Food Chemistry 136 (2013) 853–857

Contents lists available at SciVerse ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Degradation kinetics of anthocyanins in acerola pulp: Comparison between ohmic and conventional heat treatment

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ARTICLE INFO

Article history:
Received 11 June 2012
Received in revised form 10 August 2012
Accepted 13 August 2012
Available online 30 August 2012

Keywords:
Thermal processing
Ohmic heating
Anthocyanins
Acerola pulp

ABSTRACT

Degradation kinetics of monomeric anthocyanins in acerola pulp during thermal treatment by ohmic and conventional heating was evaluated at different temperatures (75–90 °C). Anthocyanin degradation fitted a first-order reaction model and the rate constants ranged from 5.9 to 19.7 $\times 10^{-3}$ min^{-1}. There were no significant differences between the rate constants of the ohmic and the conventional heating processes at all evaluated temperatures. *D*-Values ranged from 116.7 to 374.5 for ohmic heating and from 134.9 to 390.4 for conventional heating. Values of the free energy of inactivation were within the range of 100.19 and 101.35 kJ mol^{-1}. The enthalpy of activation presented values between 71.79 and 71.94 kJ mol^{-1} and the entropy of activation ranged from −80.15 to −82.63 J mol^{-1} K^{-1}. Both heating technologies showed activation energy of 74.8 kJ mol^{-1} and close values for all thermodynamic parameters, indicating similar mechanisms of degradation.

1. Introduction

Acerola fruit (*Malpighia emarginata* D.C.), also known as Barbados Cherry, is known for its high nutritional value, especially because of its substantial content of vitamin C, associated with the presence of anthocyanins, carotenoids and elements such as iron and calcium. Anthocyanins are polyphenolic pigments responsible for the red, blue, and purple colours of many fruits and vegetables. Musser et al. (2004) evaluated the anthocyanin content of mature acerola fruits from 12 genotypes harvested at three different seasons and the results showed an average variation between 3.8 and 47.4 mg/100 g. Studies carried out for identification of anthocyanin pigments in acerola pulp found that the fruit exhibited two types of anthocyanins: cyanidin 3-rhamnoside and pelargonidin 3-rhamnoside (de Rosso et al., 2008).

These brightly coloured compounds have a significant antioxidant capacity and they play a potentially important role in human health by reducing risks of cancer, cardiovascular disease, and other pathologies (Bravo, 1998; Konczak & Zhang, 2004). Nevertheless, anthocyanins easily degrade during food processing and storage, being highly sensitive to factors such as light, pH, temperature, presence of oxygen and enzymes (Fennema, 1996).

Food processing generally includes heat treatments that effectively preserve foodstuffs and also provide desirable sensory properties. However, current knowledge indicates that heat processing, particularly under severe conditions, may affect anthocyanin levels in fruit products and vegetables (Hou, Qin, Zhang, Cui, & Ren, in press; Jiménez et al., 2010; Moreira, de Azeredo, de Medeiros, de Brito, & De Souza, 2010). Therefore, over the years new thermal and non-thermal technologies have emerged to reduce or eliminate the exposure of food to heat. Ohmic heating is one alternative to thermal food processing whereby the electrical resistance of the food itself generates heat as current is passed through it. This technology allows high-temperature/short-time processing of particulates, thus avoiding excessive thermal damage to labile substances, such as vitamins and pigments (Castro, Teixeira, Salengke, Sastry, & Vicente, 2004; Palaniappan & Sastry, 1991).

The objective of the present study was to comparatively evaluate the effect of ohmic heating (OH) and conventional heating (CV) on the degradation kinetics of monomeric anthocyanins of acerola pulp at temperatures ranging from 75 to 90 °C.

2. Materials and methods

2.1. Acerola pulp

Acerola pulp was supplied by *Mais Fruta* Company (Jarinu, SP, Brazil). The product presented high moisture content, approximately 92%, pH value of 3.3 and soluble solids of 7.2 °Brix.

2.2. Ohmic heating process

The experimental setup, described in details by Mercali, Jaeschke, Tessaro, and Marczak (2012), comprises a power supply,

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http://dx.doi.org/10.1016/j.foodchem.2012.08.024

a variable transformer (*Sociedade Técnica Paulista LTDA*, model Varivolt, São Paulo, SP, Brazil), a stabilizer (*Forceline*, model EV 1000 T/2-2, São Paulo, SP, Brazil), a data acquisition system, a computer and an ohmic cell. The ohmic cell was a 400 ml water jacket glass vessel. The electric field frequency used was 60 Hz. The electrodes were made of platinum, with cross-sectional areas of 7.0 cm^2. The cell was placed on a magnetic stirrer plate (*Instrulab*, Model ARE, Brazil) for agitation of the product during heating.

The kinetic experiments were conducted at 75, 80, 85 and 90 °C. Samples were withdrawn at various heating times (0, 15, 30, 45, 60, 75 and 90 min). In order to eliminate the heating time as a variable during the experiments, the time–temperature histories in conventional and ohmic processes were matched using the following control strategy. A temperature-controlled water bath (*Lauda*, model T, Germany) was connected to the ohmic cell to heat the sample at one degree above the desired temperature of the study. When this temperature was reached, the pump was turned off. The water in the jacket was removed while the temperature of the sample gradually decreased. When the sample reached the desired temperature, the first sample, associated with time zero, was collected. Then, the ohmic heater was turned on using 25 V to maintain the desired temperature inside the cell during 90 min.

Although one of the advantages of ohmic heating over the conventional process is that food exposure to heat is significantly reduced due to more rapidly temperature increments, this heating procedure was necessary to evaluate the non-thermal effects of electricity during the thermal treatment. Fig. 1 presents plots of temperature against time for ohmic and conventional heating experiments conducted at 75 and 90 °C. The time–temperature histories at 80 and 85 °C showed a similar plot behaviour.

2.3. Conventional heating process

The conventional heating process was carried out in the ohmic cell without the presence of the electrodes. The same thermostatic water bath (*Lauda*, model T, Germany) was used to heat the samples. The experiments were conducted at the same range of temperatures (75–90 °C) and the samples were withdrawn at same heating times (0–90 min).

2.4. Determination of monomeric anthocyanin content

The monomeric anthocyanin content of the samples was analyzed by UV–Visible spectroscopy using the pH-differential method (Lee, Durst, & Wrolstad, 2005). Briefly, the samples were centrifuged (*Cientec*, model 500R, Piracicaba, SP, Brazil) at 5 °C (10 min, 3000×*g*). Then, two dilutions of the sample were prepared using the supernatant: one with potassium chloride buffer, pH 1.0; and the other with sodium acetate buffer, pH 4.5. These dilutions were sat out at room temperature for 20 min. The absorbance of the samples was calculated using Eq. (1):

$$A = (A_{520} - A_{700})_{pH1,0} - (A_{520} - A_{700})_{pH4,5} \quad (1)$$

where A_{520} is the absorbance at the wavelength 520 nm and A_{700} is the absorbance at the wavelength 700 nm.

The monomeric anthocyanin content of the sample was calculated using Eq. (2):

$$\text{Anthocianins (mg/L)} = \frac{A \times MW \times DF \times 10^3}{\varepsilon \times l} \quad (2)$$

where *MW* is the molar weight (g mol^{-1}), *DF* is the dilution factor, ε is the molar absorptivity (L mol^{-1} cm^{-1}) and *l* is pathlength of the cuvette (cm).

2.5. Determination of kinetic parameters

In accordance with previous studies, anthocyanins follow first-order degradation kinetics:

$$C = C_0 \exp(-k \cdot t) \quad (3)$$

where *t* is the time (min), *k* is the first order kinetic rate constant (min^{-1}), C_0 and *C* are the anthocyanin content (mg L^{-1}) at time zero and *t*, respectively.

The decimal reduction time (*D*-value), which is the time needed for a tenfold reduction of the initial concentration at a given temperature, is related to *k*-values according to Eq. (4):

$$D = \frac{\ln(10)}{k} \quad (4)$$

The half-life ($t_{1/2}$) value of degradation is given by Eq. (5):

$$t_{1/2} = \frac{\ln(2)}{k} \quad (5)$$

2.6. Thermodynamic analysis

The activation energy was obtained by nonlinear regression using Eq. (6), which is the combination of the first-order model and Arrhenius equation. In this manner, a more precise estimation is obtained since all data is used at once to estimate the activation energy.

$$\frac{C}{C_0} = \exp\left\{-k_{Ref} \cdot \exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{Ref}}\right)\right] \cdot t\right\} \quad (6)$$

where T_{Ref} is the reference temperature (82.5 °C), k_{Ref} is the anthocyanin loss rate at T_{Ref} (min^{-1}), E_a is the activation energy (J/mol), *R* is the ideal gas constant (8.314 J mol^{-1} K^{-1}) and *T* is the temperature (K).

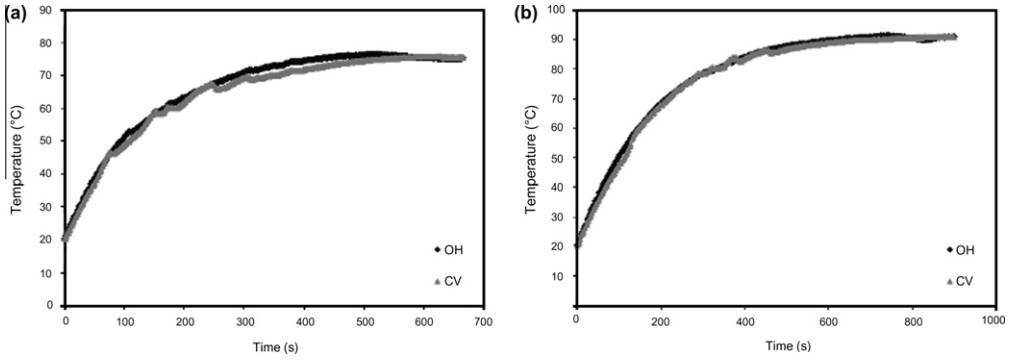

Fig. 1. Time–temperature histories in the conventional and ohmic heating processes for experiments carried out at (a) 75 and (b) 90 °C.