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ORIGINAL ARTICLE

Kinetics of ascorbic acid loss during hot water blanching of fluted pumpkin (*Telfairia occidentalis*) leaves

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Abstract The kinetics of thermal degradation of ascorbic acid in fluted pumpkin leaves were investigated from 60 to 90°C (pH 5.0 to 6.5). Ascorbic acid degradation was modeled as a first order rate reaction with the rate constants increasing with increase in pH of the medium. The pH and temperature dependence of the rates of destruction gave highly significant correlations when analyzed by the thermal resistance and activated complex reaction rate methods. Activation energy (Ea) ranged from 41.2 to 18.2 kJ/mol while D-values ranged from 103.3 to 22.4 min. The changes in activation energy affected K_o values which ranged from 5.98×10^4 to 41.7 min^{-1}.

Keywords Thermal degradation · Fluted pumpkin · Activation energy · D-value · Frequency factor

Vegetables are low in fat and energy with high carbohydrate and fibre contents, providing significant levels of some micronutrients. Fluted pumpkin popularly called "Ugu" in Igbo speaking areas of Nigeria is a major leafy vegetable in Nigerian dishes (Lucas 1988). The ascorbic acid content in raw vegetable ranges from 160 to 180 mg/100 g (Ifon and Bassir 1979). Traditionally, the leaves are used for preparing soups, yam and cocoyam porridges. Ascorbic acid is valuable for its antioxidant effect, stimulation of the immune system, inhibition of formation of cancer-causing N-nitroso compounds in the stomach and these health benefits are being actively investigated and reported (Hussein et al. 2000).

During processing in homes and in institutional cooking, the fresh vegetables receive some heat treatment, in water media in which diffusion mass transport may increase loss of vitamin C to 50% or more (Benterud 1977; Paul and Southgate 1988). Losses in vitamin C content of some Nigerian leafy vegetables during traditional and pilot-plant scale cooking have been reported (Fafunso and Bassir 1976, Onayemi and Badifu 1987; Badifu 1991). The information is only partial because initial and final vitamin C concentration values are only reported and intermediate predictions are difficult to make.

Kinetic parameters, such as reaction order, rate constant and activation energy, are essential for predicting food quality loss during storage as well as thermal processing (Nisha et al. 2005). Also kinetic data are essential for predicting vitamin, C retention in vegetable processing and preservation. The degradation kinetics of ascorbic acid in model systems conforms to first order kinetics with the activation energy being a linear function of pH; the degradation is also affected by temperature as well as enzymes such as polyphenol oxidases and ascorbic acid oxidases (Ariahu et al. 1997). Information on the effect of temperature and pH of medium on ascorbic acid retention in fluted pumpkin leaves is lacking.

The objective of this study was to improve on ascorbic acid retention during processing of fluted pumpkin leaves using predictive kinetic approach. The specific objectives were to determine (a) the effect of heating temperatures (60 to 90°C) and pH (5.0 to 6.5) on ascorbic acid retention in

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fluted pumpkin leaves and (b) the rate constants and activation energies that characterize ascorbic acid degradation in fluted pumpkin leaves as influenced by pH.

Materials and methods

Fresh fluted pumpkin leaves used for this study were obtained locally from Wurukum market, in Makurdi, Nigeria. It was kept in polythene bag and immediately transported to the laboratory for treatments and analyses within 1 h after purchase. The vegetable was thoroughly washed in clean tap water to remove dirt or bruised leaves, and hard stems were also trimmed off. The fresh portion of fluted pumpkin leaves were weighed (120 g) and the samples were divided into 6 equal lots labeled as I, II, III, IV, V and VI, and immersed in 100 ml slightly acidified deionized water of varying pH (5.0, 5.5, 6.0 and 6.5). Lot 1 was used as control to obtain initial ascorbic acid content in the fluted pumpkin leaves. Lots 11, 111, 1 V, V and V1 were blanched at temperature ranging from 60 to 90°C for 10, 15, 20, 25 and 30 min respectively. Each lot was cooled, blended in a Kenwood blender (Philips, HR 1702, Borehamwood, England, UK) and filtered with cheesecloth. The liquid extracts were used to assess the kinetics of ascorbic acid loss during hot water blanching.

Extraction of L-ascorbic acid The treated samples were cooled and extraction of ascorbic acid was carried out according to AOAC (1995). Twenty grams of each treated sample was blended in a Kenwood blender (Philips, HR 1702, Borehamwood, England, UK). Ten milliliter of each

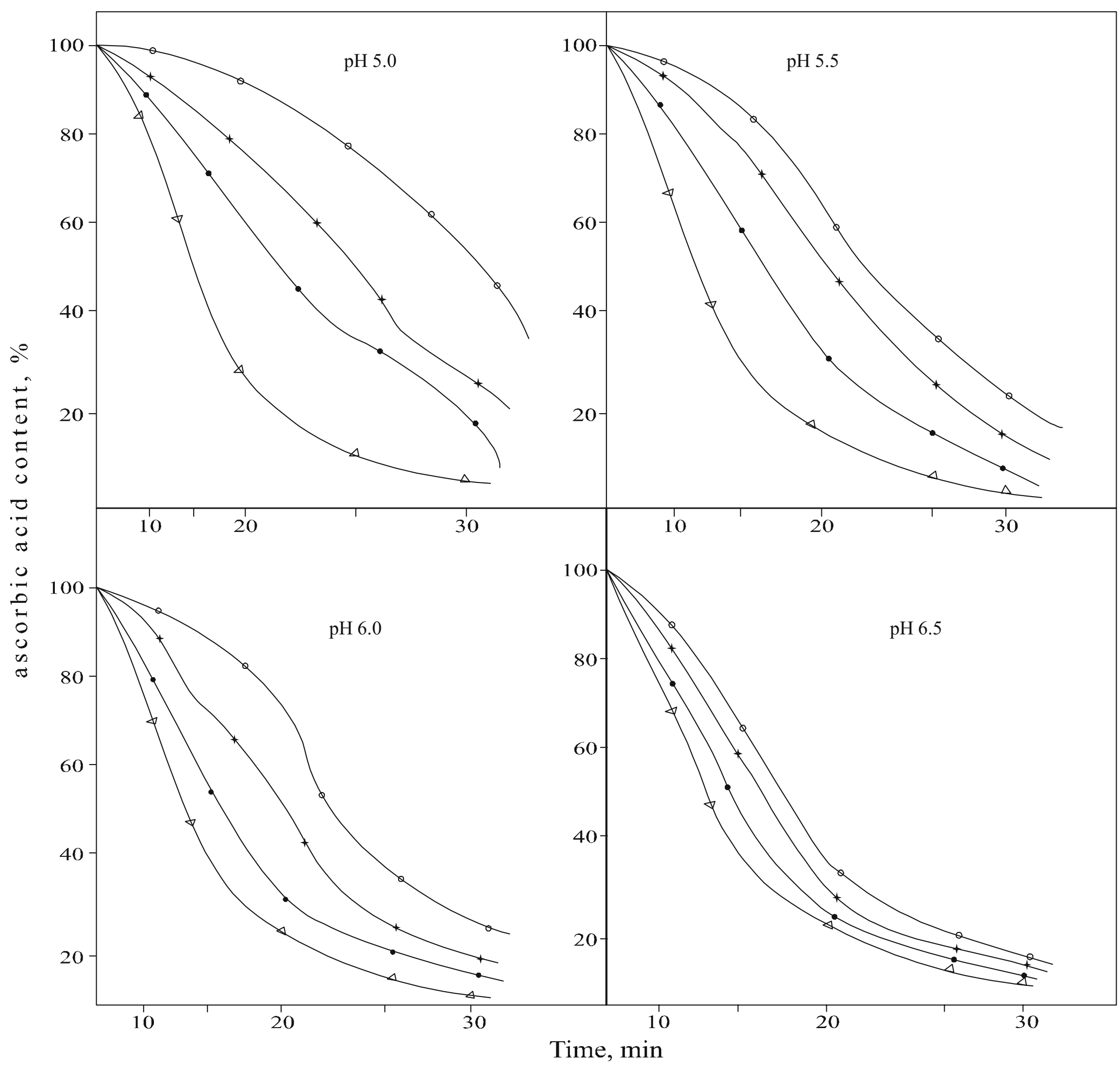

Fig. 1 Percentage retention of ascorbic acid in fluted pumpkin leaves at various pH and heating temperatures (60°C (o), 70°C (+), 80°C (•), 90°C (▵))

sample was mixed with 2 ml of freshly extracted solution, 5% trichloroacetic acid and was filtered rapidly with cheese cloth and the filtrate was the ascorbic acid extract.

Determination of vitamin C This was done according to the method described by AOAC (1995). Extracts from treated samples were separately treated with 0.8 g of activated charcoal to remove chlorophyll which might interfere with titration and filtered with cheese cloth. Ten milliliter of the aliquots was dispensed into conical flasks. The solutions were then titrated against 2, 6-dichloroindophenol solution until the solution turned to a slight pink colour which persisted for 15-sec (end points), thus indicating that enough dye has been added to react with the ascorbic acid in the extract which was calculated from the quantity of the dye added.

Kinetic data analysis A modified steady state procedure (Nunes and Swartzel 1991) was used in which data were generated only in the isotherm portion of heating. Samples were heated to reach the processing temperature and held for the desired time. A two-step method was used to calculate activation energy. This method of analysis required the determination of the relationship between percent of ascorbic acid remaining and time (t) to fit a kinetic model:

$$dC/dt = KC^n$$

where C = concentration of ascorbic acid, K = reaction rate constant, n = order of reaction, t = time.

For zero order reaction:

$$C_o - C = Kt$$

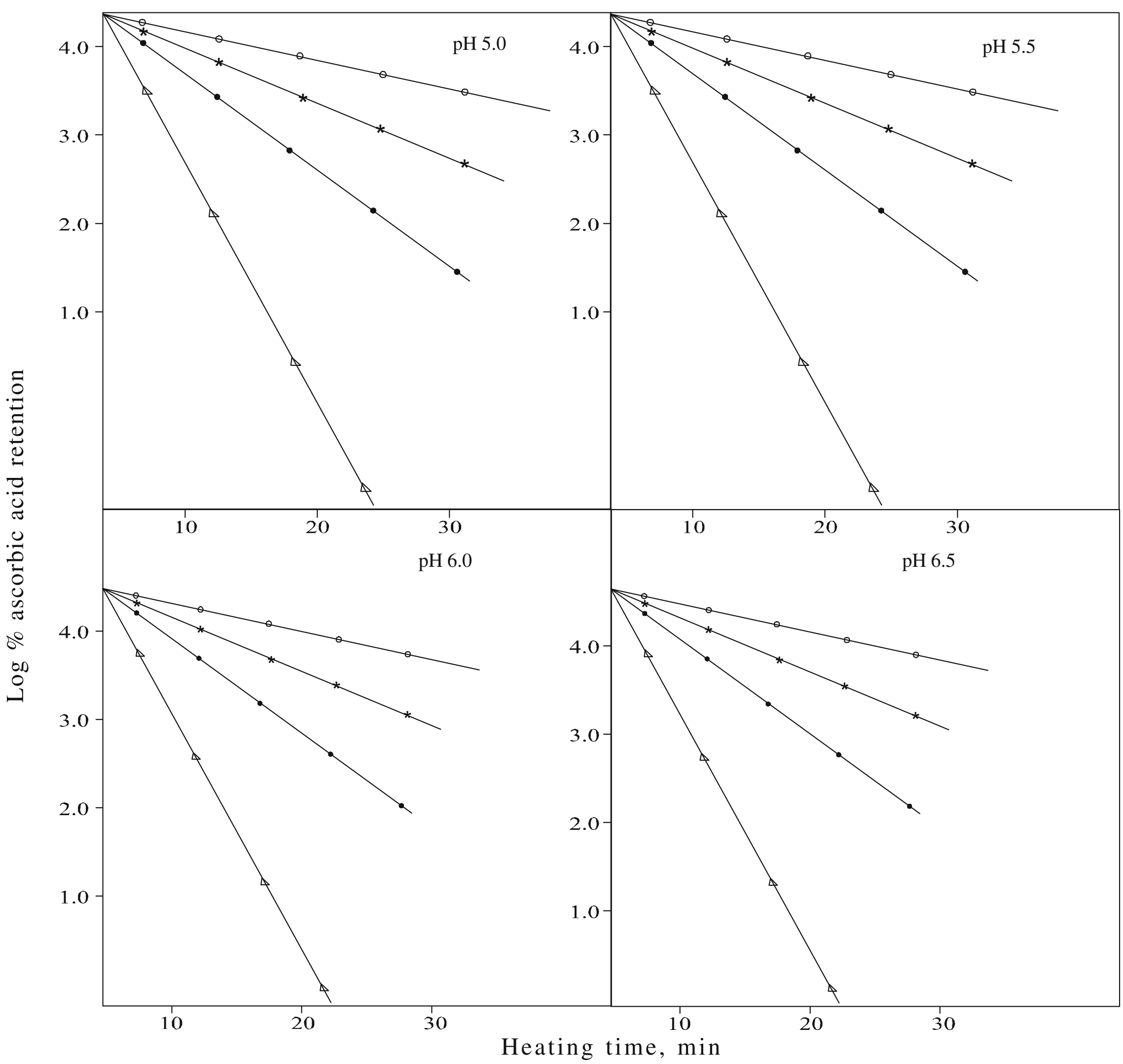

Fig. 2 Percentage retention of ascorbic acid in fluted pumpkin leaves at various pH and heating temperatures (60°C (o), 70°C (+), 80°C (•) 90°C (▵))

Table 1 Regression parameters for first order reaction kinetics of ascorbic acid degradation in fluted pumpkin leaves at various pH of blanch water

Regression parameter	Temperature (°C)			
	60	70	80	90
pH 5.0				
r^2	0.882	0.864	0.954	0.974
Standard error	0.08	0.10	0.16	0.11
Intercept	4.7058	4.5125	4.5886	4.4661
Slope(min^{-1})	0.0223	0.0271	0.0548	0.0692
D-value(min)	103.4	81.9	42.0	33.3
pH 5.5				
r^2	0.992	0.989	0.984	0.976
Standard error	0.07	0.07	0.06	0.15
Intercept	4.5870	4.5195	4.5250	4.3090
Slope(min^{-1})	0.0486	0.0680	0.0699	0.0819
D-value(min)	47.4	36.7	33.0	28.1
pH 6.0				
r^2	0.996	0.985	0.998	0.977
Standard error	0.05	0.11	0.04	0.13
Intercept	4.5490	4.6264	4.5862	4.3329
Slope(min^{-1})	0.0518	0.0692	0.0802	0.0899
D-value(min)	44.5	33.3	28.7	25.6
pH 6.5				
r^2	0.992	0.989	0.984	0.976
Standard error	0.07	0.07	0.06	0.15
Intercept	4.5870	4.5195	4.5250	4.3090
Slope(min^{-1})	0.0486	0.0680	0.0699	0.0819
D-value(min)	47.4	36.7	33.0	28.1

For first order reaction:

$$\ln C_o/C = -Kt$$

The reaction rate constants were obtained from least square linear regression analysis and related to temperature by Arrhenius equation:

$$\ln K = \ln K_o - E_a/R(1/T)$$

where, Ea is activation energy, R is the universal gas constant (8.3145 J/mol. °K), K_o is the frequency factor and T is absolute temperature. From a plot of the logarithm of the rate constants versus 1/T, the slopes and the intercepts were obtained using least square linear regression (Gupta 1978). Activation energy, E_a/R was determined from the slope of the lines while the intercepts gave the frequency factors.

The decimal reduction times or D-values (i.e. the time required to reduce the ascorbic acid concentration by 90%) was determined using the TDT-method as described by Ariahu et al. (1997) using the equation:

$$D = 2.303/K$$

where, K = rate constant

Results and discussion

Kinetics of ascorbic acid degradation Figure 1 shows a non-linear relationship, and an obvious degradation, therefore the zero order plot was insufficient to predict reaction rates. The first order plots of Log_e% ascorbic retention with respect to time for each temperature was made as shown in Fig. 2. Increase in temperature, pH and heating time caused a reduction in ascorbic acid retention in fluted pumpkin leaves. The loss of ascorbic acid was enhanced probably by the activity of ascorbic acid oxidase, which is strongly dependent on pH of the vegetable. The plots showed a pseudo first order kinetics. For a first order reaction model, it can be shown that:

$$\text{In } C_0/C = Kt.$$

Table 1 shows the regression parameters for the degradation of ascorbic acid in fluted pumpkin at the various processing pH and temperature conditions studied.

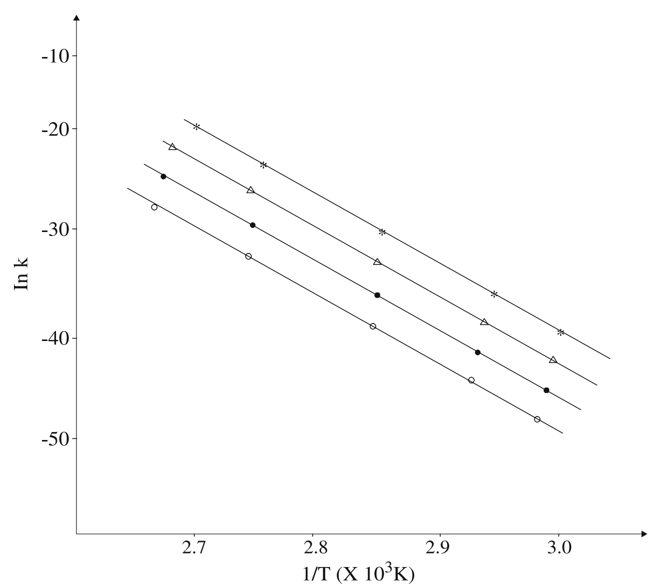

Fig. 3 Arrhenius plot for degradation of ascorbic acid in fluted pumpkin leaves at various pH 5.0 (o), 5.5 (•), 6.0 (*), 6.5 (△)

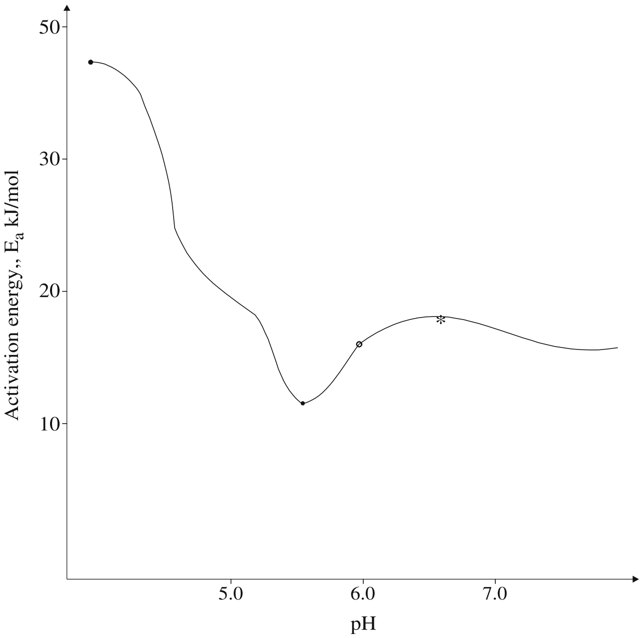

Fig. 4 Arrhenius parameters for thermal (60–90°C) degradation of ascorbic acid in fluted pumpkin leaves at various pH values

The rate constants, K, increased slightly with increase in pH and temperature. Rate constants ranged from 0.0223 to 0.1028 min^{-1}. The thermal susceptibility of ascorbic acid in fluted pumpkin is clearly illustrated by the destruction rate curves. The high correlation coefficients ($r \geq 0.996$) in addition to the straight lines for pseudo first order kinetics suggested that the model was satisfactory in describing thermal degradation of ascorbic acid in fluted pumpkin at various pH values of processing. Zero and second order models did not posses any significant advantages over the first order model. The D-values ranged from 22.4 to 103.3 min and decreased with increase in pH value and temperature.

Temperature dependency Figures 3 and 4 shows that degradation of ascorbic acid is temperature dependent at a given pH. Table 2 shows the regression parameters for Arrhenius relationships between the degradation reaction rate constants and pH variations in the fluted pumpkin leaves. Arrhenius relationship was empirically derived to describe the temperature dependence of simple chemical reactions. It has proven to be very worthwhile in chemical kinetics. It relates the rate constant, K, of a reaction to absolute temperature T.

The activation energy can be seen as the energy barrier that molecules need to cross in order to be able to react. Activation energy value varied between 16.9 and 41.2 kJ/mol. Activation energy values for ascorbic acid degradation are in agreement with reported ranges by Mauri et al. (1989). Higher activation energy implies that a smaller temperature change is required to degrade a specific compound more rapidly. Therefore, ascorbic acid is more susceptible to thermal degradation at higher pH values than at lower pH values. Thus, the effect of the critical pH 5.5 can be observed; this pH produces effects which are not in line with the overall relationship between increasing acidity and heat resistance observed.

Conclusion

Ascorbic acid degradation in fluted pumpkin can be predicted by first-order kinetics. High pH blanching of fluted pumpkin leaves showed more degradation of ascorbic acid, thus it increased the heat sensitivities of the ascorbic acid content. Hence low pH coupled with high temperature short time processing would retain more ascorbic acid than low temperature long time at high pH values of processing. Fluted pumpkin leaves being a low acid vegetable, increasing its acidity helps to retain more of its ascorbic acid content during industrial processing as well as conventional home processing.

Table 2 Arrhenius regression parameters for ascorbic acid loss in fluted pumpkin leaves during blanching in hot water of varying pH values

Regression parameter	pH			
	5.0	5.5	6.0	6.5
N	4	4	4	4
r^2	0.944	0.975	0.981	0.997
Standard error	0.13	0.02	0.03	0.01
Intercept	10.998	3.0946	3.6551	3.7552
K_o (min^{-1})	5.98×10^4	22.08	38.67	42.70
Slope	-4952.02	-2027.91	-2188.74	-2191.34
E_a (kJ/mol)	41.2	16.9	18.2	18.2

n number of points, E_a activation energy, K_o frequency factor, r^2 regression coefficient

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