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Ascorbic acid degradation of papaya during drying: Effect of process conditions and glass transition phenomenon

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ABSTRACT

The aim of the present work was to study the degradation of ascorbic acid during hot air drying of papaya cubes and to verify its relationship with glass transition. A convective tray dryer was used in the drying experiments, which were carried out at air temperatures (T_{air}) of 40, 50, 60 and 70 °C and air velocities of 1.0 and 1.32 m/s. The lowest T_{air} induced higher retention of this nutrient at end of drying. At 70 °C, papaya sample remained in the rubbery state until the end of drying, since product temperature (T_p) was above the glass transition temperature (T_g) along the process. This state is characterized by great molecular mobility inside the food, which facilitates the degradation. At 40 °C, the rate of nutrient degradation was very slow as T_g was close to T_p and papaya has suffered phase transition from rubbery to glassy state.

1. Introduction

In tropical and subtropical countries, a large amount of fruits and vegetables is produced, which are very attractive from a commercial point of view. However, in association with the seasonal problem, most of these products present high water content, making them susceptible to decomposition by microorganisms, chemical and enzymatic reactions. These products are extremely perishable and it is difficult to be marketed or exported as fresh produce.

In Brazil, the loss of tropical and subtropical fruits is very high, reaching about 5 million ton/year (Soares, 2009). Among these fruits, there is the papaya (*Carica papaya* L.), where approximately 30% of local production is lost (Soares, 2009). Papaya is an important fruit crop grown widely in tropical and subtropical countries, and Brazil is the second world producer, with a total of 1.871 million ton/year in 2010 (FAO, 2012). This fruit is full of nutrients, rich in minerals (calcium, iron, potassium and sodium), provitamin A and vitamin C (ascorbic acid), β-carotene and β-cryptoxanthin (Wall, 2006). It is commonly used to make juices, pulp, jam, fruit-candies in syrup, crystallized fruit, dried fruit and other products.

Therefore, it is essential to process this fruit to improve its shelf life and prevent post-harvest losses. Amongst the several methods employed for preservation, drying is a process in which the water activity of the food is reduced by water removal by vaporization or sublimation, minimizing enzymatic and microbiological reactions. Furthermore, food dehydration is applied to reduce weight and volume, in order to decrease transport and storage costs.

Although air-drying offers dehydrated products that can have an extended shelf life like one year, quality of conventionally dried foods is significantly influenced by changes which occur during manufacturing and/or storage and can be drastically reduced from that of the original foodstuff. Therefore, it is interesting to minimize chemical changes, such as enzymatic reactions, non-enzymatic browning and oxidation of lipids and pigments, and to maximize nutrients retention during drying.

Ascorbic acid is very important for human nutrition, since is an essential substance that prevents diseases like scurvy, and it plays the role of biological antioxidant. As humans have no capability to synthesize this component, it should then be supplied by the diet. However, its stability in food is related to the process and storage conditions and to the composition of the matrix. The vitamin C can be degraded, depending on many variables such as temperature, pH, light, time, presence of enzymes, oxygen and metallic catalysers (Santos and Silva, 2008). This nutrient is usually considered as an index of nutrient quality during processing and storage of foods, since, if it is well retained, the other nutrients are also well retained (Santos and Silva, 2008). Therefore, many authors have been evaluated the influence of the hot-air drying on retention of ascorbic acid for several fruits, such as acerola residue (Duzzioni et al., 2013), apricot (García-Martínez et al., in press), pineapple (Ramallo and Mascheroni, 2012; Santos and Silva, 2009), red

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Nomenclature

a_w	water activity	$T_{g,s}$	glass transition temperature of dry matter (°C)
C_0	content of ascorbic acid at initial drying time (mg/g solid)	$T_{g,w}$	glass transition temperature of water (°C)
C	content of ascorbic acid at drying time t (mg/g solid)	T_p	product temperature (°C)
D	decimal reduction time (h)	V_E	experimental value
k	first-order reaction rate constant (h^{-1})	V_P	predicted value
k'	constant of Gordon–Taylor model	w_s	weight fraction of dry matter (g/g total)
N	population of experimental data	w_w	weight fraction of water (g/g total)
t	time (min)	X_0	initial moisture content (g/g solids)
$t_{1/2}$	half-life time (h)	X_t	moisture content at drying time t (g/g solids)
T_{air}	air-drying temperature (°C)	X_e	equilibrium moisture content (g/g solids)
T_g	glass transition temperature (°C)		

pepper (Vega-Gálvez et al., 2009), pear (Mrad et al., 2012) and tomato (Demiray et al., 2013; Abano et al., in press; Marfil et al., 2008).

The free volume and the molecular relaxation time (time necessary for adapting structure when there is a temperature variation) of the food structure could affect chemical changes. They are related to the molecular mobility, which changes diffusivity of molecular species. The glass transition temperature (T_g) has been used as indicator of this molecular mobility, and it is defined as the temperature at which an amorphous system changes from the glassy to the rubbery state. In the glassy state, molecular mobility is extremely slow, due to the high viscosity of the matrix (about 10^{12} Pa s), and available free volume has been estimated 2.5% of the total volume (Roos, 2010). In the rubbery state, the molecular mobility of the matrix and the reactants are accelerated, which results in an increased rate of physical chemical properties of the products (Roos, 2010).

Thus the T_g can be taken as a reference parameter to characterize properties, quality, stability and safety of food systems. At most drying conditions, a significant amount of the dried product remains in the amorphous state, mainly due to insufficient time for crystallization to occur at the given drying condition. Fruit samples, due to its high moisture content, are in rubbery state at the start of the drying and could remain likewise as process progresses or suffer phase transition for glassy state, since the removal of water increases the glass transition temperature of the product significantly (Nicoleti et al., 2007).

The aim of the present work was to study the degradation of ascorbic acid (*AA*) during hot air drying of papaya cubes and to verify its relationship with glass transition. The specific objectives were: to model the kinetics of degradation and to evaluate the effect of air temperature and air velocity on the *AA* stability.

2. Materials and methods

2.1. Material

Papayas (*C. papaya* L.) of similar ripeness (10–12°Brix) were purchased in a local market (Campinas, SP, Brazil). Fruits were selected in order to obtain samples of uniform shape, size (length of 25–30 cm and weight of 1.2–1.6 kg), and ripening grade, based on skin color (80–90% of yellowness). The selected fruits were hand-peeled and cut into cubes of (20 × 20 × 20) mm. The composition of the papaya (wet basis), obtained according to AOAC (1995), was: moisture content of 87.8 ± 0.6%, total sugar content of 7.4 ± 0.1%, reducing sugar content of 5.7 ± 0.1%, fiber content of 3.2 ± 0.4% and ash of 0.4 ± 0.03%.

2.2. Glass transition temperature

About 10 mg of papaya pieces were placed into differential scanning calorimeter (DSC) aluminum pans (20 µl) and equilibrated over saturated salt solutions in desiccators at 25 ± 1 °C until equilibrium was reached. Then, samples were hermetically sealed with lids and weighed. The mass of each sample pan was matched in advance with the mass empty reference pan to within ±0.1 mg. DSC analyses were carried out in a TA-MDSC-2920 (Ta Instruments, New Castle, DE, USA). For temperatures below −70 °C, liquid nitrogen was used; otherwise, a mechanical refrigeration system (RCS-Refrigerated Cooling Accessory) was applied. Equipment calibration was performed with indium (T_{melting} = 156.6 °C) and verification with azobenzol was done (T_{melting} = 68.0 °C). Dry helium, 25 ml/min, was used as purge gas. After cooling the sample at 10 °C/min up to −70 °C, measurement of glass transition temperature was carried out and thermo-analytical curves obtained by heating the sample at 10 °C/min up to 80 °C (or other values of initial and final temperatures, according to the samples). The second scanning of each sample was performed to reduce the enthalpy relation of the amorphous product which appears in the first scan. All analyses were done in triplicate and the data were treated by the software Universal Analysis 2.6 (TA Instruments, New Castle, DE, USA).

2.3. Convective hot air-drying experiments

A convective tray dryer was used in the experiments, which were carried out at air temperatures of 40 °C, 50 °C, 60 °C and 70 °C and air velocities of 1.0 m/s and 1.32 m/s. The dryer system consisted of a vertical airflow through the trays and was arranged as a closed circuit. For the air heating, electric resistances (3000 W) were used, manually set into operation by a digital thermostat. During drying, the sample was weighed using a semi-analytical balance (resolution of 0.01 g) at intervals of 15 min during the first and second hours of drying, 30 min for the next 2 h and then 1 h until sample weight became constant. When this condition is reached, there is a dynamic equilibrium between the sample equilibrium moisture content X_e and drying air humidity. The sample moisture and solids contents were gravimetrically determined using a vacuum oven at 70 °C for 24 h. Five samples were taken at each predetermined time interval to determine the ascorbic acid content. Thermocouples connected to a data acquisition (Testor 171 model, Testo, Lenzkirch, Germany) were placed on the trays and inside three papaya cubes to analyze the evolution of air temperature (T_{air}) and temperature into the product (T_p) during the experiments.