



## Ascorbic acid degradation and color changes in acerola pulp during ohmic heating: Effect of electric field frequency



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### ABSTRACT

The effect of the electric field frequency on ascorbic acid degradation and color changes in acerola pulp during ohmic heating was evaluated and this technology was compared with the conventional heating process. The electric field frequency was evaluated in the range between 10 and 10<sup>5</sup> Hz. The use of low electric field frequency (10 Hz) led to greater ascorbic acid degradation and higher color changes probably due to the occurrence of electrochemical reactions. Above 100 Hz these reactions were minimized and, as a result, ohmic and conventional heating processes showed similar degradation rates of ascorbic acid and similar color changes. The use of high electric field frequency did not affect the degradation kinetics of ascorbic acid and pigment compounds. This indicates that the ascorbic acid molecule predisposition for hydrogen donation in redox reactions was not affected by the rapidly varying electric field.

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## 1. Introduction

Acerola (*Malpighia emarginata* D.C.) is a tropical fruit of great nutritional value because of its high content of vitamin C (1000–4000 mg/100 g) and the presence of other nutrients such as anthocyanins, carotenoids, iron and calcium. Loss of its vitamins and pigments due to thermal treatment during food processing is a major concern, which may be potentially mitigated by alternative pasteurization processes such as ohmic heating.

Ohmic heating is based on the passage of an alternating current through a sample which responds by generating heat internally due to its inherent resistance (Fryer et al., 1993; Palaniappan and Sastry, 1991a). The energy generation is proportional to the square of the local electric field strength and the electrical conductivity of the product (Goullieux and Pain, 2005; Ruan et al., 2001). This technology is one alternative to thermal processing that allows high-temperature/short-time processing (de Alwis and Fryer, 1992; Stirling, 1987). Ohmic heating can provide a fast and uniform heating with the ability to start/stop thermal processing instantaneously (Bansal and Chen, 2006). These advantages allow reaching the desired holding temperature of the process in a short time, usually few seconds, reducing the treatment time that is critical to avoid excessive thermal damage to labile substances.

The ohmic heating consists of the application of AC voltage to electrodes in contact with the product. When an electric field is applied to a sample, each molecule in the field suffers a slight distortion of the electron distribution, called electronic polarization (North, 1972). The electric field distorts the negative cloud of electrons around the positive atomic nuclei in a direction opposite to the field. This slightly separation of charges make one side of the atom somewhat positive and the opposite side negative. The consequence of each molecular dipole along the direction of the field is a polarization of the whole sample. The rate of the polarization process is determined by the charge mobility. This is irrelevant if the electric field changes slowly, but if the electric field is altered rapidly (as a high frequency alternating voltage) there is not time for an equilibrium polarization to be established (North, 1972).

Studies have been performed to evaluate the effect of the electric field frequency during moderate electric field treatments on food properties and process parameters (Bansal and Chen, 2006; Imai et al., 1995; Kulshrestha and Sastry, 2006; Lima et al., 1999b; Shynkaryk et al., 2010), diffusion and extraction of certain constituents of foodstuffs (Kulshrestha and Sastry, 2003; Lakkakula et al., 2004; Lima and Sastry, 1999; Wang and Sastry, 2002), stimulation of microbial growth (Loghavi et al., 2008, 2009) and inactivation kinetics of spores (Somavat et al., 2012). However, little is known about the effect of the electric field frequency on nutrient stability during ohmic heating.

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The nutritional components of the acerola pulp, such as ascorbic acid and pigment compounds, are subjected to an electric field distortion when the ohmic heating technology is applied. High electric field frequencies do not allow the polarization to reach the equilibrium and this phenomenon may influence on their degradation kinetics. For this reason, the objective of this work was to evaluate the effect of the electric field frequency (from 10 to  $10^5$  Hz) on ascorbic acid degradation and color changes in acerola pulp during ohmic heating and also to compare this technology with the conventional heating process.

## 2. Materials and methods

### 2.1. Acerola pulp

The acerola pulp was supplied by *EcoFruits* Company (South Jordan, USA). The nutritional properties of the product were evaluated. The total dry matter and moisture content were determined by the gravimetric method (AOAC, 2005). The soluble solid content and pH values were determined using a refractometer (*Sper Scientific*, model 300017, Scottsdale, AZ, USA) and a pH meter (*Mettler Toledo*, pH-/Cond-/DO-/ISE-Meter model, USA), respectively. Monomeric anthocyanins were analyzed using the pH-differential method (Lee et al., 2005). Total phenolic content was determined by the Folin–Ciocalteu method (Waterhouse, 2003). All analyses were performed at least in triplicate.

### 2.2. Ohmic heating process

The ohmic heating apparatus comprised a power amplifier (*Industrial Test Equipment*, model 500A, Port Washington, NY, USA), a function generator (*Tektronix Inc.*, model AFG3252, Richardson, Tex, USA), an Agilent 34970A data acquisition unit and HP BenchLink Data Logger software (*Agilent Technologies Inc.*, Palo Alto, CA, USA), a computer and an ohmic cell. A schematic diagram of the ohmic heating setup is presented in Fig. 1. The ohmic cell consisted of a 500 ml jacketed glass vessel. The electrodes were made of titanium. The electrodes were curved to conform to reactor dimensions. The maximum inter-electrode gap was 7.5 cm and the minimum gap was 5.7 cm. Electrode height was 5 cm and reactor height was 9.9 cm. The temperature was measured by 2 type-T thermocouples. One of the thermocouples was located close to the electrode and the other away from the electrodes. Temperature distribution in the sample during heating was homogeneous. The difference between the two measurements was less than 2 °C. This homogeneity was achieved due to the intense agitation of the product (magnetic stirrer plate, *Fisher Scientific*, Model Isotemp, USA). The current flowing through the circuit was monitored by

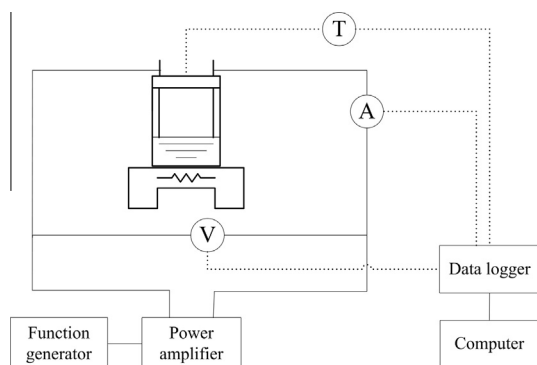


Fig. 1. Schematic diagram of the ohmic heating setup (V = voltage measurement; A = current transformer and T = temperature sensor).

a Pearson current transformer (*Pearson Electronics Inc.*, model 150, Palo Alto, CA, USA) with a working range of 40 Hz–20 MHz.

The kinetic experiments were conducted at 85 °C for up to 2 h, using 30 V and 75 °C water in the jacket, simultaneously. This was necessary to match the time–temperature histories of the conventional and ohmic heating processes. This procedure allows the evaluation of the non-thermal effects of the electricity during the thermal treatment. Fig. 2 presents a plot of temperature against time for the ohmic and conventional heating experiments conducted at 85 °C. The time required to reach the desired holding temperature was approximately 13 min.

The experiments were carried out using 350 g of acerola pulp. Samples were withdrawn at various heating times (0, 20, 40, 60, 80, 100 and 120 min) and their ascorbic acid concentration and moisture content were determined. The ascorbic acid content after the sample reached the desired holding temperature was considered the initial ascorbic acid content. This was required to eliminate the effect of heating the sample until reaching the desired start-up temperature as a variable during the experiments. Trials were conducted in triplicate for each frequency evaluated (10,  $10^2$ ,  $10^3$ ,  $10^4$  and  $10^5$  Hz).

### 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 (*Brookfield Engineering Laboratories*, model EX-100, MA, USA) was used to heat the samples. The kinetic experiments were conducted at the same temperature (85 °C) and the samples were withdrawn at same heating times (from 0 to 120 min).

### 2.4. Determination of ascorbic acid content

The ascorbic acid content of the samples was determined using a high performance liquid chromatograph (*Hewlett–Packard*, HP Agilent 1100 system, Norwalk, CT, USA). The column used was a reverse  $C_{18}$  Luna® (5  $\mu$ m, 250 × 4.6 mm, *Phenomenex*, Torrance, CA, USA). Isocratic chromatographic separation was carried out using a mobile phase of  $KH_2PO_4$  (5%). The eluent flow-rate was 0.7 ml/min and the column temperature was 25 °C. Ascorbic acid was identified by comparing the retention time of the sample peak with that of the ascorbic acid standard at 254 nm.

The extraction of ascorbic acid consisted of adding 1.5 g of sample to 7.5 ml of 4.5% (w/v) *meta*-phosphoric acid solution. The mixture was then homogenized for 30 s and centrifuged (5 min, 10 °C, 1500 × g). The supernatants were filtered through a 0.45- $\mu$ m PTFE membrane, diluted and injected into the HPLC system. Samples were protected from light during all procedures.

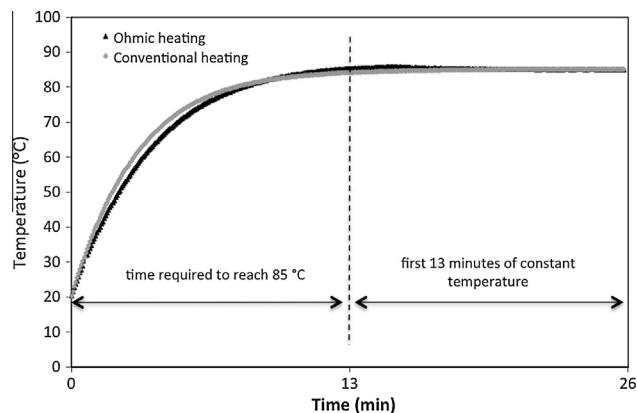


Fig. 2. Thermal histories of acerola pulp during ohmic and conventional heating treatments.

## 2.5. Color measurement

Color measurements were performed using a ColorQuest XE colorimeter (Hunter Assoc. Laboratory, VA, USA). The CIELAB parameters  $a^*$ ,  $b^*$  and  $L^*$  were obtained with the light source D65 and observation angle of  $10^\circ$ , using the reflectance specular included mode. The  $L^*$  coordinate represents the lightness of the color ( $L^* = 0$  denotes black and  $L^* = 100$  denotes white),  $a^*$  indicates the position between green and red ( $a^*$  varies from  $-80$  to  $+100$ ) and  $b^*$  is the extent of blueness/yellowness ( $b^*$  varies from  $-50$  to  $+70$ ).

Total color difference ( $\Delta E^*$ ) was calculated using the Hunter–Scotfield equation (Hunter, 1975):

$$\Delta E^* = (\Delta a^{*2} + \Delta b^{*2} + \Delta L^{*2})^{1/2} \quad (1)$$

where  $\Delta a^* = a^* - a_0^*$ ,  $\Delta b^* = b^* - b_0^*$  and  $\Delta L^* = L^* - L_0^*$ ; subscript '0' indicates color at time zero.

## 2.6. Determination of the kinetic parameters

The results obtained for ascorbic acid degradation and color changes were fitted to the first-order kinetic model:

$$C = C_0 \exp(-k \cdot t) \quad (2)$$

where  $t$  is the time (min),  $k$  is the rate constant ( $\text{min}^{-1}$ ),  $C_0$  and  $C$  are the quality parameters at time zero and time  $t$ , respectively.

The decimal reduction time ( $D$ -value) is the time needed for a tenfold reduction of the initial concentration at a given temperature. It is related to  $k$ -values according to the following equation:

$$D = \frac{\ln(10)}{k} \quad (3)$$

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

$$t_{1/2} = \frac{\ln(2)}{k} \quad (4)$$

## 2.7. Statistical analysis

Three independent experiments were carried out for each frequency studied during ohmic heating and also for the conventional heating. The results were fitted to the first-order model by nonlinear estimation using Statistica 7.0 software for Windows (Statsoft @, Tulsa, OK, USA). Statistical significance was determined by Tukey test (5% of confidence level).

## 3. Results and discussion

### 3.1. Sample characterization

The nutritional properties of acerola pulp are presented in Table 1. The product showed a good content of vitamin C,  $1657 \pm 45$  mg/100 g. This result is in agreement with those found by Vendramini and Trugo (2000). These authors investigated the ascorbic acid content of acerola in three different stages of maturity and found values between 1074 and 2164 mg/100 g. The soluble solids content of the acerola pulp was approximately  $11^\circ\text{Brix}$ . Monomeric anthocyanins and phenolic contents were  $2.16 \pm 0.17$  mg/100 g and  $1445 \pm 35$  mg/100 g, respectively. Lima et al. (2005) analyzed the total phenolic content of acerola fruits at three maturation stages harvested in dry and rainy seasons. The values range from 536 to 4524 mg/100 g. de Rosso et al. (2008) analyzed total anthocyanin content of two Brazilian acerola varieties and found higher values than the one found in this study: Waldy variety showed total anthocyanin content of 6.5–7.6 mg/100 g; while 7.9–8.4 mg/100 g were found for Olivier variety.

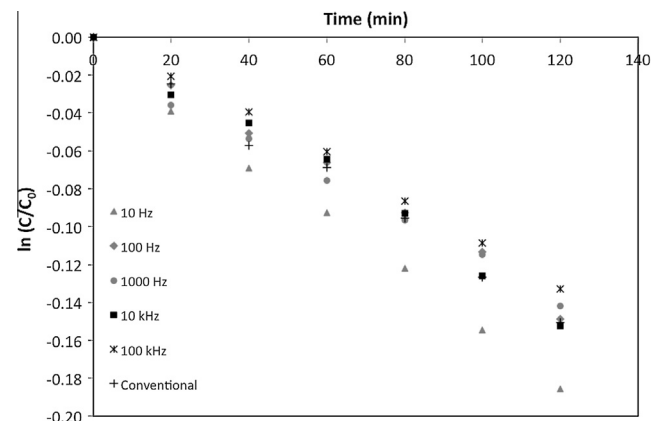
**Table 1**

Nutritional properties of acerola pulp.

Property	Mean value
Total solids content (g/100 g)	$12.81 \pm 0.33$
pH	$3.27 \pm 0.03$
Vitamin C (mg/100 g)	$1657 \pm 45$
Monomeric anthocyanin (mg/100 g)	$2.16 \pm 0.17$
Phenolics (mg/100 g)	$1445 \pm 35$
Soluble solids content ( $^\circ\text{Brix}$ )	$11.3 \pm 0.3$

### 3.2. Ascorbic acid degradation

Thermal stability of ascorbic acid from acerola pulp was evaluated using different frequencies during ohmic and conventional heating treatment. The relationship between the ascorbic acid concentration and time for all treatments is presented in Fig. 3. Error bars were not added because it would be impossible to distinguish between the different treatments. The standard deviations were lower than 3%. The ascorbic acid degradation percentage after 120 min of ohmic heating at 10 and  $10^5$  Hz were approximately 17% and 13%, respectively. For the conventional heating process, the degradation percentage after 120 min was 14%. The impact of temperature and time on ascorbic acid degradation was lower than the expected. It is possible that the oxygen dissolved in the medium is a limiting reactant since the vitamin C content in acerola pulp is very high. Lima et al. (2010) also found that temperature impact on ascorbic acid degradation in ground cashew apples was not as high as expected. They observed that after heat treatment at  $100^\circ\text{C}$  for 120 min, ascorbic acid content was only 30% lower than the initial value. Lima et al. (1999a) used ohmic heating to heat orange juice for 30 min at  $90^\circ\text{C}$  and ascorbic acid degradation was approximately 21%. Leizeron and Shimoni (2005) found that the reduction of vitamin C maintained at 15% ( $p > 0.05$ ) for orange juice treated with ohmic heating at temperatures of 90, 120, and  $150^\circ\text{C}$  for 1.13, 0.85, and 0.68 s. Mercali et al. (2012) evaluated ascorbic acid degradation in acerola pulp during thermal treatment by ohmic heating varying the solids content of the pulp (2 and 8 g/100 g) and the heating voltage (120 and 200 V); the degradation rates varied between 3.1% and 10.6% for a heating treatment at  $85^\circ\text{C}$  for 3 min. Clearly, the literature values for ascorbic acid degradation in food products vary. Studies have shown that its stability is influenced by the intrinsic properties of the product and the process characteristics (Eison–Perchonok and Downes, 1982; Esteve et al., 1999; Louarme and Billaud, 2012; Mercali et al., 2012; Odriozola-Serrano et al., 2008; Serpen and Gökmen, 2007; Vikram et al., 2005). Vitamin C degradation can occur through aerobic and/



**Fig. 3.** Ascorbic acid degradation during ohmic and conventional heating processes. The standard deviations were lower than 3%.

or anaerobic pathways, depending on a number of factors such as pH, acidity, metal ions, light, humidity, water activity, temperature, presence of amino acids, carbohydrates, lipids and enzymes, among others (Gregory, 1996).

The results of ascorbic acid concentration against time were fitted to the first-order equation by nonlinear estimation. The determination coefficients ( $R^2$ ) presented values higher than 0.98 for all treatments. Table 2 summarizes the kinetic parameters obtained for each frequency evaluated during ohmic heating and also for the conventional process. The kinetic rate constants ranged from 1.1 to  $1.6 \times 10^{-3} \text{ min}^{-1}$ . The rate constant for the ohmic heating process at 10 Hz was higher than the rate constants for all other treatments. There was no statistical difference ( $p > 0.05$ ) between ascorbic acid degradation rates of the experiments carried out with field frequencies ranging from 100 to  $10^5$  Hz.

Two mechanisms of ascorbic acid degradation are commonly encountered in food processing: chemical oxidation and chemical degradation via the anaerobic pathway (Gregory, 1996). The first case, and the dominant mechanism, is characterized by reversible oxidation of ascorbic acid into dehydroascorbic acid, which also has biological activity. Further oxidation generates diketogulonic acid, which has no biological function. (Furusawa, 2001; Gregory, 1996; Lee and Kader, 2000). After diketogulonic acid hydrolysis, additional oxidation, dehydration, polymerization and reaction with amino acids and proteins generate various nutritionally inactive products (Gregory, 1996; Lee and Kader, 2000). The degradation of vitamin C under anaerobic condition is not yet elucidated due to its complexity (Gregory, 1996).

Another relevant mechanism of degradation during the ohmic heating process is electrochemical degradation by reactions at the electrodes, such as electrolysis of water and electrode corrosion. Electrolysis of water releases hydrogen and oxygen in the medium which may cause additional oxidation of the ascorbic acid. On the other hand, electrode corrosion release metal ions that also catalyze the oxidation process (Assiry et al., 2003).

Some experimental observations may be explained by the above mentioned mechanisms of degradation. Higher degradation rates at 10 Hz may be due to the occurrence of electrochemical reactions, mainly electrolysis of water. Samaranayake and Sastry (2005) noticed corrosion of electrodes and apparent (partial) electrolysis of the heating medium with most types of electrodes at low-frequency alternating currents. They demonstrated that although the titanium electrodes showed a relatively high corrosion resistance, apparent electrolysis was seen at all the pH values. In addition, experiments conducted by Assiry et al. (2006) showed that at a given power level, higher electric field strengths are conducive to increased incidence of faradaic reactions during ohmic heating of pH 5.7 buffer solution. Moreover, some studies have shown that electrochemical reactions are accelerated by the use of high voltage and low frequency (Assiry et al., 2003; Mercali et al., 2012; Palaniappan and Sastry, 1991b; Qihua et al., 1993).

**Table 2**  
Kinetic parameters of the first-order model for ascorbic acid degradation in acerola pulp during ohmic and conventional heating.

Frequency (Hz)	$R^2$	$K$ ( $\text{min}^{-1}$ ) <sup>a</sup>	$D$ (min) <sup>a</sup>	$t_{1/2}$ (min) <sup>a</sup>
10	1.00	$0.0016 \pm 0.0001^a$	$1480 \pm 72^a$	$446 \pm 22^a$
$10^2$	0.99	$0.0012 \pm 0.0001^b$	$1948 \pm 50^b$	$587 \pm 15^b$
$10^3$	0.98	$0.0012 \pm 0.0001^b$	$1927 \pm 183^b$	$580 \pm 55^b$
$10^4$	0.99	$0.0012 \pm 0.0001^b$	$1889 \pm 124^b$	$569 \pm 37^b$
$10^5$	1.00	$0.0011 \pm 0.0001^b$	$2145 \pm 179^b$	$646 \pm 54^b$
Conventional	0.99	$0.0012 \pm 0.0001^b$	$1860 \pm 151^b$	$560 \pm 45^b$

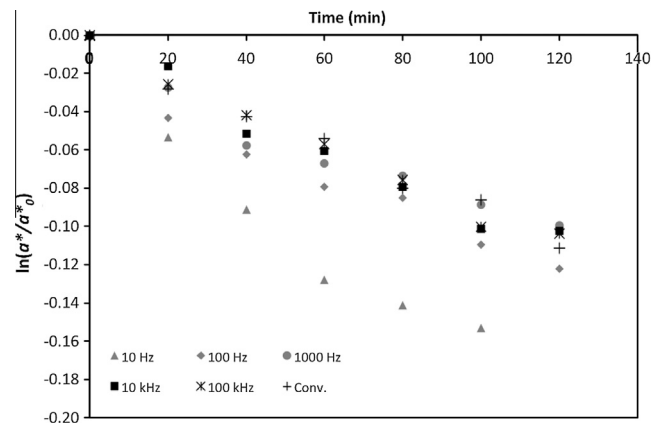
<sup>a</sup> Mean of three replicates  $\pm$  standard error; Means in the same column with different lowercase letters (a and b) are significantly different ( $p < 0.05$ ).

The rate constant for the conventional treatment was similar to the ones found for the ohmic heating process using frequencies from 100 to  $10^5$  Hz (Table 2). This indicates that above 100 Hz the electrochemical reactions were probably minimized and the mainly mechanism of degradation is the oxidation. Experiments conducted by Bansal and Chen (2006) suggested the use of a high frequency power supply can be a useful tool in controlling the corrosion of electrode surfaces during ohmic heating. Leizeron and Shimoni (2005) evaluated the effect of ultrahigh-temperature continuous ohmic heating treatment on fresh orange juice in comparison to the conventional pasteurization; the results showed similar ascorbic acid degradation for both technologies when the thermal histories were matched. Lima et al. (1999a) examined ascorbic acid degradation in pasteurized orange juice during conventional and ohmic heating matching the time–temperature histories and the type of heating had no significant effect on vitamin C degradation. Castro et al. (2004) found that the presence of an electric field ( $<20 \text{ V cm}^{-1}$ ) does not affect ascorbic acid degradation during ohmic heating of strawberry products. Vikram et al., 2005 evaluated the kinetic degradation of vitamin C during infrared, ohmic ( $42 \text{ V cm}^{-1}$  electric field) and microwave heating in comparison with conventional heating. The destruction of vitamin C was influenced by the heating method and the temperature of processing. Out of the four methods studied, ohmic heating gave the best result, with better vitamin C retention at all temperatures.

In this study, the use of electric field frequencies above 100 Hz during ohmic heating did not affect the degradation kinetics of ascorbic acid. The ascorbic acid molecule predisposition for hydrogen donation in redox reactions was not affected by rapidly varying electric field. As field frequency increases, the time interval between reverse movements in field polarity gradually becomes of a similar order to the relaxation times of the molecules. Changes in the time available for the molecules to respond and orientate in accordance to the direction of field changes did not influence how molecules react in the medium. In this manner, the hypothesis that high electric field frequencies could influence on its degradation kinetics was not confirmed.

### 3.3. Color changes

The acerola pulp showed initial  $L^*$  value of  $44.07 \pm 0.41$ ,  $a^*$  value of  $7.84 \pm 0.22$  and  $b^*$  value of  $20.05 \pm 0.51$ , which characterizes the acerola pulp tonality as orange/red. Figs. 4–7 show color changes during ohmic and conventional heating. Error bars were not added because it would be impossible to distinguish between the different treatments. The standard deviations were lower than 2%, 5% and 6% for  $L^*$ ,  $a^*$  and  $b^*$  parameters, respectively. The color



**Fig. 4.** Color changes ( $a^*$  values) for acerola pulp during ohmic and conventional heating treatments. The standard deviations were lower than 5%.

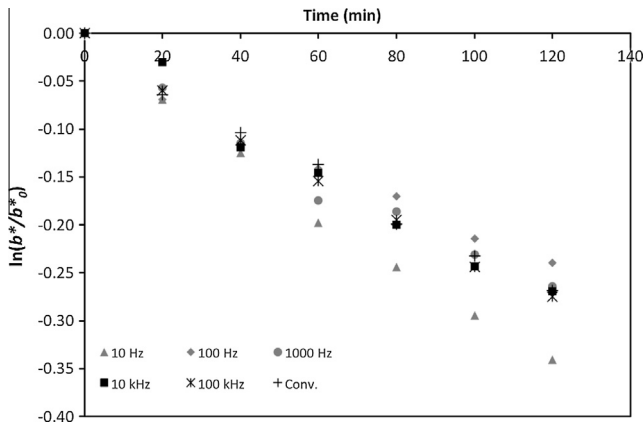


Fig. 5. Color changes ( $b^*$  values) for acerola pulp during ohmic and conventional heating treatments. The standard deviations were lower than 6%.

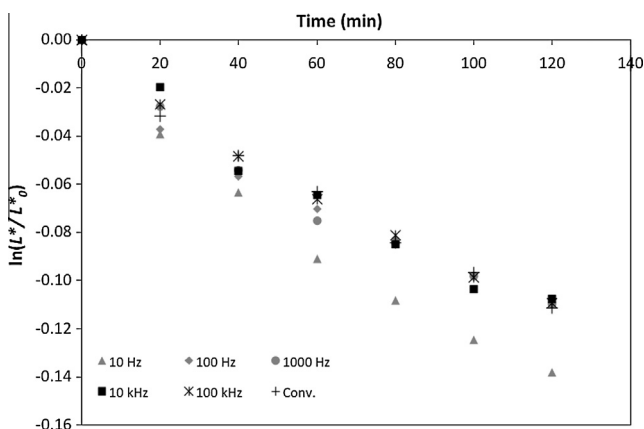


Fig. 6. Color changes ( $L^*$  values) for acerola pulp during ohmic and conventional heating treatments. The standard deviations were lower than 2%.

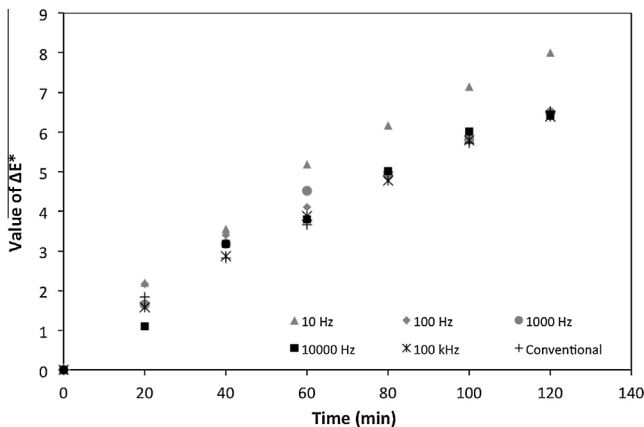


Fig. 7.  $\Delta E^*$  values for acerola pulp during ohmic and conventional heating treatments.

parameters values were fitted to the first-order model. The determination coefficients ( $R^2$ ) presented values higher than 0.89 for all treatments. This suggests the first-order model satisfactorily described color changes in acerola pulp during ohmic and conventional heating. The kinetic parameters for  $L^*$ ,  $a^*$  and  $b^*$  values obtained for each frequency evaluated during ohmic heating and also for the conventional process are presented in Table 3.

Color is an important quality indicator to evaluate the extent of deterioration due to thermal processing. As shown in Figs. 4–7,  $L^*$ ,  $a^*$  and  $b^*$  parameters decreased over time for all treatments. This indicates that samples were less red and yellow and also were darker after the heating process. The kinetic parameters (Table 3) can be used as an alternative tool for estimating the degradation of nutritional compounds during processing. Non-enzymatic browning of citrus beverages is an important quality deterioration factor. More than one type of mechanism may be involved in the formation of brown pigments, such as the reactions between amino acids and reducing sugars (Maillard reactions) and the aerobic and anaerobic degradation of the ascorbic acid with further reactions of the carbonyl compounds to yield brown pigments (Fustier et al., 2011). In acerola pulp,  $L^*$  parameter can be associated with non-enzymatic browning especially due to ascorbic acid degradation. The rate constant for  $L^*$  values ranged from 0.0010 to 0.0013  $\text{min}^{-1}$ . The experiment using the lowest frequency (10 Hz) showed the highest rate constant. Moreover, data showed no statistically significant difference between all others treatments. These results are comparable to the ones found for ascorbic acid degradation.

Sant'Anna et al. (2013) summarized studies that showed a good correlation between the CIELAB parameters and the presence of bioactive compounds in a broad range of foods. According to these authors, in the last years several studies have focused on evaluating color instrumentation as an alternative to control the presence of bioactive compounds with antioxidant activities, such as carotenoids (Meléndez-Martínez et al., 2007; Spada et al., 2012), anthocyanins and other polyphenols (Jiménez-Aguilar et al., 2011; Larrauri et al., 1997), betalain (Esquivel et al., 2007), and chlorophyll (Koca et al., 2006). Acerola is a good source of anthocyanins which are the responsible for the red color of the pulp. During food processing, anthocyanins can easily degrade resulting in color changes in the final product. The  $a^*$  parameter is a good indicator of anthocyanin degradation. The gradual degradation of red color, visually observed during the heating process of the acerola pulp, was confirmed by the decrease of  $a^*$  values (Fig. 4). The rate constants for the  $a^*$  parameter ranged from 0.0009 to 0.0018  $\text{min}^{-1}$  (Table 3).

Acerola pulp also has a good amount of carotenoid pigments which account for the natural yellow, orange or red colors of many foods. Mezadri et al. (2005) identified 17 carotenoid pigments in acerola fruit, in which the four major carotenoids were the yellowish ones:  $\beta$ -carotene,  $\beta$ -cryptoxanthin, lutein, and violaxanthin. These yellowish carotenoids when isolated presented positive values of  $b^*$  (Fustier et al., 2011). In this manner, the  $b^*$  parameter can be correlated with the degradation of these important pigments. As shown in Table 3, the rate constants for changes in  $b^*$  values ranged from 0.0022 to 0.0030  $\text{min}^{-1}$ , being the color parameter most affected by the heating processing.

Overall, the behavior of the  $L^*$ ,  $a^*$  and  $b^*$  parameters with frequency was similar. The experiment conducted at 10 Hz showed the highest color changes (highest rate constants) for  $L^*$ ,  $a^*$  and  $b^*$  parameters. This result is confirmed by total color difference ( $\Delta E^*$ ) curves shown in Fig. 7.  $\Delta E^*$  values were obtained taking in consideration the three coordinates of the CIELAB space. This result may be due to the occurrence of electrochemical reactions that accelerate the degradation of the acerola pulp pigments. On the other hand, for all color parameters, no statistical differences (5% confidence level) were observed between the experiments carried out at frequencies ranging from 100 to 10<sup>5</sup> Hz. As shown in Fig. 7, the total color difference curves of these experiments were very close to each other. Moreover, no statistical differences were observed between the two heating technologies when frequencies higher than 100 Hz were used.

**Table 3**  
Kinetic parameters of the first-order model for color changes in acerola pulp during ohmic and conventional heating.

FQ (Hz)	$L^*$ parameter			$a^*$ parameter			$b^*$ parameter		
	$k$ (min <sup>-1</sup> )	$D$ (min)	$R^2$	$k$ (min <sup>-1</sup> )	$D$ (min)	$R^2$	$k$ (min <sup>-1</sup> )	$D$ (min)	$R^2$
10	0.0013 ± 0.0002 <sup>a</sup>	1812 ± 230 <sup>a</sup>	0.95	0.0018 ± 0.0002 <sup>a</sup>	1318 ± 154 <sup>a</sup>	0.93	0.0030 ± 0.0002 <sup>a</sup>	772 ± 54 <sup>a</sup>	0.99
10 <sup>2</sup>	0.0010 ± 0.0001 <sup>b</sup>	2280 ± 130 <sup>b</sup>	0.90	0.0011 ± 0.0001 <sup>b</sup>	2062 ± 171 <sup>b</sup>	0.90	0.0022 ± 0.0001 <sup>b</sup>	1065 ± 51 <sup>b</sup>	0.95
10 <sup>3</sup>	0.0010 ± 0.0000 <sup>b</sup>	2255 ± 85 <sup>b</sup>	0.94	0.0009 ± 0.0002 <sup>b</sup>	2568 ± 562 <sup>b</sup>	0.89	0.0024 ± 0.0003 <sup>b</sup>	976 ± 122 <sup>b</sup>	0.96
10 <sup>4</sup>	0.0010 ± 0.000 <sup>b</sup>	2285 ± 122 <sup>b</sup>	0.97	0.0010 ± 0.0001 <sup>b</sup>	2416 ± 230 <sup>b</sup>	0.96	0.0024 ± 0.0002 <sup>b</sup>	965 ± 69 <sup>b</sup>	0.98
10 <sup>5</sup>	0.0010 ± 0.0000 <sup>b</sup>	2324 ± 59 <sup>b</sup>	0.97	0.0009 ± 0.0001 <sup>b</sup>	2481 ± 357 <sup>b</sup>	0.98	0.0024 ± 0.0001 <sup>b</sup>	948 ± 35 <sup>b</sup>	0.99
Conv.	0.0010 ± 0.0000 <sup>b</sup>	2313 ± 102 <sup>b</sup>	0.96	0.0009 ± 0.0001 <sup>b</sup>	2476 ± 176 <sup>b</sup>	0.98	0.0024 ± 0.0001 <sup>b</sup>	981 ± 49 <sup>b</sup>	0.99

<sup>a</sup> Mean of three replicates ± standard error; Means in the same column with different lowercase letters (a and b) are significantly different ( $p < 0.05$ ).

#### 4. Conclusions

This work studied the effect of electric field frequency on degradation kinetics of ascorbic acid and color changes in acerola pulp during thermal treatment by ohmic heating. Ascorbic acid degradation fitted a first-order reaction model and the rate constants ranged from 1.1 to 1.6 × 10<sup>-3</sup> min<sup>-1</sup>. Color parameters  $L^*$ ,  $a^*$  and  $b^*$  decreased over time for all treatments, which indicates color changes during the heating treatment.

Low electric field frequency (10 Hz) showed higher ascorbic acid degradation and higher color changes probably due to occurrence of electrochemical reactions. Electrolysis of water releases oxygen in the medium, which catalyzes the degradation pathways of these compounds. Ohmic heating using frequencies above 100 Hz and conventional heating showed similar degradation rates of ascorbic acid. This might be an indication that above 100 Hz the electrochemical reactions were minimized and the mainly mechanism of degradation is the oxidation. The use of electric field frequencies above 100 Hz during ohmic heating did not affect the degradation kinetics of ascorbic acid. This was observed even at high frequencies where the time interval between reverse movements in field polarity becomes of a similar order to the relaxation times of the molecules. In this manner, high electric field frequencies did not influence how ascorbic acid molecules react in the medium. Further work in this area is required to achieve a better understanding of the effect of the electric field frequency during ohmic heating on the kinetic reactions of nutritional compounds.

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#### References

AOAC, 2005. Official methods of analysis, eighteenth ed., AOAC International, Gaithersburg, MD, USA.

Assiry, A., Sastry, S.K., Samaranayake, C., 2003. Degradation kinetics of ascorbic acid during ohmic heating with stainless steel electrodes. *Journal of Applied Electrochemistry* 33, 187–196.

Assiry, A.M., Sastry, S.K., Samaranayake, C.P., 2006. Influence of temperature, electrical conductivity, power and pH on ascorbic acid degradation kinetics during ohmic heating using stainless steel electrodes. *Bioelectrochemistry* 68 (1), 7–13.

Bansal, B., Chen, X.D., 2006. Effect of temperature and power frequency on Milk fouling in an ohmic heater. *Food and Bioprocess Processing* 84 (C4), 286–291.

Castro, I., Teixeira, J.A., Salengke, S., Sastry, S.K., Vicente, A.A., 2004. Ohmic heating of strawberry products: electrical conductivity measurements and ascorbic acid degradation kinetics. *Innovative Food Science and Emerging Technologies* 5 (1), 27–36.

de Alwis, A.A.P., Fryer, P.J., 1992. Operability of the ohmic heating process: electrical conductivity effects. *Journal of Food Engineering* 15 (1), 21–48.

de Rosso, V.V., Hillebrand, S., Montilla, E.C., Bobbio, F.O., Winterhalter, P., Mercadante, A.Z., 2008. Determination of anthocyanins from acerola (*Malpighia emarginata* DC.) and açai (euterpe oleracea Mart.) by HPLC–PDA–MS/MS. *Journal of Food Composition and Analysis* 21, 291–299.

Eison-Perchonok, M.H., Downes, W., 1982. Kinetics of ascorbic acid autoxidation as a function of dissolved oxygen concentration and temperature. *Journal of Food Science* 47, 765–767.

Esquivel, P., Stintzing, F.C., Carle, R., 2007. Pigment pattern and expression of colour in fruits from different *Hylocereus* sp. Genotypes. *Innovative Food Science and Emerging Technologies* 8, 451–457.

Esteve, M.J., Frigola, A., Martorell, L., Rodrigo, C., 1999. Kinetics of green asparagus ascorbic acid heated in a high-temperature thermoresistometer. *Z Lebensm Unters Forsch A* 208, 144–147.

Fryer, P.J., de Alwis, A.A.P., Koury, E., Stapley, A.G.F., Zhang, L., 1993. Ohmic processing of solid-liquid mixtures: heat generation and convection effects. *Journal of Food Engineering* 18, 101–125.

Furusawa, N., 2001. Rapid high-performance liquid chromatographic identification/quantification of total vitamin C in fruit drinks. *Food Control* 12, 27–29.

Fustier, P., St-Germain, F., Lamarche, F., Mondor, M., 2011. Non-enzymatic browning and ascorbic acid degradation of orange juice subjected to electroreduction and electro-oxidation treatments. *Innovative Food Science and Emerging Technologies* 12, 491–498.

Goullieux, A., Pain, J.P., 2005. Ohmic Heating. In: Sun, D.-W. (Ed.), *Emerging technologies for food processing*. Elsevier Academic Press, Italy, p. 549.

Gregory, J., 1996. Vitamins. In: Fennema, O.R., Srinivasan, D., Parkin, K.L. (Eds.), *Food Chemistry*, 4th ed. CRC Press, New York, USA, p. 1144.

Hunter, R.S., 1975. Scales for measurements of color differences. *Measurement of Appearance*. Wiley-Interscience, NY, p. 133.

Imai, T., Uemura, K., Ishida, N., Yoshizaki, S., Noguchi, A., 1995. Ohmic heating of Japanese white radish *Rhaphanus sativus* L. *International Journal of Food Science & Technology* 30 (4), 461–472.

Jiménez-Aguilar, D.M., Ortega-Regules, A.E., Lozada-Ramírez, J.D., Pérez-Pérez, M.C.I., Vernon-Carter, E.J., Welti-Chanes, J., 2011. Color and chemical stability of spray-dried blueberry extract using mesquite gum as wall material. *Journal of Food Composition and Analysis* 24 (6), 889–894.

Koca, N., Karadeniz, F., Burdurlu, H.S., 2006. Effect of pH on chlorophyll degradation and colour loss in blanched green peas. *Food Chemistry* 100 (2), 609–615.

Kulshrestha, S., Sastry, S.K., 2003. Frequency and voltage effects on enhanced diffusion during moderate electric field (MEF) treatment. *Innovative Food Science and Emerging Technologies* 4 (2), 189–194.

Kulshrestha, S.A., Sastry, S.K., 2006. Low-frequency dielectric changes in cellular food material from ohmic heating: Effect of end point temperature. *Innovative Food Science & Emerging Technologies* 7 (4), 257–262.

Lakkakula, N.R., Lima, M., Walker, T., 2004. Rice bran stabilization and rice bran oil extraction using ohmic heating. *Bioresource Technology* 92 (2), 157–161.

Larrauri, J.A., Rupérez, P., Saura-Calixto, F., 1997. Effect of drying temperature on the stability of polyphenols and antioxidant activity of red grape pomace peels. *Journal of Agricultural and Food Chemistry* 45, 1390–1393.

Lee, S.K., Kader, A.A., 2000. Preharvest and postharvest factors influencing vitamin C content of horticultural crops. *Postharvest Biology and Technology* 20, 207–220.

Lee, J., Durst, R.W., Wrolstad, R.E., 2005. Determination of total monomeric anthocyanin pigment content of fruit juices, beverages, natural colorants, and wines by the pH differential method: Collaborative study. *Journal of AOAC International* 88 (5), 1269–1278.

Leizerson, S., Shimoni, E., 2005. Effect of ultrahigh-temperature continuous ohmic heating treatment on fresh orange juice. *Journal of Agricultural and Food Chemistry* 53 (9), 3519–3524.

Lima, M., Sastry, S.K., 1999. The effects of ohmic heating frequency on hot-air drying rate and juice yield. *Journal of Food Engineering* 41, 115–119.

Lima, M., Heskitt, B.F., Burianek, L.L., Nokes, S.E., Sastry, S.K., 1999a. Ascorbic acid degradation kinetics during conventional and ohmic heating. *Journal of Food Processing and Preservation* 23 (5), 421–443.

Lima, M., Heskitt, B.F., Sastry, S.K., 1999b. The effect of frequency and wave form on the electrical conductivity-temperature profiles of turnip tissue. *Journal of Food Process Engineering* 22 (1), 41–54.

Lima, V.L.A.G., Mélo, E.A., Maciel, M.I., Prazeres, F.G., Musser, R.S., Lima, D.E.S., 2005. Total phenolic and carotenoid contents in acerola genotypes harvested at three ripening stages. *Food Chemistry* 90 (4), 565–568.

Lima, J.R., Elizondo, N.J., Bohuon, P., 2010. Kinetics of ascorbic acid degradation and colour change in ground cashew apples treated at high temperatures (100–180°C). *International Journal of Food Science and Technology* 45, 1724–1731.

- Loghavi, L., Sastry, S.K., Yousef, A.E., 2008. Effect of moderate electric field frequency on growth kinetics and metabolic activity of *Lactobacillus acidophilus*. *Biotechnology Progress* 24, 148–153.
- Loghavi, L., Sastry, S.K., Yousef, A.E., 2009. Effects of moderate electric field frequency and growth stage on the cell membrane permeability of *Lactobacillus acidophilus*. *Biotechnology Progress* 25 (1), 85–94.
- Louarme, L., Billaud, C., 2012. Evaluation of ascorbic acid and sugar degradation products during fruit dessert processing under conventional or ohmic heating treatment. *LWT - Food Science and Technology* 49, 184–187.
- Meléndez-Martínez, A.J., Britton, G., Vicario, I.M., Heredia, F.J., 2007. Relationship between the colour and the chemical structure of carotenoid pigments. *Food Chemistry* 101 (3), 1145–1150.
- Mercali, G.D., Jaeschke, D.P., Tessaro, I.C., Marczak, L.D.F., 2012. Study of vitamin C degradation in acerola pulp during ohmic and conventional heat treatment. *LWT - Food Science and Technology* 47 (1), 91–95.
- Mezadri, T., Pérez-Gálvez, A., Hornero-Méndez, D., 2005. Carotenoid pigments in acerola fruits (*Malpighia emarginata* DC.) and derived products. *European Food Research and Technology* 220 (1), 63–69.
- North, A.M., 1972. Dielectric relaxation in polymer solutions. *Chemical Society Reviews* 1 (1), 49–72.
- Odrizola-Serrano, I., Soliva-Fortuny, R., Gimeno-Añó, V., Martín-Belloso, O., 2008. Kinetic study of anthocyanins, vitamin C, and antioxidant capacity in strawberry juices treated by high-intensity pulsed electric fields. *Journal of Agricultural and Food Chemistry* 56 (18), 8387–8393.
- Palaniappan, S., Sastry, S.K., 1991a. Electrical conductivities of selected solid foods during ohmic heating. *Journal of Food Process Engineering* 14 (3), 221–236.
- Palaniappan, S., Sastry, S.K., 1991b. Electrical conductivity of selected juices: influences of temperature, solids content, applied voltage, and particle size. *Journal of Food Process Engineering* 14 (4), 247–260.
- Qihua, T., Jindal, V.K., Van Winden, J., 1993. Design and performance evaluation of an ohmic heating unit for liquid foods. *Computers and Electronics in Agriculture* 9, 243–253.
- Ruan, R., Ye, X., Chen, P., Doona, C.J., 2001. Ohmic heating. In: Richardson, P. (Ed.), *Thermal Technologies in Food Processing*. Woodhead Publishing Limited, Londres.
- Samaranayake, C.P., Sastry, S.K., 2005. Electrode and pH effects on electrochemical reactions during ohmic heating. *Journal of Electroanalytical Chemistry* 577 (1), 125–135.
- Sant'Anna, V., Gurak, P.D., Marczak, L.D.F., Tessaro, I.C., 2013. Tracking bioactive compounds with colour changes in foods – a review. *Dyes and Pigments* 98 (3), 601–608.
- Serpen, A., Gökmen, V., 2007. Reversible degradation kinetics of ascorbic acid under reducing and oxidizing conditions. *Food Chemistry* 104, 721–725.
- Shynkaryk, M.V., Ji, T., Alvarez, V.B., Sastry, S.K., 2010. Ohmic heating of peaches in the wide range of frequencies (50 Hz–1 MHz). *Journal of Food Science* 75 (7), E493–E500.
- Somavat, R., Mohamed, H.M.H., Chung, Y.-K., Yousef, A.E., Sastry, S.K., 2012. Accelerated inactivation of *Geobacillus stearothermophilus* spores by ohmic heating. *Journal of Food Engineering* 108 (1), 69–76.
- Spada, J.C., Noreña, C.P.Z., Marczak, L.D.F., Tessaro, I.C., 2012. Study on the stability of  $\beta$ -carotene microencapsulated with pinhão (*Araucaria angustifolia* seeds) starch. *Carbohydrate Polymers* 89 (4), 1166–1173.
- Stirling, R., 1987. Ohmic heating – a new process for the food industry. *Power Engineering Journal* 1 (6), 365–371.
- Vendramini, A.L., Trugo, L.C., 2000. Chemical composition of acerola fruit (*Malpighia puniceifolia* L.) at three stages of maturity. *Food Chemistry* 71, 195–198.
- Vikram, V.B., Ramesh, M.N., Prapulla, S.G., 2005. Thermal degradation kinetics of nutrients in orange juice heated by electromagnetic and conventional methods. *Journal of Food Engineering* 69, 31–40.
- Wang, W.-C., Sastry, S.K., 2002. Effects of moderate electrothermal treatments on juice yield from cellular tissue. *Innovative Food Science & Emerging Technologies* 3 (4), 371–377.
- Waterhouse, A.L., 2003. Determination of total phenolics. In: Wrolstad, R.E. (Ed.), *Current Protocols in Food Analytical Chemistry*. Wiley, New York.