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Research Article

Comparative Study of Degradation Kinetics of Ascorbic Acid (Vitamin C) in Tray Drying, Solar Drying and open Sun Drying of Pineapple Slices

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Abstract

A comparison of degradation kinetics of ascorbic acid was done on tray, solar and open sun drying of pineapples. Thin slices of 10mm±3 thickness were equally weighed and divided into three samples of 300g each. One 300g sample was placed in a tray dryer and dried at a temperature of 60oC, the next 300g sample was placed in the solar dryer and another 300g sample was placed on a tile for open sun drying and dried under fluctuating temperatures. Samples were taken at half hour intervals and analysed for vitamin C content over the drying period using the 2,6 dinitrophenolindophenol dye titration method. The residual vitamin C content in tray drying was least at 11.25 mg/100g of sample. This was followed by sun drying with a residual vitamin C content of 19.5mg/100g of sample. Solar dried sample showed the highest vitamin C retention with 29.25mg/100g of sample weight. The degradation kinetics were analysed using the first order fractional Model and the Weibull Model. The correlation coefficient (R2) was calculated for goodness of fit. The Weibull model had the best fit. However deviation from first order degradation kinetics of vitamin C was noted.

Keywords: Vitamin C; Ascorbic Acid; Dehydoxyascorbic acid; Degradation kinetics; Solar Drying

Introduction

The ultimate goal of food technology and food processing is to deliver safe, wholesome and nutritious food to the consumer. Wholesomeness and nutritive value denote the preservation of inherent nutrients which may otherwise be depleted during processing and or storage. Vitamins are a susceptible group of nutrients which require care during processing to avoid loss. Of particular interest in this study is Ascorbic Acid (Vitamin C). Its scientific name is L-3-keto-threo-hexuronic acid-γ-lactone [1], or 2-oxo-L-threo-hexono-1,4-lactone-2,3-endiol [2]. It is synthesised in most plants and some animals where humans and apes are an exception. These have to rely on diet to supply adequate amounts of vitamin C [2,3]. L ascorbic acid (AA) as it is often referred to be one of the most important anti oxidants obtained from fruits and vegetables [4]. The recommended daily intake ranges from 50-55mg for infants and it peaks to 100mg for 15 year olds to adults with lactating mothers requiring up to 150mg [1]. L-Ascorbic acid (Vitamin C) is water soluble and is heat labile. It is easily absorbed in the body but cannot be stored. High concentrations of vitamin C are found in the adrenal and pituitary glands. Several metabolites of the vitamin such as dehydroxy ascorbic acid, 2, 3-diketogluconic acid and oxalic acid can be found in the body [2,5]. They are lost through urine in various amounts. 3% is lost as ascorbic acid, 20-25% as dehydroxy-ascorbic acid and 50-55% as oxalic acid [1]. The benefits of ascorbic acid are multifold. They include anti-oxidant properties and free radical scavenging, anti-atherogenic, and anti-carcinogenic and immunomodulator [1,2,6]. The most important function of ascorbic acid is the prevention of scurvy [7].

Vitamin C degradation has been studied intently and various authors have attempted to characterise and fully describe the degradation kinetics. This is because vitamin C degradation is an important quality index due to its sensitivity to degradation during processing and storage [4,8]. According to Viera, [9] and Lee [8] the degradation of AA occurs in aerobic and anaerobic conditions and is specific for a particular system. In aerobic conditions, the L ascorbic acid is oxidized reversibly and the reaction can either follow a catalysed (by metals) or uncatalysed pathway. This yields L-dehydroxy-ascorbic acid (DHAA) which still exhibits the biological activity of AA. The DHAA can undergo further oxidation irreversibly to yield 2, 3-deketogulonic acid (DKGA) which has no vitamin C biological activity. Viera [9], further explained the AA degradation in anaerobic conditions where AA undergoes ketonisation to form an intermediate keto-tautomer called keto-ascorbic acid (KAA) which exists in equilibrium with its anion keto-monoanion-ascorbic acid (KMAA). Further delactonisation yields DKGA which as stated does not have the biological activity of vitamin C. Heat and oxygen are the major factors affecting the oxidation of AA to DHAA. Other factors affecting AA degradation during storage have been reported as low relative humidity, physical damage, pH, sucrose, enzymes and amino acids [8-11]. In this study an attempt was made to understand the degradation kinetics of ascorbic acid basing on the different temperature regimes namely constant temperature drying in an electric oven and comparing it with fluctuation temperature drying in open sun and indirect solar drying of pineapples.

Pineapples were used in this study due to their high content of vitamin C and the all year availability. Pineapple (Ananas comosus)

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Table 1: Two Mathematical models used in the comparative study.

Sr. No.	Mathematical Model Name	Formula
1	First order fractional Model	$P/P_0 = e^{-kt}$
2	Weibull Model	$C_{AA}/C_{AA0} = e^{\left(\frac{-t}{\alpha}\right)^{\beta}}$

- Where P is the ascorbic acid concentration at instantaneous time (t) for the fractional first order model, P0 is the ascorbic acid concentration at time t = 0 and k is the rate constant.
- Where CAA is ascorbic acid concentration at instantaneous time (t), CAA0 is ascorbic acid concentration at time t = 0, β is the shape parameter and α is the scale parameter in the Weibull Model.

is a non-citrus tropical fruit rich in vitamin C. Some sources claim it can be as high as 40-50mg/100g [12].

The drying of fruits has been and still remains an important preservation method throughout the history of mankind. It was the objective of this study to investigate and compare the degradation kinetics of ascorbic acid in the three modes of drying.

Materials and Methods

Fruit selection and preparation

Mature pineapples *(Ananas comosus)* of green-yellow colour were obtained from the fruit market in Chennai, Tamil Nadu, India, with an average weight of 150g±7g, a moisture content of 87%±5%. The fruits were peeled, sliced to an average thickness of 10mm±3 and cored. They were divided into three lots and the lots were dried in the solar dryer, tray dryer and in open sun drying.

Laboratory scale solar dryer prototype design

A laboratory scale solar dryer was designed and fabricated for this study. It had a capacity of 1kg. The dryer was constructed using sheet metal of thickness 4mm which had an insulated drying cabinet to prevent secondary heating from the walls. The dryer was intended to dry products from an average moisture content of 90% to 10% or less which caters for a wide range of fruits and vegetables.

The solar collector was a "flow above" flat bed collector with a black metal absorber covered with a 4mm transparent glass. The tilt angle was determined for the Chennai area where the latitude and longitude were determined based on data from NASA Langley Centre for Atmospheric Science (2002).

Psychrometry of drying air was considered so as to estimate the moisture carrying capacity of the air; the volume required hence the dimensions of the dryer. The Vernmaces HDP by psych Chart 7.5.6© software was used. From these calculations the dryer dimensions were determined. The dryer was classified as an active, indirect and forced convection cabinet solar dryer. It used heated air as the only heat source and air velocity for mass transfer [13]. A PID temperature controller was incorporated to aid in temperature measurement of the drying air in the solar cabinet. The heating mode was the indirect heating as reported by Belessiotis & Delyannis [13].

Open sun drying

Pineapple slices were spread (uni-layer) on a flat wooded surface and exposed to direct solar radiation. The drying process involved heat transfer by convection from the surrounding air and by direct absorption of solar incidence and diffuse radiation on the surface of the pineapples which caused the drying to occur [13]. A dry bulb thermometer was mounted to record the ambient air temperatures.

Tray dryer

An electric heated convective mode tray dryer was used as the third drying method. Pineapple slices were placed in perforated trays and dried at 60°C as suggested by [13] to be the mean drying temperature for most foods.

Ascorbic acid determination

The Ascorbic acid was determined by the modified 2, 6-dinitrophenolindiphenol dye method as described by Kadam [14]. Standard ascorbic acid solution was prepared by weighing 50mg of ascorbic acid powder and dissolving it in 50ml of 3% phosphoric acid. From this solution, 5ml was pipette into a conical flask and volume made up to 50ml with 3% phosphoric acid to make a standard solution. 2, 6-dinitrophenolindophenol dye was made by weighing 42mg of $NaHCO_3$ and dissolving it in hot distilled water. 50mg of 2, 6-dinitrophenolindophenol dye was weighed and added to the hot solution and made up to 200ml with distilled water. 5ml from the standard ascorbic acid solution was again taken and mixed with 5ml of 3% phosphoric acid. This was then titrated against the cooled dye in the burette to a pale pink colour that lasts at least 15 seconds. The dye factor was determined from equation 1.

$$DF=0.5/titre\ vol \quad (1)$$

Where *DF* is the dye factor.

The amount of ascorbic acid in the sample was obtained by taking a 2-3g sample and grinding it in mortar and pestle while mixing with 15-20ml of distilled water. The mixture was filtered and 10ml of aliquot was pipette out and made up to 100 ml with 3% phosphoric acid. This solution was filtered again using filter paper. From the

Table 2: Vitamin C content at time (t).

Time (hrs)	Vit Cmg/100g (Tray Dryer)	Vit C mg/100g (Solar Dryer)	Vit C mg/100g (Sun Dryer)
0.0	43.00	48.75	48.75
0.5	38.00	48.75	48.75
1.0	34.00	44.85	42.90
1.5	29.00	42.90	39.00
2.0	25.00	42.90	39.00
2.5	23.00	42.90	37.05
3.0	18.50	40.95	37.05
3.5	18.00	39.00	33.15
4.0	17.00	39.00	31.20
4.5	15.00	39.00	31.20
50	15.00	35.10	29.25
5.5	12.75	35.10	29.25
6.0	12.75	35.10	29.25
6.5	11.65	33.15	25.35
7.0	11.50	33.15	23.40
7.5	11.50	33.15	23.40
8.0	11.25	31.20	21.45
8.5	11.25	31.20	21.45

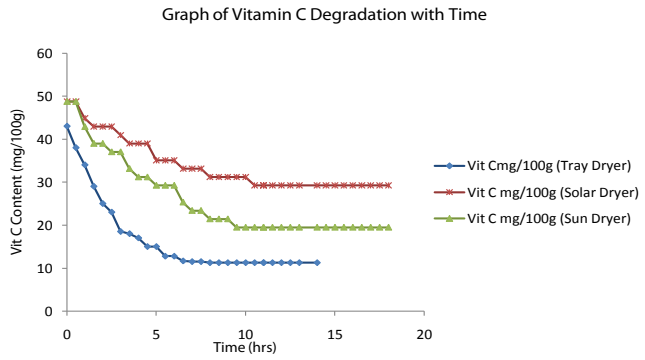

Figure 1: Comparative graph of Vitamin C with time.

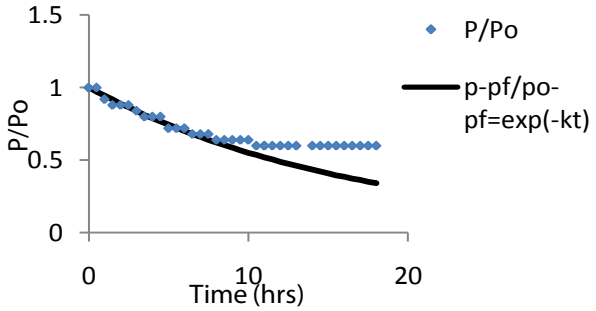

Figure 2a: Graph of Vitamin C degradation with Time and the 1st order Fractional Model Fit for solar Dryer.

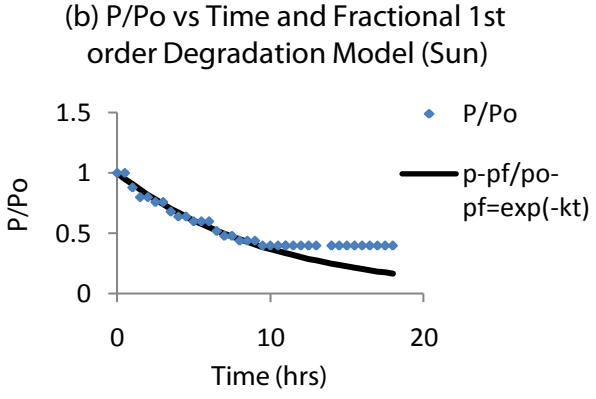

Figure 2b: Graph of Vitamin C degradation with Time and the 1st order Fractional Model Fit for Sun Dryer.

filtered aliquot, further 5ml was pipette out and blended with 50ml of 3% phosphoric acid. From the blend 2ml was pipette and titrated against the 2, 6-dinitrophenolindophenol dye in the burette. The titrations were done in triplicates. The average titre volume was noted. The amount of ascorbic acid in mg/100g sample was calculated using the method outlined in [15]. The calculation is shown in equation 2.

$$AA = \frac{\{titre\ vol \times DF \times Vol\ made\ up \times 100\}}{aliquot\ of\ extract \times weight\ of\ sample\ taken} \quad (2)$$

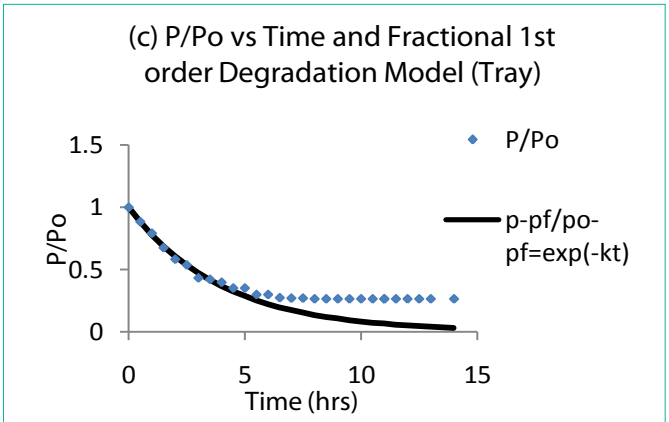

Figure 2c: Graph of Vitamin C degradation with Time and the 1st order Fractional Model Fit for Tray Dryer.

Where AA is ascorbic acid in mg/100g sample and DF is the dye factor.

Mathematical models

The ascorbic acid determination was done at half hour intervals during the drying process. The results were noted and the data was compared with two mathematical models that describe the degradation characteristics of vitamin C namely the first order fractional model and the Weibull model [16-18]. The models used are shown in Table 1.

Statistical analysis

From the modeling data values, Regression analysis was used to determine the correlation coefficient (R^2) using SPSS© and Excel Data Analysis Tool© and the root mean square error (RMSE) was calculated using Excel and the model with the higher R^2 value and the least RMSE was chosen as the best fit [19]. From the models, the model constants were determined and compared for the three treatments namely solar, sun and tray drying.

Results and Discussion

Table 2 shows the vitamin C content (mg/100g of sample) at half hour intervals during the drying period in tray, solar and sun dryer respectively. From this table the comparative graphs of vitamin C degradation were generated as shown in Figure 1.

Figures 2 a, 2b and 2 c show the dimensionless ascorbic acid concentration Ratio (P/P_o) vs. time using the 1st order fractional model. P is the ascorbic acid concentration at time (t) and P_o is concentration at t=0. From graph 2a, the solar dryer process shows a 1st order degradation up to 0.6 units and a time of about 10 hours then a deviation is noted [18]. Similar kinetics were noted in the sun dryer process as well. For the tray dryer operating at constant temperature, the deviation was noted earlier, at 0.4 units (P/P_o) and a time of 5 hours. This deviation may be attributable to the reversible ascorbic acid-dehydroxy-ascorbic acid degradation kinetics [16,18].

Figures 3a, 3b and 3c show the same degradation kinetics using the Weibull Model taking into consideration the shape and scale parameters. The kinetics followed 1st order degradation up to 0.6, 0.5 and 0.4 units for solar, sun and tray drying respectively before deviating. The dimensionless ratio concentrations used were C_{AA}/

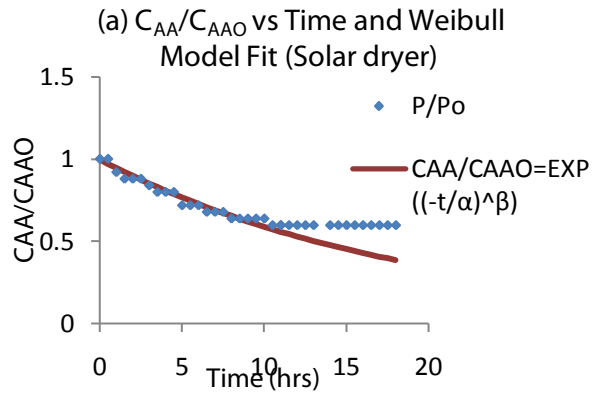

Figure 3a: Vitamin C Degradation with Time Graph and the Weibull Model Fit for Solar Dryer.

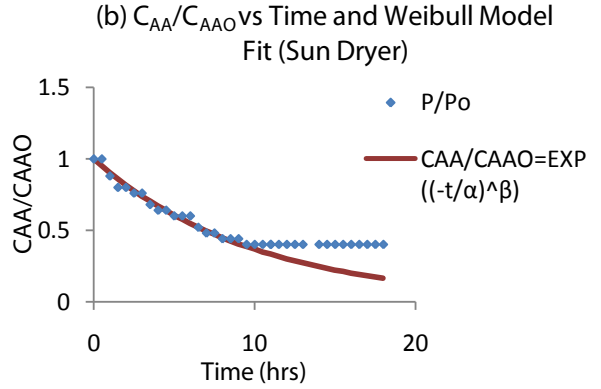

Figure 3b: Vitamin C Degradation with Time Graph and the Weibull Model Fit for Sun Dryer.

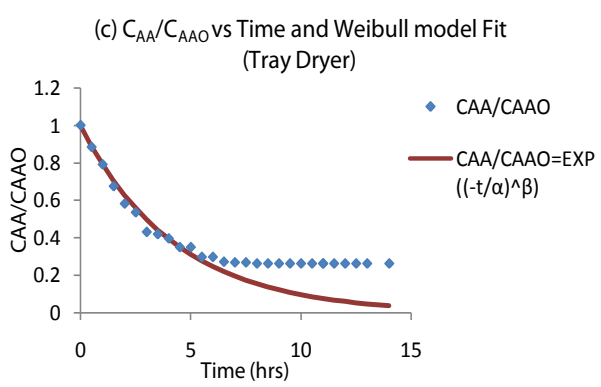

Figure 3c: Vitamin C Degradation with Time Graph and the Weibull Model Fit for Tray Dryer.

C_{AA0} where C_{AA} is the ascorbic acid concentration at time (t) and C_{AA0} is concentration at time (t=0).

From Table 3 the degradation rate constant k was determined using the 1st order fractional model. It proved higher in the tray dryer at 0.25mg/min indicating a higher loss of vitamin C in the tray drying process. The sun dryer had the second highest rate of 0.1mg/min. The solar dryer had the smallest degradation rate constant of 0.06mg/min. This showed the highest vitamin C retention (supported by the graph in Figure 1). The shape parameter β and scale parameter α were also determined. Knowing these values aid in prediction calculations. Statistical analysis using SPSS and Microsoft Excel showed the correlation coefficients (R^2) of both models. The higher the R^2, the better the fit to accurately describe the degradation kinetics [3]. The Weibull model had higher values of R^2 in all three treatments (solar, sun and tray drying).

Table 3: Summary of the Statistical analyses and Rate constant estimation.

Model	Treatment	Model Constants			R^2	RMSE
		k	α	β		
First Order fractional Model	Solar dryer	0.06			0.979441805	0.121552731
	Sun Dryer	0.1			0.945564836	0.101880165
	Tray dryer	0.25			0.841681566	0.135661241
Weibull Model	Solar Dryer		19	1	0.984065657	0.125089642
	Sun Dryer		10	1	0.945564836	0.108801651
	Tray Dryer		4.3	1	0.858744691	0.091785978

Where k is the rate constant, α is the scale parameter and β is the shape factor

Conclusion

It was noted that though some authors [3,7,16] and many others suggested that Vitamin C degradation followed a 1st order kinetic model, it was not the case in this study. The results obtained were similar to the work done by Vieri et al. [9] who noted that a deviation from 1st order kinetics exists after a dimensionless Ascorbic acid concentration ratio of 0.4 units at constant temperature. In this study, similar results were obtained in the case of the tray dryer which was operated at constant temperature of 60°C (Figures 2c and 3c). The mathematical models compared using R^2 showed that though a deviation existed; the Weibull model had the better goodness of Fit in modeling the degradation kinetics of Ascorbic acid [17,18]. The rate constant k, the shape parameter and scale parameter β and α respectively were also estimated using the mathematical models. Most importantly the solar dried pineapple slices had the highest residual vitamin C (Figure 1 and Table 1). This was due to the indirect solar heating mechanism prevailing in the solar dryer, which protected the pineapples from direct sunlight [13].

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