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Convective drying kinetics of strawberry (*Fragaria ananassa*): Effects on antioxidant activity, anthocyanins and total phenolic content

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ABSTRACT

The thermal drying effects on strawberries were investigated in terms of the kinetics of antioxidant activity (AA), anthocyanins (A) and total phenolic compound content (TPC), as well as the final colour. The evaluated drying temperatures were 50 and 60 °C with an air rate of 1.5 m/s. The 2,2-diphenyl-2-picryl-hydrazyl, pH differential and Folin–Ciocalteu methods were used to assess the antioxidant properties. The kinetics of TPC and AA showed an initial and final period of degradation attributed to inhibition of enzymes. A plateau between these two periods suggests that under certain conditions of temperature and water content, no degradation reactions occurred. Final losses of up to 74, 45 and 78% were found for AA, A and TPC, respectively. The total colour change (ΔE) was lesser degree at 60 than 50 °C. Thermal degradation of the antioxidant compounds followed a first-order reaction kinetics and the degradation rate constants (k) were calculated.

1. Introduction

Consumption of fruit and vegetables, has been associated with reduced risk of chronic degenerative diseases, cancer and cardiovascular diseases. Numerous evidences suggest that these health benefits are linked to antioxidant phytochemicals which play an important role in the prevention and treatment of chronic diseases caused by oxidative stress induced by free radicals. Antioxidant compounds (phytochemicals), such as phenolic compounds, act through various mechanisms, such as scavenging of free radicals, compound-deactivating enzymatic activity and the chelation of metal ions. However, the mechanisms of the synergetic effects of antioxidants have not yet been fully elucidated. Some hypotheses about their mechanisms of action include the regeneration of primary antioxidants through the transfer of hydrogen from the molecules that interact synergistically, reduction of oxidation of metal ion complexing initialisation by scavenging singlet oxygen and improvement of stability of primary antioxidant environments by acidification (Bzducha & Wołosiak, 2006).

The phenolic compounds are secondary metabolites in plants that have been identified as major antioxidants in fruits. Flavonoids are a subset of phenolic compounds. The most important subcategory of flavonoids are anthocyanins, which are water-soluble glycosides of anthocyanidins (Craft, Kerrihard, Amarowicz, & Pegg, 2012), with strong *in vitro* and *in vivo* antioxidant activity, as well as other beneficial physicochemical and biological properties (Juroszek, Lumpkin, Yang, Ledesma, & Ma, 2009; Li et al., 2012). Moreover, they are responsible for the reddish to purple pigmentation in plants.

Strawberries have high levels of antioxidant activity, which is associated with their phenolic compounds contents, including phenolic acids and flavonoids (Panico et al., 2009).

In strawberry, the major anthocyanins are pelargonidin-3-glucoside, cyanidin-3-glucoside and pelargonidin-3-rutinoside, while the main flavonoids are quercetin, kaempferol and myricetin (Wang & Lewers, 2007). Quercetin has the highest antioxidant activity among these bioactives.

Evaluations of antioxidant capacity and phenolic compounds have been performed on fresh strawberries (Panico et al., 2009; Rekika et al., 2005; Wang & Lewers, 2007), products of strawberry-type juice and leathers dehydrated from fresh purees (Concha-Meyer, D'Ignoti, Saez, Diaz, & Torres, 2016; Klopotek, Otto, & Böhm, 2005), while changes in physical properties have been evaluated in strawberries exposed to convective drying (Alonzo-Macías, Cardador-Martínez, Mounir, Montejano-Gaitán, & Allaf, 2013; Askari, Emam-Djomeh, & Mousavia, 2009). The influence of drying conditions on bioactive compounds in fresh and dried strawberries has been evaluated by Wojdyło, Figie, and Oszmianski (2009), however, there is no previous report published

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on the kinetics of degradation of antioxidant compounds in strawberries during thermal drying processes. Thermal processing of vegetables and fruits, mostly degrade, or decrease the content of antioxidant compounds, although, contrastingly, some authors have reported an increased in antioxidant activity (Patras, Brunton, Butler, & Gerard, 2008; Patras, Tiwari, Brunton, & Butler, 2009).

The degradation of phenolic compounds during drying has been attributed to either the binding of polyphenols with other compounds or to alterations in the chemical structure (Martín-Cabrejas et al., 2009). Heat treatment at 70 °C for 20 min, resulted in a 4% decrease in the phenolic content of vacuum-packaged strawberries (Patras et al., 2009), while the phenolic content of strawberries decreased from 88 to 12%, following drying at 50 °C and 1.2 m/s air flow for 24 h, reaching a final content of 16.18 gallic acid equivalents (GAE)/g_{ds}, where *ds* refers to dry solid (Alonzo-Macías et al., 2013).

A plethora of studies have evaluated the effects of processing on anthocyanins due to their high instability and reactivity. Their stability depends on the processing conditions (light and oxygen), temperature and intrinsic properties of the products, such as pH, the presence of enzymes, the structure and concentration of the anthocyanins, as well as the presence of other compounds including other flavonoids, proteins and minerals (Zoric, Dragovic-Uzelac, Pedisic, Kurtanjek, & Garofulic, 2014). Among the many factors that can influence anthocyanin stability, the most significant is temperature (Moldovan, David, Chisbora, & Cimpoiu, 2012).

In tests performed on controlled dehydration of grapes, Marquez, Perez-Serratosa, Varo, and Merida (2014) found that the temperature influences the final content of anthocyanins. The opening of the pyrylium ring structure and chalcone formation was described as the first degradation step of anthocyanins, whereas hydrolysis of the sugar moiety and aglycone formation was the initial step in the degradation of anthocyanins. Zoric et al. (2014) suggest that cleavage of covalent bonds and enhanced oxidation reactions of anthocyanins, or even their conjugates, causes their fragmentation into smaller molecules like aldehydes and benzoic acid derivatives, during heat treatment.

In addition to the chemical changes, physical alterations, such as those produced during the preparation process of the materials (cutting) releases precursors and water, altering the pH and facilitating closeness of reactants like peroxide enzymes, pectin methyl esterase and polyphenol oxidase (PPO) that can degrade anthocyanins. Disintegration of the membrane and cell content spillage are also favoured by the loss of water (Nunes, Brecht, Morais, & Sargent, 2005), moreover, high drying temperatures can increase the permeability of membranes (Chaovanalikit & Wrolstad, 2004). Physical changes, such as collapse, shrinkage and porosity, favour the exposure of the compounds to oxygen and light. Thus, the overall effect of thermal processing on the antioxidant compound retention depends upon the complexity of the physical and chemical phenomena that occur.

Moreover, further interactions of compounds in foods make it difficult to predict the drying conditions that inhibit or reduce the loss of antioxidant compounds. This work aimed to obtain the kinetics of degradation of the antioxidant activity, phenolic compounds and anthocyanins in strawberries during convective drying at 50 and 60 °C.

2. Materials and methods

2.1. Sample preparation

Completely ripe (fully red) strawberries, cultivar Diamante, grown in Puebla, Mexico (latitude: 19°02′3602″ N; longitude: −98°12′6.95″), were acquired at a local market and immediately transported to the laboratory.

Flawless strawberries were selected, washed and disinfected with 5% chlorine solution for 10 min. The samples were then cut into 1-cm cubes and pre-treated in 1% calcium chloride ($CaCl_2$) at 25 °C for 15 min to inhibit the action of both PPO and pectin methyl esterase enzymes, which are responsible for the degradation of anthocyanins. The cubes were drained and uniformly distributed on perforated trays, as a single layer.

2.2. Drying conditions

The trays were placed in the sample holder of a hot air recirculating tray dryer (Pat. 304462, Mexico) coupled to a modular measurement and control system supplier (FieldPOINT®, National Instruments, Austin, Texas, USA) programmed in LabVIEW® (Austin, Texas, USA). The air was heated with two resistors of 20 Ω (2.4 kW) and was kept constant using a proportional-integral-derivative controller. Air flow was provided by a centrifugal blower (A-SQ, Armee, Chicago, Illinois, USA) connected to a frequency variator to regulate the air speed. A transmitter (HUMICAP®, Vaisala, Helsinki, Finland) with a built-in sensor was used to measure relative humidity (RH) and temperature of the drying air (T_a). The air rate was measured with an air velocity transducer (Alnor, AVT 55, USA). Furthermore, an electronic balance with analogue output (GX-06, A&D San Jose CA, USA) was used to determine the mass of the sample in real time. The internal and surface temperatures of the sample were measured with type-T thermocouples. The final drying time (t_f) was determined when the moisture content of the material was in equilibrium with the RH of the drying air.

2.3. Final moisture content and dried mass

The A.O.A.C. (1990) 934.01 method was used to determine the water content of the samples during (X_t) and at the end (X_f) of the process. The dry solids (DS) content, expressed as grams of dry solid (g_{ds}), was calculated using Eq. (1), as follows:

$$DS = w_t(1 - X_{wb}) \quad (1)$$

where: X_{wb} is the water content, wet basis (g_{water}/g_{ws}) at time t and w_t is the sample weight (g) at time t.

In order to determine the moisture content and prepare extracts, samples were taken every 15 min during the first hour and every 30 min during the subsequent hours. Water content analyses were performed in triplicate. The results were expressed as the average values.

2.4. Colour determination

The L*, a* and b* colour parameters were determined before and after drying using a Hunter Lab Mini scan EZ (Reston VA, USA). Colour differences between the dry and fresh samples were used to describe the colour change during drying, defined using Eq. (2), as follows:

$$\Delta E = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2} \quad (2)$$

where: L* represents on the scale CIELAB the lightness of the sample ranging from 0 (black) to 100 (white), coordinate a* represents red colour (+) or green (−), and coordinate b* represents yellow colour (+) or blue (−). Subscript 0 refers to the colour of the fresh sample. High ΔE values indicate large colour changes relative to the reference.