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MODELLING OF THERMAL DEGRADATION KINETICS OF ASCORBIC ACID IN PAWPAW AND POTATO

SAMUEL E. AGARRY AND MUJIDAT O. AREMU

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ABSTRACT

Ascorbic acid (vitamin C) loss in thermally treated pawpaw and potato was modelled mathematically. Isothermal experiments in the temperature range of 50 -80 ^{o}C for the drying of pawpaw and 60 -100 ^{o}C for the blanch-drying of potato were utilized to determine the kinetics of ascorbic acid loss in both fruit and vegetable. Changes in ascorbic acid degradation followed first-order reaction kinetics. Temperature dependence of the rate constant during thermal processing of pawpaw and potato obeyed the Arrhenius relationship with activation energy of 12.1 and 19.3 KJ/ mole for pawpaw and potato, respectively. A correlation between the loss of ascorbic acid and moisture loss in pawpaw was established with satisfactory statistical predictions(R= 0.996)

KEYWORDS: Ascorbic acid; drying; blanching; degradation; kinetics; pawpaw; potato

1.0 INTRODUCTION

Fruit and vegetables are important and low-cost food containing low levels of fat and high levels of vitamins, minerals and fibres (Masrizal et al., 1997) and a variety of substances and specific compounds with properties that can be healthy for humans. However, since the discovery of the basic vitamins and their many forms, efforts have been made to retain them in foods during post–harvest handling, commercial processing, distribution, storage and preparation (Gregory, 1996). During the last few years, the nutritional importance of antioxidants in foods such as ascorbic acid (vitamin C) has found increased interest due to their possible role in the prevention of human diseases such as cancer, atherosclerosis and immune depression (Byres and Perry, 1992). The status of vitamins during processing is receiving more attention. A comprehensive overview of the effect of processing on the vitamin status is given by Karmas and Harris (1988).

Fruits and vegetables are unusually processed under normal atmosphere. Hence, dried, cooked, canned and frozen fruit and vegetables are a very important part of our food supply. However, the processing of these foods leads to a loss of relevant compounds such as vitamins and carotenoids thereby lowering the nutritional quality of the product (Ramesh et al., 1999). The main vitamin losses occur due to water solubility and mass transfer, heat sensitivity and enzymatic oxidation (Rumm-Kreuter and Demmel, 1990). However, ascorbic acid (vitamin C) is a water soluble and heat or temperature-sensitive molecule that serves to influence oxidation-reduction reactions (Uddin et al., 2002) compared to most other nutrients and as a result may cause problems during the preservation of fruit and vegetables (Belitz and Grosch, 1988).

The oxidation of food ingredients such as ascorbic acid (vitamin C) and aroma compounds is one of the most important causes of quality loss during processing of food and the main deteriorative reaction in microbiologically safe foods like dry and frozen foods (Anderson and Lingnert, 1997). Ascorbic acid degradation is specific to particular systems (Faramade, 2007; Tiwari et al., 2009) as it depends on several factors stemming from either an anaerobic or aerobic pathway (Esteve et al., 1999; Vieira et al,

Samuel E. Agarry, Biochemical Engineering Research Laboratory, Department of Chemical Engineering, Ladoke Akintola University of Technology, Ogbomoso, Nigeria.
Mujidat O. Aremu, Biochemical Engineering Research Laboratory, Department of Chemical Engineering, Ladoke Akintola University of Technology, Ogbomoso, Nigeria.

2000). In the aerobic pathway, because of the presence of metals or some other pathways, oxidation ensues. In the anaerobic pathway, ascorbic acid undergoes ketonization (Vieira et al., 2000). Kinetic models of thermal catabolism are often considered to be essential to design new processes to ensure a safe food product and give maximum retention of quality (Avila and Silva, 1999).

The objective of this present study was to mathematically model the thermal degradation of ascorbic acid in pawpaw (Carica papaya) and potato (Ipomoea batata), by using an isothermal method to assess process impact on the product quality. A correlation between moisture loss (removed) and loss of ascorbic acid was also determined for pawpaw.

2.0 MATERIALS AND METHODS

Preparation of Raw materials

Fresh samples of pawpaw and potatoes were obtained from a local market in Ogbomoso town of Nigeria. They were peeled, cut, sliced and washed in clean tap water, then blotted dry with tissue paper prior to use. Each sample was divided into three: (i) for moisture content analysis (ii) for the determination of ascorbic acid in the fresh samples and (iii) for blanching and drying purposes.

Blanch-drying of Potato

Approximately 50g sliced samples (5mm diameter in size) of fresh potato were put in a 250ml beaker containing water and blanched at predetermined temperatures (60,70,80,90,100)^{o}C and time (3,5,8,10 minutes) combinations using a thermostatically controlled water-bath (DK-420 Glufex Medical and Scientific, England) according to the method described by Okoli et al. (1988) after which the samples were removed at each predetermined temperature-time combination from the water and blotted dry using a tissue paper in order to remove the excess water and were analyzed for ascorbic acid. Samples were analyzed in duplicates.

The blanched samples obtained at the predetermined temperature-time combinations were then dried in an oven dryer at temperatures of 60, 70, 80 90, 100 ^{o}C for 2 hrs, respectively. There after, samples were withdrawn for ascorbic acid analysis.

Drying of Pawpaw

Approximately 50g sliced samples (5mm diameter in size) of fresh papaw were spread on a metal tray and placed in an hot air oven dryer (Uniscope SM 9053, A laboratory oven, Surgifriend Medicals, England). The samples were dried at different temperatures of 50, 60, 70 and 80 ^{o}C for 2hrs, respectively. Samples were removed from the drier every 30 minutes for the determination of ascorbic acid and moisture content. This was carried out in duplicates.

Determination of moisture content

The moisture content of the fresh and dried samples were determined according to the AOAC method (AOAC, 1990).

Determination of Ascorbic Acid

The ascorbic acid contents of both the fresh, the blanched and dried samples were determined by the 2-6-dichloro phenol indophenols titration method as described by Pearson (1991).

Mathematical Modeling of Ascorbic Acid Thermal Degradation

The change in the quality of a foodstuff either positively or negatively at a constant temperature over a period of time can be described by a relationship (Esteve et al., 1998; Manso et al., 2001; Karhan et al., 2004) as given:

$$C = C_o \exp(K_T t) \quad \text{------------------------------------} \quad (1)$$

Where C_o is the total initial ascorbic acid in content (mg/100g), K_T is the degradation rate constant (min^{-1}), C is the ascorbic acid content at time t (mg/100g) and t is the time (min). On the basis of a first-order reaction for the degradation changes of ascorbic acid in the blanched potato and dried pawpaw, Equation (1) becomes:

$$\ln(\frac{C}{C_o}) = -K_T t \quad \text{------------------------------------} \quad (2)$$

Thus, Equation (2) allows the natural logarithmic plots of experimental values of C/C_o versus process time, t in which straight lines obtained are indications of the validity of first-order reaction kinetics for the food system under consideration. According to Labuza and Riboh (1982) and Cohen et al. (1994) the intensity of heat on degradation of moist nutrient in foods can be described by the Arrhenius model such that temperature dependence of K_T closely follows the equation:

$$K_T = K_R \exp[-\frac{E_a}{R}(\frac{1}{T} - \frac{1}{T_R})t] \quad \text{---------------} \quad (3)$$

Where K_R is pre-exponential constant at the reference temperature (min^{-1}), E_a is the activation energy (KJ/mol), R is the ideal gas constant (8.314 J/mol.K). T is the actual temperature (K), T_R is the reference temperature (K) and t is the time (min). The regression of the natural logarithm of the degradation rate constant (K_T) against ($\frac{1}{T} - \frac{1}{T_R}$) in which a straight line curve is obtained indicates that the Arrhenius model was fulfilled and slope of this curve (Arrhenius plot) is equal to E_a/R and allowed calculation of the activation energy.

Half-life times for each temperature degrees ($t_{1/2}$) were determined according to Villota and Hawkes (1992)

$$t_{1/2} = \frac{\ln(2)}{K_T} \quad \text{-- (4)}$$

The time required to reduce the ascorbic acid concentration by 90% (D values) and the temperature required for a 90% decrease in D values (Z values) was estimated according to Ariahu and Ogunsua (2000):

$$D = \frac{K_T}{2.303} \quad \text{-- (5)}$$

and

$$Z = \frac{T_2 - T_1}{\ln(D_1/D_2)} \quad \text{------------------------------------- (6)}$$

Where D_1 and D_2 are decimal reduction time at temperature T_1 and T_2.

The degradation effect of drying due to successive moisture removal or loss from the pawpaw and the corresponding ascorbic acid losses were correlated by considering a simple linear regression model of the form:

$$Y = b_o + b_1 X \quad \text{--------------------------------------- (7)}$$

Where Y is the ascorbic acid loss, X is the moisture or water loss, b_o is a constant of regression, and b_1 is the viable coefficient due to moisture or water loss. Hence, the empirical value of b_o and b_1 were obtained from a plot of Y against X where the slope of the curve is equal to b_1 and the intercept is equal to b_o (Fig. 5). This could be used for the prediction of loss (or otherwise the retention) of ascorbic acid in pawpaw.

3.0 RESULTS AND DISCUSSION

L- Ascorbic acid content of potato and pawpaw were found be 19 mg/100g and 60 mg/100g, respectively. Nevertheless, the amounts determined were reasonably comparable with those of other fruits such as citrus fruits, guava (Vieira et al., 2000; Uddin et al., 2002) and leafy vegetables such as African Spinach (Amaranthus hybridus) (Omueti and Adepoju, 1988).

Mathematical Modeling of Ascorbic Acid Degradation

To establish the kinetic model, a two-step mathematical method was used. In the first step, a linear regression analysis was applied to calculate the degradation rate constant for each experiment. Figs.1 and 2 respectively shows the decrease in ascorbic acid content of potato and pawpaw during heat treatment with time by fitting to a first-order reaction equation. The kinetics of degradation followed a first-order reaction in confirmation of those previously reported (Johnson et al. 1995; Lee and Chen, 1998; Manso et al., 2001; Karhan et al., 2004).

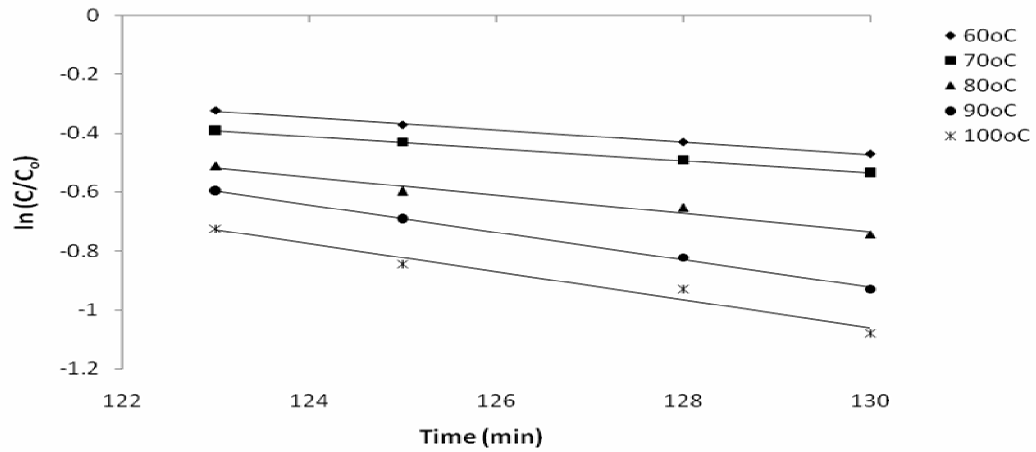

Fig. 1: Loss of ascorbic acid content of potato with time during blanch-drying at different temperature

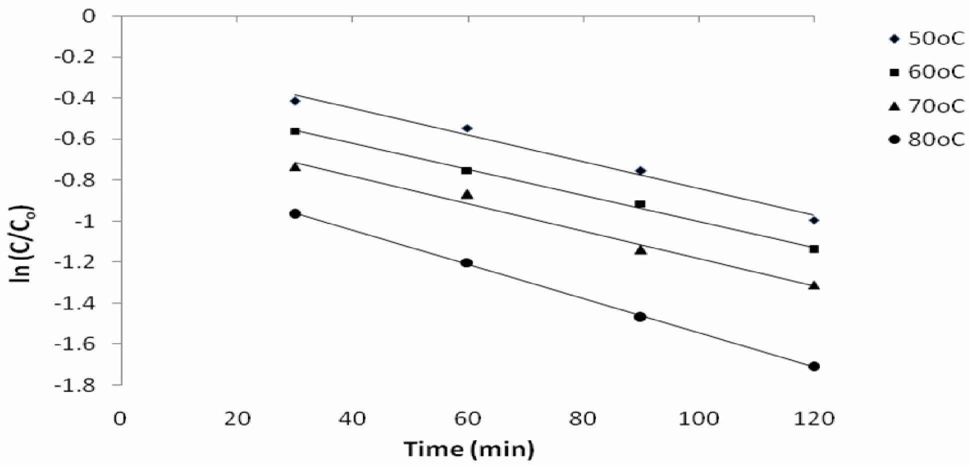

Fig. 2: Loss of ascorbic acid content of pawpaw with time during drying at different temperature

The degradation rate constants determined from the slopes of the regression lines are presented in Table 1. The low values of the rate constant for pawpaw were indications of the ease of thermal degradation of ascorbic acid as compared to the potato as shown in Table 1. This factor is important in the optimization of process control applicable to blanching and drying. More also, the degradation rate constants for both potato and pawpaw increased with temperature. A similar observation has been reported for ascorbic acid degradation in tomato (Marfil et al., 2008) and in orange juice (Manso et al., 2001).

Table 1: Rate Constants for Thermal Degradation of Ascorbic Acid in Potato and Pawpaw at Various Temperatures.

Food Material	T °C	$K_T x10^{-3}(\min^{-1})$	R^2
POTATO	60	21.1	1.00
	70	20.6	1.00
	80	31.0	0.97
	90	46.6	0.99
	100	47.0	0.97
PAWPAW	50	6.50	0.98
	60	6.30	1.00
	70	6.70	0.98
	80	8.30	1.00

In the second step, to define the temperature dependence of the degradation rate constants, the Arrhenius equation was used (Equation 3) as shown in Figs. 3 and 4 for pawpaw and potato, respectively.

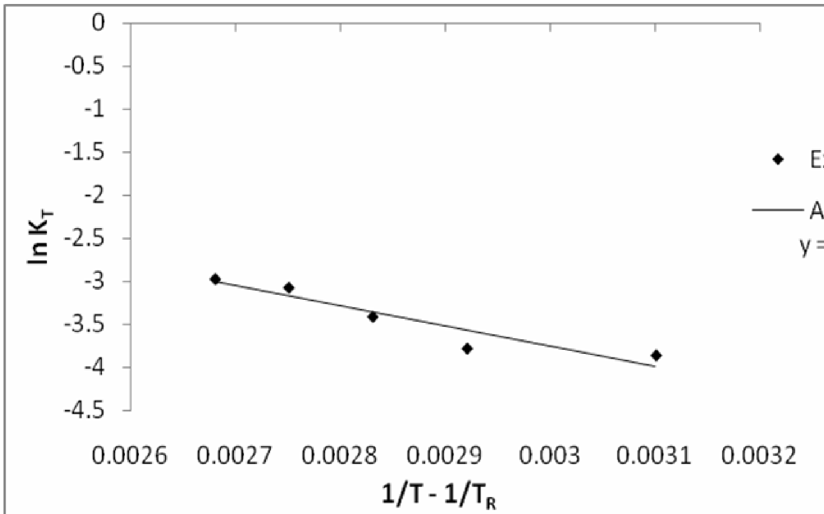

Fig. 3: Plot to determine activation energy of ascorbic acid degradation in pawpaw

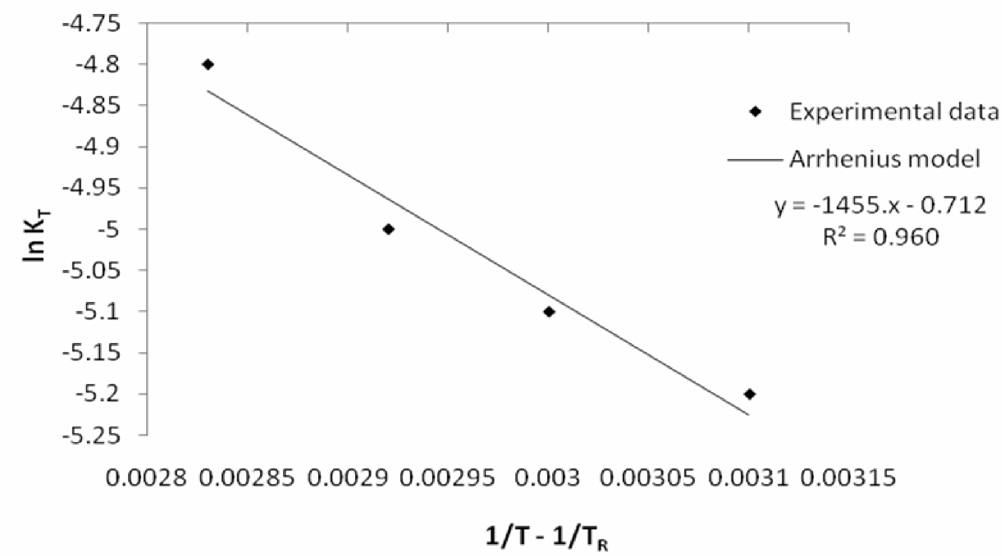

Fig. 4: Plot to determine the activation energy of ascorbic acid degradation in potato

The temperature-dependent effects of blanch-drying and drying without blanching on activation energy (E_a) showed different numerical values for potato (19.0 KJ/mol) and pawpaw (12.1 KJ/mol), respectively, as shown in Table 2. The activation energy (E_a) is an entropy potential which evaluates the quality changes in the food system from the estimates of the rate constant using process temperature as the cause-and-effect driving force.

Table 2: Activation Energy **(**E_a**),** D**,** Z and $T_{1/2}$ Values of Ascorbic Acid during Blanch-Drying of Potato and Drying of Pawpaw

Food Material	T °C	D (min)	E_a (KJ/mol)	Z (°C)	$T_{1/2}$ (min)
POTATO	60	108			32
	70	101			30
	80	70	19.3	117	21
	90	49			15
	100	45			13
PAWPAW	50	415			125
	60	358			108
	70	340	12.1	52	102
	80	280			84

The E_a values of 19.0 KJ/mol and 12.1 KJ/mol obtained for potato and pawpaw respectively in this study are lower than the values of 115.5KJ/mol (Johnson et al., 1995) and 38.6 KJ/mol (Manso et al., 2001) for orange juice and 75 KJ/mol for cupuacu (Vieira et al.,. 2000) but in good agreement with the values of 14.4 - 47.4 kJ/mol for guava fruits stored at 30 and 50°C (Uddin et al., 2002) and 14.99 -36.00 KJ/mol obtained for tropical green leafy vegetables (ewedu (Corchorus olitorus), tete (Amaranthus hybridus) and ugu (Telfaira accidentalis)) during blanching at 55 – 90°C (Solanke and Awonorin, 2002). The E_a value of pawpaw is lower than that of potato which implies that ascorbic acid in pawpaw is more easily susceptible to thermal processes as compared to potato; however, the low activation energy for both pawpaw and potato indicates that they are quite susceptible to thermal processes.

In addition to the E_a values obtained from the Arrhenius plot, the D, $t_{1/2}$ and Z values obtained for potato and pawpaw are each lower that those previously reported for grape fruit, lemon and tangerine juices (Vieira et al., 2000), orange juice (Johnson et al., 1995) and Rose Hip (Karhan et al., 2004), while the D values for pawpaw are higher than that of Rose Hip (Karhan 2004). The Z values of potato and pawpaw are higher than the Z values obtained for asparagus (Esteve et al., 1998) and canned peas (Rao et al., 1981). Fig. 5 shows the correlation between water or moisture loss (X) and ascorbic acid loss (Y) for pawpaw and this yielded the following result from Equation (7): $Y = 13.5 + 0.762X$ (R = 0.996)

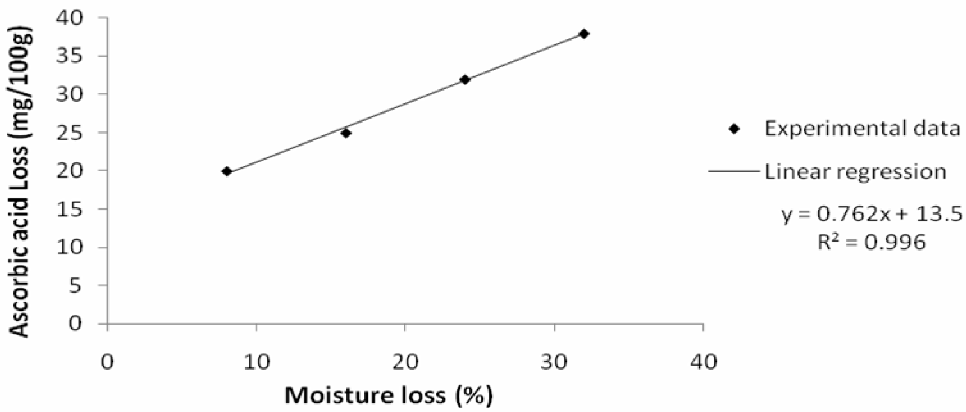

Fig. 5:The linear correlation between the ascorbic acid loss and moisture loss in pawpaw during drying

4.0 CONCLUSION

The losses of ascorbic acid depended on changes induced by thermal intensity of blanching and drying to disintegrate the fruit and vegetable (pawpaw and potato) structurally rather than composition of each fruit and vegetable because other components which constitute the product quality may also be affected differently in each of the samples. The thermal degradation of ascorbic acid as mathematically evaluated using the first order kinetic and Arrhenius model was found to be accurate for the potato and pawpaw as a function of process temperature and time.

The degradation rate constant for ascorbic acid degradation increases with increase in temperature and these values were high for potato than papaw. The activation energy (E_a) for ascorbic acid degradation in potato is higher than that of pawpaw; however, by a factor that is less than two. The D values and $t_{1/2}$ values of pawpaw are higher than that of potato, while the Z value of potato is higher than that of pawpaw. The empirical correlation of ascorbic losses with moisture loss predicted closely to the experimental results and can be used as indicator parameters to execute the changes of processing conditions for a desired ascorbic retention involving pawpaw.

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