International Food Research Journal 16: 555-560 (2009)

A dynamic method for kinetic model of ascorbic acid degradation during air dehydration of pretreated pineapple slices

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Abstract: A dynamic method was developed for kinetic model parameter estimation of ascorbic acid degradation during air-dehydration of pretreated (sucrose and sulphiting pretreatments) pineapple slices. Pineapple slices were pretreated in sucrose solution of 40% and 60% and SO_2 solution of 1500ppm and 2500ppm SO_2 respectively before air-dried in a cabinet dried for 10h at 70^0C temperature. Ascorbic acid concentration was monitored as a function of moisture lost during dehydration. The model showed that there was a linear degradation of ascorbic acid with moisture loss during drying. The samples pre-treated at 40% and 60% sucrose recorded 2.60 and 2.42mg/100g as rate of ascorbic acid degradation respectively, while the sulphite pretreated slices recorded 1.38 and 0.84mg/100g for 1500ppm and 2500ppm SO_2 respectively. The data obtained were used to estimate optimal parameters in a kinetic model describing the rate of degradation of ascorbic acid as a function of moisture content and time.

Keywords: pineapple, kinetic model, drying, pretreatment

Introduction

Pineapple (*Ananas comosus*) is one of the common non-citrus tropical and subtropical fruit, largely because of its attractive flavour and refreshing sugar-acid balance and a very rich source of vitamin C and organic acids (Bartolomew *et al., 1995*).

Vitamin C is water soluble, highly unstable and a primary function is to prevent scurvy. However, during processing, most especially with the application of heat, which causes destruction of the vitamin thus, drying of fruits like pineapple may lead to loss of the vitamin (Kaushal, 1990; Solanke and Awonorin, 2002; Osundahunsi, 2008). Reports have shown during fruits and vegetable preparation, losses of vitamin C may be high, and this may sometimes exceed those caused by drying operation. Early report showed that losses of the vitamin C during preparation of apple flakes were 8% during slicing, 62% from blanching; 10% from pureeing and 5% from drum drying. Reports have also that shown that vitamin C degradation could be as high as 80-95% during air-dehydration of fruits (Miskin *et al.,* 1984; Karim, 2005). This limits the air-dehydration of fruits (McMinn and Magee, 1997). The removal of moisture during drying is attributed to the changes on the dried products. To alleviate this problem of air-dehydration of fruit, pretreatment of fruit slices with sucrose-osmosis and sulphiting (SO_2) have been proved effective (Levi *et al.,* 1980; Alvarez *et al.,* 1999; Karim, 2005).

Many researchers have investigated the effect of osmotic dehydration prior to conventional drying on the rate of moisture transport and product quality (Vaccarezza *et al.,* 1974; Raoult-Wack, 1994; Karim, 2005; Karim *et al.,* 2008). Sulphur dioxide (SO_2) pretreatment inhibits enzymatic and non-enzymatic darkening during drying. Invariably as these pretreatment influenced the drying rate and moisture transport, the consequential Vitamin C degradation during drying may be impaired.

An obstacle in the path of maximizing nutrient retention during drying is the lack of adequate kinetic models. In general, the degradation kinetics of nutrients is a function of moisture and temperature. Unfortunately, a food product traverses a large range of temperature and moisture during drying. Thus, a kinetic model must necessarily be representative over this range. Usually, such modeling is done using data from static experiments using a balanced matrix design (Miskin *et al.,* 1984). The study was designed to determine the influence of pretreatments with sulphur dioxide and sucrose (osmosis) on the degradation of vitamin C during drying at 70^oC by developing a mathematic model to describe the path. The study was conducted using the proposed

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dynamic methods (Miskin *et al*., 1984; Karim, 2005) to develop a kinetic model for description of the ascorbic acid degradation during air-dehydration of pretreated pineapple slices.

Materials and Methods

Freshly harvested pineapple fruits (*Ananas comosus* L.) from Ajanla farm via, Ibadan, Nigeria were used for the study. The fruit had a good indication of physiological maturity and eating quality of flat 'eyes', with a slight hollowness at the centre; enlarged fruit, less firm and more aromatic. The fruits were kept at 18^0C and 80-90% relative humidity until used and processed within the 48 h of arrival at the laboratory.

Experimental design

A two-factor factorial experimental design was used for the study. The factors were 3-levels of two pre-treatment methods of sucrose (osmosis) and sulphiting (SO_2) treatment and drying conditions (temperature/time) of 70^0C/10h. This resulted into (3 x 3) 9 samples for the study. The experimental ranges of factors were 0, 40 and 60% sucrose and 0, 1500 and 2500 ppm of SO_2 which were established from preliminary experiment and from published research. (Forni *et al.,* 1991).

Pre-treatment of pineapple slices

A batch each of 5 kg of pineapple slices was pre-treated with sucrose solution, and chemical treatment with SO_2 solution**.** Pineapple slices were osmotically treated by immersing into aqueous solution of 40% w/w or 60% w/w of sucrose (Food grade of 98% purity) for 10 min. The samples were drained on wire mesh and re weighed. The slices were also dipped in 1500 ppm and 2500 ppm sulphurdioxide solution made from potassium-meta bisulphate solution for 6 min and reweighed.

Analysis

Each sample was weighed before pre treatment and after. The samples were also analysed for pH; titrable acidity; and moisture using (A.O.A.C. 2000) methods after treatment. The ascorbic acid was determined by titration method of Ruck (1969) by macerating 5.25g of pineapple fruit in a blender. Ten grams of the sample aliquot was transferred into 250 ml volumetric flask made up to volume with 0.4% oxalic acid and then filtered. 15ml of 0.4% oxalic acid was added to 5 ml aliquot of the filtrate and titrated with standardized 0.04% dye (sodium 2, 6-dichloro phenol indophenol) to a faint pink point lasting for 5 seconds to 10 seconds. The result was presented as mg/100g ascorbic acid.

Calculation:

$$\text{Mg/100g ascorbic acid} = \frac{\text{dye equivalent x titre x dilution x 100}}{5}$$

$$= \frac{\text{dye equivalent x titre x 25 x 100}}{5}$$

$$= \text{dye equivalent x titre x 5 x 100}$$

NB: Dye equivalent = 0.189 ± 0.005.

Hot air-drying of pineapple slices

The pre-treated pineapple slices were dried in cabinet dryer (Gallenkamp hotbox oven size 2, England) under standard conditions on perforated stainless steel trays, of tray loading 1kg with cross-through airflow. The cabinet dryer consists of an insulated chamber. Hot air was circulated through the cabinet at 1.2m/s per square metre tray area. The cabinet has an automatically controlled air temperature and humidity, and at constant air velocity. The 9 samples of pineapple slices from the experimental design were dried simultaneously, in order to ensure uniform drying conditions.

As drying progressed, weight changes were recorded every hour from the difference between the initial and final weight of the slice. At the end of drying, the final product weight was recorded and its moisture content determined. The weight changes recorded during drying was used in calculating moisture in percentage dry weight basis and drying rate as a function of weight loss per unit dry matter per drying hour respectively. For this purpose, the drying container was removed, rapidly weighed and returned into the drier. A very good reproducibility between pairs of drying runs performed under identical conditions was found.

Kinetics of moisture transport and ascorbic acid degradation

The method of Alvarez *et al.* (1995) was used to monitor the kinetics of moisture transport during the drying of pineapple slices of 82.41% w/w moisture content. The volume of each pineapple slice (v) was measured using a pycnometer (with water as the fluid) and the equivalent spherical radius (Re) was then calculated from the formula for the volume of a sphere ($v = 4 \pi R^3e/3$) using the pineapple slice volume. As drying progressed, the ascorbic acid content was measured at every hour by titration method as described for the fresh slices. Analyses were determined in triplicate.

Table 1. Chemical qualities of fresh pineapple slices

Quality	Value
pH	3.52± 0.02
Titrable acidity (g citric/100g f.w)	1.15 ± 0.01
Moisture (% f.w.)	82.41± 0.42
Ascorbic acid (mg/100g f.w.)	32.50± 0.25

Each value represent mean of three replicates, f.w. – fresh weight, ± standard deviation.

Table 2. Rate of ascorbic acid degradation during air drying of pre-treated pineapple slices

Pretreatment method	Rate mg/100g
Control	2.72 ± 0.02
40% Sucrose	2.60 ± 0.01
60% Sucrose	2.42 ± 0.01
1500% ppm SO_2	1.38 ± 0.02
2500ppm SO_2	0.83 ± 0.01
40% Sucrose/1500ppm SO_2	1.64 ± 0.01
40% Sucrose/2500ppm SO_2	0.85 ± 0.01
60% Sucrose/1500ppm SO_2	1.62 ± 0.02
60% Sucrose/2500pmm SO_2	0.84 ± 0.01

Mean values of triplicate analysis. + - standard deviation.

Kinetic model for ascorbic acid degradation during air-drying of pineapple slices was obtained using a dynamic test approach (Saguy *et al*., 1978; Mishkin *et al*., 1982; Mishkin, 1983). An empirical first-order kinetic model was used.

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

where C is the concentration of ascorbic acid (normalized with respect to initial concentration). The first-order rate constant (k) is Arrhenius temperature dependence,

$$k = k_o \exp [- E_a/RT] \quad (2)$$

where k_o and E_a have moisture functionality,

$$\text{In } k_o = P_1 + P_2M + P_3M^2 \quad (3)$$

$$E_a = P_4 + P_5M + P_6M^2 + P_7M^3 \quad (4)$$

and water M is the moisture content in g/g-solids.

Results and Discussion

The initial moisture content of the fruit was 82.41% while the ascorbic acid was found to be 32.5/mg/g, TTA value was 1.17% and pH was 3.5 as presented in Table 1. The effect of sucrose (osmosis) and sulphiting pre-treatment on ascorbic acid degradation of pineapple slices during drying at 70^0C temperatures are shown in Figure 1. This revealed that there was significant degradation of ascorbic acid. A constant fall in the ascorbic acid content was noted for all samples. The control sample had the steepest curve and highest rate of reduction of ascorbic acid as 2.72 mg/100g/h (Table 2). The pattern of the curve may be due to the significant effect of application of heat on ascorbic acid. The sulphited samples showed a significant protective effect on the ascorbic acid throughout the drying period. The average ascorbic acid degradation was 1.38 and 0.83 for 1500 ppm and SO_2 respectively. However, due to evaporation of SO_2 along with the moisture during drying, the protective nature of SO_2 reduces as drying time increased.

The reduction in ascorbic acid observed during drying indicates instability of ascorbic acid at elevated temperatures (Solanke and Awonorin, 2002; Osundahunsi, 2008). The sucrose (osmosis) pre-treatment did not show much protective effect on the ascorbic acid loss during drying.

However, the sulphited samples had better retention of ascorbic acid content, which was due to the earlier observed protective effect of sulphiting pre-treatment on ascorbic acid content of food (Levi *et al*., 1980). The 60% sucrose/1500ppm SO_2 recorded the highest value of 1.62 mg/100g while the 60% sucrose/2500ppm SO_2 had 0.8 mg/100g. The significant difference in the values of sulphited pre-treated samples relative to control explains the protective nature of SO_2 on ascorbic acid during drying. This was why there was high retention of ascorbic acid during the first five hours of drying. The SO_2 exhibited a great protection on ascorbic acid.

This is in agreement with the findings of Roberts and Weeny (1972), Levi *et al.* (1980), Bhardwaj and Kaushal (1990), Alvarez *et al.* (1995) on the protective nature of SO_2 on ascorbic acid. However, the residual/retained SO_2 decreased as drying progressed thus, degradation of the ascorbic acid increased with drying. The combination effects of sucrose and SO_2

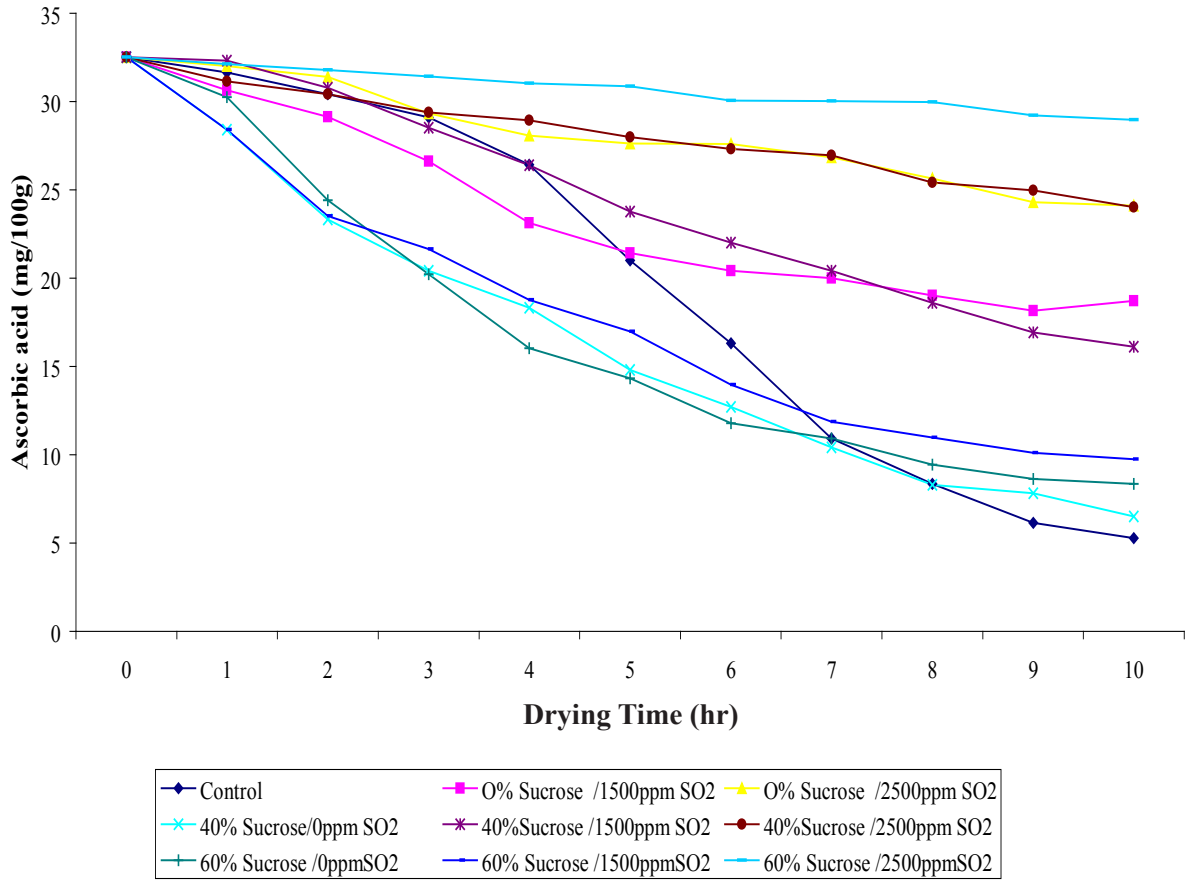

Figure 1. Effect of Sucrose and Sulphiting on ascorbic acid degradation of pineapple slice at 70°C drying

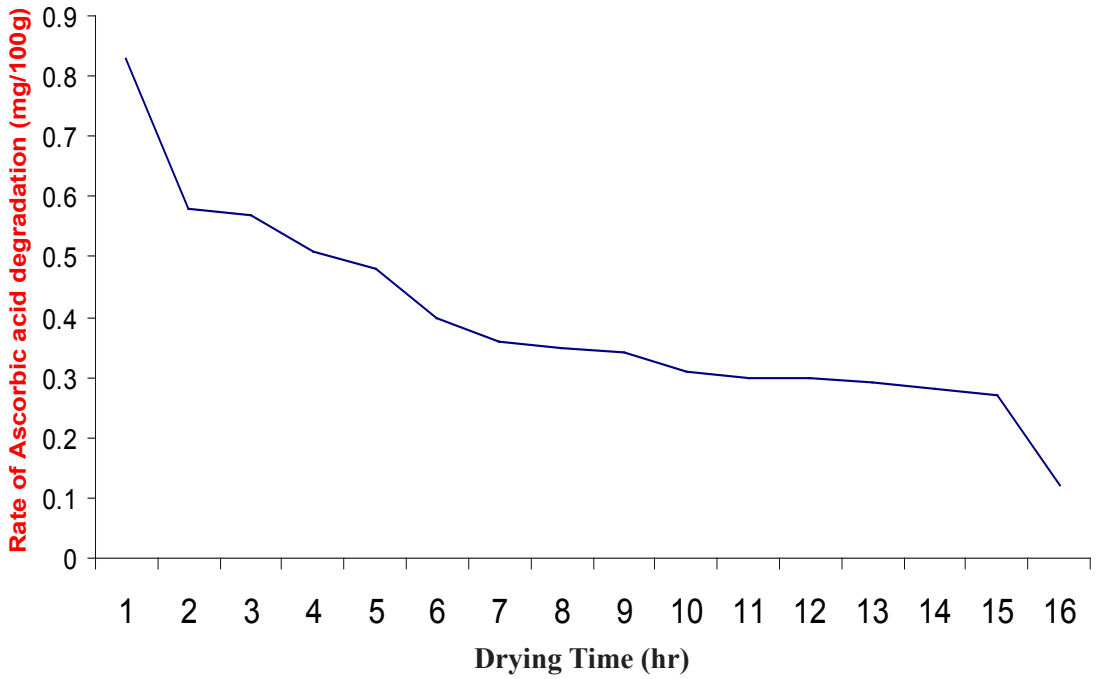

Figure 2. Effect of pre-treatment methods on quality attributes of dried pineapple slices at 70°C drying

Table 3. Ascorbic acid kinetic model parameter values for Eq. 3 and 4

Parameter	Value
P1	16.95
P2	1.921
P3	1.911
P4	14931.3
P5	241.1
P6	656.2
P7	3326.8

(Simulated results for data for the estimated parameters are shown in Figure 2 along with the data for the experiments)

observed on the degradation of ascorbic acid also corroborate the explanation of Levi *et al.* (1980) on possible protection from enzymatic destruction. The linear degradation of ascorbic acid with time is an indication of instability of ascorbic acid in fruit slices; it is water soluble and heat sensitive.

During the early stages of drying, the membrane integrity of the pineapple tissue was substantially intact, protecting the ascorbic acid from deleterious cell components. As drying proceeded and the moisture content of the slices dropped (and the internal temperature of the slices increased) the compartmentation of the slices might have been lost resulting in accelerated kinetics of ascorbic acid degradation. It is also possible that endogenous antioxidative constituents may be responsible for the initial low rate of ascorbic acid reduction experienced by the samples. However the two combinations of the pre-treated methods exhibited a significant effect on the rate of ascorbic acid degradation. The variation in the quantity of SO_2 used for pre-treatment also exhibited a marked influence on the ascorbic acid content during drying. The sample pretreated with 2500 ppm SO_2 exhibited a greater protection on the ascorbic acid than the sample pretreated with 1500 ppm $SO_{2.}$ The higher the value of SO_2 used for pre-treatment, the lower the degradation of the ascorbic acid.

The kinetic model employed for the description of ascorbic acid degradation during drying showed that there was a linear degradation of ascorbic acid. The dynamic test approach of Saguy *et al.,* (1978); Miskin *et al.,* (1984) on empirical first-treatment methods also showed a significant effect on the model and values of P_1 –P_7 of equations 3 and 4 are parametic constants estimated using the proposed modeling method shown in Table 3.

There was a rapid decrease in the rate constant at high moisture levels due to the physical circumstances under which the kinetic data were obtained. The model views the phenomena of the ascorbic acid degradation as a diminished rate at high moisture levels. The kinetic model developed in this study and in particular the estimated parameters are representatives of the particular batch of pineapple slices used.

Conclusion

Due to the complexity of plant tissue there is likelihood of different ascorbic acid degradation kinetic among varieties of pineapple fruits. However, this model has shown that the ascorbic acid degradation can be described using first order kinetics using the average moisture content loss during drying.

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