E_a and k_o in equations (6) or (7) are of fundamental interest since they both represent the activation energy and pre-exponential constant associated with a reference absolute temperature for activation reaction, respectively. Both values were obtained from the plots of Lnk versus l/T values. Activation energies E_a (kJ /mol) was calculated as a product of universal gas constant, R (8.314kJ/mol.K) and the slope of the graph obtained by plotting 'Lnk' versus '1/T'. Fig. 3 and 4 shows the Arrhenius plots for ascorbic acid degradation in baobab drink under pasteurization and storage conditions.

Temperature quotient (Q_{10}) values, the number of times ascorbic acid degrades with a 10 ^oC change in temperature, were also calculated for the temperature ranges of -5–40 ^oC and 60–90 ^oC It is expressed as (Toledo, 1991):

$$Q_{10} = e^{(E_a/R)(10T_{21}/\ ]T)} \quad (8)$$

The z value, the temperature change needed to change ascorbic acid degradation rate by a factor of 10. The z value has also been used to express the temperature dependence of degradative reactions occurring in foods during processing and storage. The z value expressed in terms of the Q_{10} is as follows:

$$z = 10\ln(10)/\ln(Q_{10}) \quad (9)$$

2.6 Statistical Analysis

Each sample was analyzed in triplicate then averaged. Linear regression analysis was used to obtain kinetic parameters of Baobab drink samples using Microsoft Excel software (Version 7, Microsoft Corporation, Redmond, WA, USA).

III. Results And Discussion

3.1. Amount of ascorbic acid in baobab drink at isothermal conditions.

TABLES 1 and 2 show the effect of heat treatments at different temperatures -5 – 40 ^oC (storage) and 60 – 90 ^oC (pasteurization) over different time periods on the initial concentration of ascorbic acid. Initial ascorbic acid contents of baobab drink varied between 125.00 and 137.29 mg/100ml (TABLE 1 and 2). This confirmed the significance of baobab fruit pulp as a popular ingredient in local drinks amongst rural dwellers in areas where they are found and exploited [39]. Ascorbic acid content of the samples decreased to 103.17, 74.67, 59.17, 39.00 mg/100ml and 22.83,11.38, 5.50, 1.50 mg/100ml after a five week storage at -5, 5, 25 and 40 ^oC and holding at potential pasteurization temperatures of 60, 70, 80, 90 ^oC respectively. It was observed as expected from the study that ascorbic acid decreased with increasing temperature [31]and retention of ascorbic acid (%) in those samples at -5, 5, 25 and 40 ^oC were 82.53, 59.73, 47.33, 31.22 and 16.63, 8.29, 4.01, 1.09 respectively. At pasteurization temperatures, the loss of ascorbic acid in baobab drink was highest especially at 90^oC compared to the loss at storage temperatures. Moreover, half-life of ascorbic acid in the drink was found higher at storage temperature of -5^oC.

3.2. Kinetic data for loss of ascorbic acid in baobab drink.

A first order degradation was assumed in order to determine the reaction rate constants. The plot of natural logarithm of remaining concentration of ascorbic acid i.e. 'Ln (C/C_o)' versus time't' (Fig. 1 & 2), from which rate

Table 1: Ascorbic acid degradation in baobab drink during storage (mg/100 ml)*

Temperature ^{o}C	Time (days)					
	0	7	14	21	28	35
-5	125.00 (0.500)	121.54 (0.711)	117.33 (0.577)	113.083 (1.377)	109.54 (0.315)	103.17 (0.688)
5	125.00 (0.500)	110.42 (0.629)	99.88 (0.650)	87.63 (0.696)	81.75 (1.639)	74.67 (0.764)
25	125.00 (0.500)	104.92 (0.722)	88.46 (0.938)	77.33 (0.577)	69.54 (0.641)	59.17 (1.041)
40	125.00 (0.500)	90.29 (4.490)	75.33 (1.607)	65.17 (0.289)	56.00 (2.000)	39.00 (0.750)

Determined at pH and soluble solids of 3.20 and 9.00 oBrix

Numbers in parenthesis are standard deviations

Table 2: Ascorbic acid degradation in baobab drink during pasteurization (mg/100 ml)

Temperature ^{o}C	Time (minutes)						
	0	30	60	90	120	150	180
60	137.29 (0.711)	123.42 (0.878)	99.58 (1.010)	75.33 (1.258)	58.17 (0.764)	40.17 (1.155)	22.83 (0.577)
70	137.29 (0.711)	101.75 (0.750)	81.33 (0.289)	55.92 (0.722)	31.67 (0.764)	22.50 (1.000)	11.38 (0.545)
80	137.29 (0.711)	91.92 (0.722)	63.96 (0.072)	41.58 (0.520)	17.54 (0.286)	8.66 (0.764)	5.50 (0.500)
90	137.29 (0.711)	87.50 (1.000)	63.63 (1.192)	31.17 (0.577)	9.33 (0.289)	3.46 (0.938)	1.50 (0.500)

*Determined at pH and soluble solids of 3.20 and 9.00 oBrix

Numbers in parenthesis are standard deviations

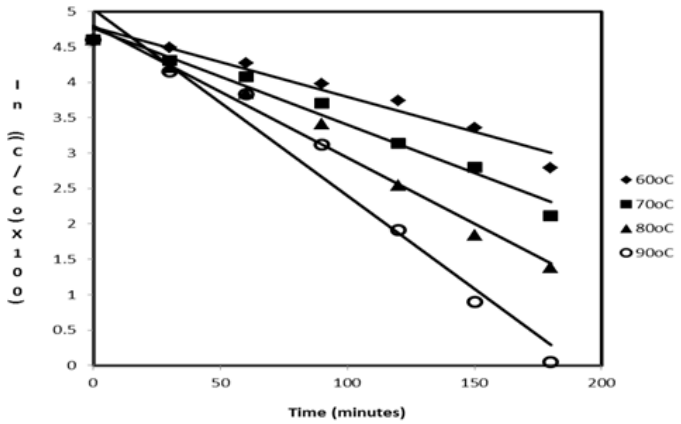

Fig.1: Kinetics of ascorbic acid loss in baobab drink at pasteurization temperatures

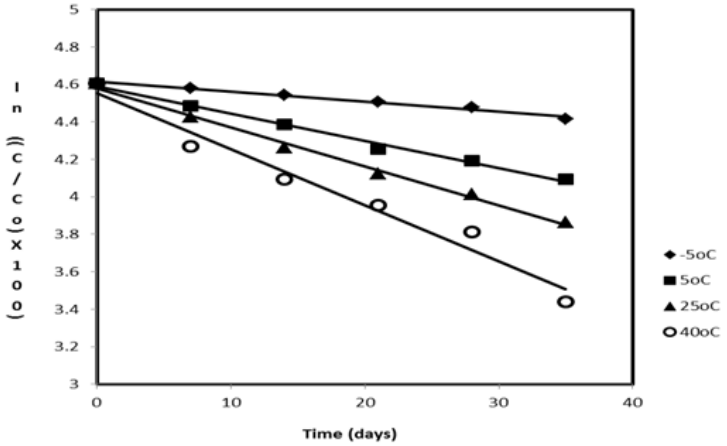

Fig.2: Kinetics of ascorbic acid loss in baobab drink at storage temperatures

constant, 'k' was determined as the slope of the straight line. In addition, the plot yielded high determination coefficients (R^2 value) between 0.976 and 0.997 from the regression analyses which are indications of validity of first order reaction kinetics for the food system under consideration. This is in agreement with other studies [17,19,31,40,41]. However, it has also been reported by other researchers that ascorbic acid degradation also sometimes follows a zero-order [42] or second-order reaction [20,40].

Under storage condition, rate constant, 'k' increased from 5.26 x 10^{-3} at 0^{o}C to 29.95 x 10^{-3} /day at 40 ^{o}C. At pasteurization temperatures, k increased from 9.72 x 10^{-3} at 60^{o}C to 26.31 x 10^{-3} /minutes at 90 ^{o}C (TABLE 3 and Figs. 3 & 4). The higher values of rate constants k obtained for ascorbic acid degradation at processing temperatures were significant indications of the ease of thermal degradation of this vitamin during heat processing such as pasteurization, sterilization e.t.c. compared with degradation at storage temperatures. This fact is augmented by the low values of decimal reduction time (D_{value}) and half-life at pasteurization temperatures between 87.52 – 236.87 and 26.35 – 71.30 compare with the values at storage temperatures between 76.89 – 437.78 and 23.15 – 131.78 respectively as shown on TABLE 3.

3.3. Temperature dependency of degradation.

Activation energies were found higher at pasteurization temperatures than that of storage temperatures (TABLE 3) as calculated by using Arrhenius plots of ascorbic acid degradation in baobab drinks given in Fig. 3 & 4. It could be interpreted that degradation of ascorbic acid has stronger temperature dependency at pasteurization temperatures than at storage temperatures. This implies that the degradation will progress slowly at low temperatures but fast at high temperatures [43].

Temperature quotient (Q_{10}) values (approximately equal to 2) validate the principle of preservation that degradation of food nutrients doubles for every 10 ^{o}C change in temperature [44]. This observation reveals the marked influence of elevated temperature during processing and handling of baobab drink..

The z values (25.96 ^{o}C at storage temperatures and 33.05^{o}C at pasteurization temperatures) were related with those reported by Rao *et al.*[45].

IV. Conclusions

The influence of pasteurization and storage temperatures on the ascorbic acid degradation was evaluated in this study. Ascorbic acid in baobab drink decreased with increasing temperature. The loss of ascorbic acid in baobab drinks at all temperatures was described well by first-order kinetic model. Since ascorbic acid decomposes easily at high temperatures, baobab drinks showed the highest ascorbic acid destruction at pasteurization temperatures especially between 80 and 90 ^{o}C. The drink after pasteurization should hence, be rapidly cooled down to lower temperatures i.e. storage temperature where rate of degradation of ascorbic acid and other nutrients are low.

Table 3: Kinetic parameters for degradation of ascorbic acid in baobab drink at different temperatures

Temperature ^{o}C	k ± s.d. (x10^{-3} day^{-1})	R^2	D_{value} (day)	$t_{½}$ (day)	E_a (kJ/mol)	Q_{10}	Z_{value} ^{o}C
-5	5.26 ± 0.194	0.991	437.78	131.78			
5	14.55 ± 0.2960	0.996	158.28	47.65	24.24 (0.876)	1.06	7.96
25	20.75 ± 0.0825	0.997	110.95	33.40			
40	29.95 ± 0.346	0.985	76.89	23.15			
60	9.72 ± 0.128*	0.976	236.87**	71.30**			
70	13.62 ± 0.0757*	0.987	169.11**	50.91**	58.66 (0.868)	1.58	4.74
80	18.67 ± 1.468*	0.990	123.34**	38.51**			
90	26.31 ± 1.597*	0.982	87.52**	26.35**			

* means minutes-1

** means minutes

s.d. mean standard deviation

Figures in parenthesis in column 6 are coefficient of determinations of Arrhenius plots.

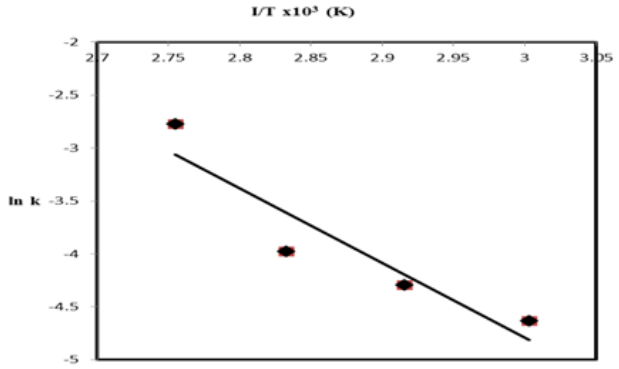

Fig. 3: Arrhenius plot of the ascorbic acid loss rate for baobab drink during pasteurization.

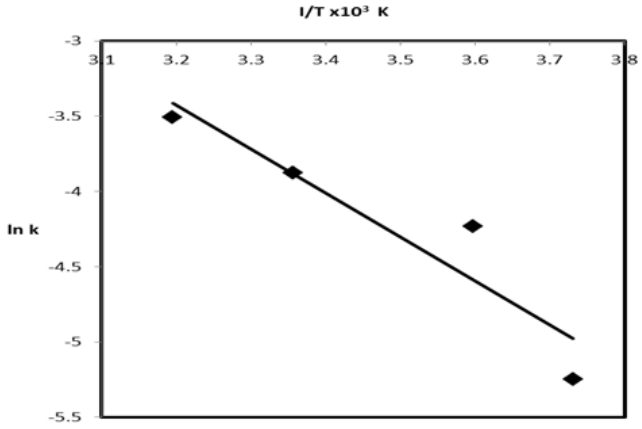

Fig. 4: Arrhenius plot of the ascorbic acid loss rate for baobab drink during storage

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