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Effects of ohmic and conventional heating on anthocyanin degradation during the processing of blueberry pulp

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ABSTRACT

The present work evaluates the anthocyanin degradation in blueberry pulp after thermal treatment using ohmic and conventional heating. The ohmic heating technology was studied using a rotatable central composite design, and the variables studied were voltage and solids content. The anthocyanin content of the samples was determined using HPLC. The results show that degradation increased with both increasing voltage and increasing solids content. The comparison between ohmic and conventional heating showed that when lower voltage levels were used, the percentage of degradation was lower or similar to those obtained during conventional heating. However, for high electric fields, the pulp processed using ohmic heating exhibited higher anthocyanin degradation.

1. Introduction

Blueberries (*Vaccinium* spp) are originally from Europe and North America and were only recently introduced in Brazil. This fruit has great nutritional value, primarily because it has high anthocyanin content. Anthocyanins are potent antioxidants and have high radical-scavenging activities, and therefore, the blueberry has become very appealing to consumers interested in functional foods. Anthocyanins are glycosylated polyhydroxyl or polymethoxyl derivatives of the 2-phenylbenzopyrylium (flavylium) cation. This basic structure, with no glucose substituents, is called anthocyanidin or aglycone and can be obtained by acid hydrolysis. The major aglycones are delphinidin, cyanidin, pelargonidin, petunidin, peonidin and malvidin. These compounds differ from each other with respect to the degrees of hydroxylation and methylation and with respect to the position and nature of their glycosyl moieties (Bravo, 1998; Francis & Markakis, 1989).

The daily consumption of blueberries and other antioxidant-rich fruits is often limited by seasonal availability, market accessibility and cost and time constraints; in addition, frozen and thermally processed products may be selected over fresh products because of the greater convenience. There is currently not sufficient knowledge about the anthocyanidin content of thermally processed fruits. Few papers have reported the quantification of anthocyanidins or the effects of food processing on these molecules (Nyman & Kumpulainen, 2001; Oliveira, Amaro, Pinho, & Ferreira, 2010; Queiroz, Oliveira, Pinho, & Ferreira, 2009; Yue & Xu, 2008). The preservation of anthocyanins is of great interest because the degradation of these compounds may considerably affect the color, the sensorial acceptance and the nutritional value of the fruit and the food products containing anthocyanin-rich fruits (Patras, Brunton, O'Donnell, & Tiwari, 2010).

Anthocyanins and the corresponding aglycones are prone to degradation. The easy oxidation of anthocyanins, due to the antioxidant properties of these molecules, leads to degradation during processing and storage (Skrede, Wrolstad, & Durst, 2000). The native enzymes polyphenoloxidase and glucosidase, which are present in blueberries, are the major enzymes responsible for anthocyanin degradation in this fruit (Kalt & Dufour, 1997; Kader, Rovel, Girardin, & Metche, 1997). Preferably, thermal processing should inactive these enzymes without reducing the content of anthocyanins. The literature suggested that thermal treatment for 45–60 s at temperatures between 90 and 100 °C is able to inactivate the primary enzymes related to anthocyanin degradation (Fennema, 2010). Kinetic parameters for the degradation of anthocyanins were estimated, and studies concluded that the rate of anthocyanin degradation is time and temperature dependent and that these compounds are especially sensitive to temperatures above 70 °C (Jimenez, Bouhon, Lima, Dornier, Vaillant, & Pérez, 2010; Sadilova, Stintzing, & Carle, 2006; Wang & Xu, 2007).

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Thermal processing is the most common method for microorganism and enzyme inactivation, and this technology has been extensively employed in food processing. Although conventional methods of thermal processing are able to ensure food safety, the high temperatures used can lead to organoleptic changes and the loss of nutrients. Because the heat transfer occurs essentially by conduction and convection, conventional thermal technologies are not homogeneous, causing the product in direct contact with the hot surfaces to overheat. Therefore, the preservation of the quality and the nutritional parameters of heat-treated fruit represents a major challenge for the traditional processing techniques for fruit pulp and other products. Innovative technologies have been widely research as alternatives to traditional thermal processing. Among these technologies are high pressure processing (Rawson, Brunton, & Tuohy, 2012; Verbeyst, Crombruggen, Van der Plancken, Hendrickx, & Van Loey, 2011), pulsed electric fields (Charles-Rodríguez, Nevárez-Moorillón, Zhang, & Ortega-Rivas, 2007; Plaza et al., 2011) and ohmic heating. Ohmic heating (OH) appear as a solution to reduce thermal damage because it heats materials in a rapid and homogeneous manner. This technique may allow improved retention of vitamins, pigments and nutrients because this type of heating is rapid and uniform, resulting in less thermal damage to labile substances (Castro, Teixeira, Salengke, Sastry, & Vicente, 2003, 2004; Eliot-Godéreaux, Zuber, & Goullieux, 2001; Ruan, Ye, Chen, Doona, & Taub, 2002; Sarang, Sastry, & Knipe, 2008).

Ohmic heating, also known as electroconductive heating, can be defined as a process in which foods are heated by passing alternating electrical current (AC) through them. Most food products contain ionic constituents, such as salts and acids, that enable the conduction of electrical current (Palaniappan & Sastry, 1991). This process can be used to generate heat within the product, transforming electrical energy into thermal energy and thus heating materials at exceptionally rapid rates without the need for a heating medium or surface (Sastry & Barach, 2000). Among ohmic heating applications in the food industry are blanching, evaporation, dehydration, pasteurization and extraction (FDA, 2000).

The aim of this study was to analyze the effect of ohmic heating on blueberry pulp anthocyanins by applying a rotatable central composite design to identify the optimal processing conditions. A two-variable full factorial central composite and star design was employed to evaluate the influence of the applied voltage and the solids content (SC) on the level of anthocyanin degradation. Finally, the ohmic heating process was compared with conventional heating.

2. Material and methods

2.1. Sample preparation

Southern Brazil cultivars of highbush blueberries (*Vaccinium corymbosum*) were used in these experiments. The samples were purchased from Italbraz Company (Vacaria, Brazil) and kept at −18 °C until analysis. The blueberry pulp used in this study was prepared by grinding the fruits and diluting the resulting material to adjust the total solids content to five different values between 4 and 16 g/100 g. To prevent precipitation, 1 g/100 g xanthan gum (Hexus Foods, Portão, Brazil) was added to the mixture. The solids contents analyzed in the experiments are presented in the experimental design section. Prior to dilution, the pulp had a pH of 3.18 ± 0.01, total solids content of 17.86 ± 0.1 g/100 g and soluble solids content (Brix) of 13.0 ± 0.5 g/100 g (Mercali, Sarkis, Jaeschke, Tessaro, & Marczak, 2011).

2.2. Chemicals

Standards of cyanidin, delphinidin, peonidin, petunidin, malvidin and pelargonidin were purchased from Sigma Aldrich (St. Louis, USA). HPLC-grade solvents including acetonitrile, methanol, *o*-phosphoric acid, acetic acid, and hydrochloric acid were obtained from Vetec (Duque de Caxias, Brazil).

2.3. Ohmic heating

2.3.1. Experimental protocol

Experiments were performed in a batch stirred reactor with ohmic heating at 60 Hz. The ohmic heating apparatus consists of: a manual transformer (0–240 V); a data acquisition system that recorded temperature, current and voltage data (data logger); and an ohmic heating cell containing platinum electrodes and a water jacket. The cell was built in a Pyrex glass shape with a diameter of 8 cm. The set-up used is shown in Fig. 1 where *VT* and *A* represent the voltage and current transducers, respectively, and *T* the temperature sensors. To homogenize the pulp, the ohmic cell was placed above a magnetic stirrer, and to ensure a uniform temperature profile, the temperature was monitored in two different locations inside the ohmic cell, near the electrode and near the cell wall. For these measurements, stainless steel Pt-100 m coated with a nickel–phosphorous alloy were used.

For the ohmic heating treatments, the pulp temperature was raised applying the voltage determined by the experimental design until a temperature of 90 °C was reached. The voltage was then lowered to maintain the pulp at this temperature for 2 min. This time/temperature condition was chosen because it is suggested in literature to inactivate anthocyanin-degrading enzymes (Fennema, 2010). When the thermal treatment was complete, the product was rapidly cooled by passing cold water (4 °C) through the jacket.

2.3.2. Experimental design and statistical data analysis

The rotatable central composite design was applied to identify the influence of two variables, the applied voltage (V) and the total solids content of the blueberry pulp (g/100 g), on the percentage of anthocyanin degradation (response variable). The coded and uncoded independent variables used in the experimental design are listed in Table 1. Voltage ranges (X_1) were selected based on the limitations of the ohmic heating system, and the range of the solids content (X_2) was chosen based on the characteristics of the fruit and the stability of the diluted suspension. To determine the influence of the selected parameters on the response variable, experiments were planned according to the central composite design (CCD) using a 2^2 full factorial and star design with three central points, as shown in Table 2. For the ohmic heating experiments, the error between independent experiments was determined using the central points of the rotatable central composite design.

Multiple linear regression analysis was performed using STATISTICA 7.1 (Stat-Soft, Tulsa, USA). Experimental data were fitted to the second-order polynomial model presented in Equation (1), and regression coefficients (β's) were obtained.

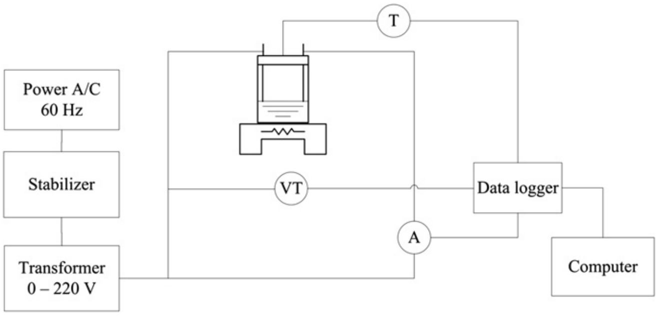

Fig. 1. Schematic of the experimental ohmic heating set-up (adapted from Mercali et al., 2012).

Table 1
Coded and uncoded levels of independent variables used in the rotatable central composite design.

Symbols	Independent variables	Coded levels				
		−1.41	−1	0	1	1.41
X_1	Voltage (V)	160	172	200	228	240
X_2	SC (g/100 g)	4	5.76	10	14.24	16

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \qquad (1)$$

where Y represents the dependent variable (estimated response) and β_0, β_1, β_2, β_{11}, β_{22} and β_{12} represent the equation coefficients. Analysis of variance (ANOVA) was performed for each response variable using the full models, and the p-values indicated whether the terms were significant. Terms that were not significant were removed from the final model. The significance of the regression was also evaluated using ANOVA.

To verify the adequacy of the models, the experimental data were compared to the values predicted by the regression models. The average error between the experimentally observed values and values predicted by the model were calculated using Equation (2)

$$E(\%) = \frac{100}{n} \sum_{i=1}^{n} \frac{\left| y_{\text{exp}} - y_{\text{pred}} \right|}{y_{\text{exp}}} \qquad (2)$$

where E is the average error, n is the number of experimental data points, y_{exp} is the experimental value and y_{pred} is the value predicted by the model.

2.4. Conventional heating

Conventional heating treatments were performed in a glass cell, and the cell content was heated by heat exchange with hot water in the jacket. The glass cell used was similar to the one employed for ohmic heating but had a 5.5 cm diameter. The time/temperature conditions were the same for both processes, and the product was cooled in the same manner. Temperature was monitored using type T thermocouples which were inserted in the center of the cell.

For the evaluation of conventional heating on anthocyanin degradation, only the central level of the design was analyzed; therefore, only blueberry pulp containing 10 g/100 g solids content was used.

2.5. Sample preparation and extraction

The anthocyanins were extracted from a 2 g sample with 20 mL of acidified methanol (0.01 mL/100 mL HCl) by homogenizing for 1 h in a shaker (Marconi, Piracicaba, Brazil). After extraction, the sample was centrifuged for 20 min at 4 °C and 4757×g, and the supernatant was collected. To prevent degradation of the pigments, samples were flushed with nitrogen before storage, and during procedures, the samples were protected from light and high temperatures.

Table 2
Rotatable central composite design setting for the voltages and solids content (SC) analyzed, anthocyanin content pre- and post-ohmic heating (OH) and experimental results for anthocyanin degradation.

Run	X_1 voltage (V)	X_2SC (g/100 g)	[Acy] pre OH (mg/100 g)	[Acy] post OH (mg/100 g)	Y anthocyanin degradation (%)
1	172	5.76	62.6 ± 1.0	58.1 ± 1.0	7.3
2	172	14.24	114.1 ± 0.9	102.5 ± 1.0	10.2
3	228	5.76	62.7 ± 1.0	54.1 ± 1.0	13.6
4	228	14.24	99.4 ± 1.0	86.1 ± 1.0	13.4
5	160	10	87.0 ± 0.9	82.0 ± 0.5	5.7
6	240	10	92.6 ± 0.1	79.0 ± 1.1	14.7
7	200	4	60.6 ± 0.9	54.1 ± 1.0	10.7
8	200	16	130.5 ± 0.9	114.7 ± 1.0	12.1
9	200	10	89.1 ± 1.0	79.0 ± 1.0	11.3
10	200	10	87.0 ± 0.9	76.5 ± 1.0	12.1
11	200	10	87.0 ± 0.9	76.2 ± 1.1	12.4

Acid hydrolysis was performed according to the methodology of Rodriguez-Saona and Wrolstad (2001) with the modifications proposed by Lima, Pinheiro, Nascimento, Gomes, and Guerra (2006). The methanolic extract, prepared as previously described, was used to hydrolyze the anthocyanins to aglycones by adding 3 mL of extract to 10 mL of a 2 mol L^{-1} HCl solution. The flask containing the mixture was flushed with nitrogen and immersed in boiling water for 1 h. After hydrolysis, the samples were cooled in an ice bath in the dark for 10 min prior to use.

The hydrolyzed extract was passed through a sorbent C$_{18}$ solid phase extraction (SPE) cartridge (Waters, Milford, USA). Anthocyanidins were adsorbed onto the cartridge, and water-soluble compounds were washed off. The pigments were eluted using acidified methanol (0.01 mL/100 mL HCl), which was subsequently evaporated using a stream of nitrogen until a more concentrated sample was obtained. Finally, the concentrated extract was filtered through a 0.45 μm membrane filter (Millipore) and injected into the HPLC system for analysis.

2.6. HPLC analysis

The extracts were analyzed by HPLC using a chromatography system equipped with a quaternary pump, a UV–Vis detector and a column oven (series 200, PerkinElmer, Waltham, USA). Separation was conducted on a C$_{18}$ reversed-phase 5 μm (250 × 4.6 mm i.d., PerkinElmer) column coupled to a C$_{18}$ 5 μm (15 × 3.2 mm i.d., PerkinElmer, Waltham, USA) guard column. The injection volume was 20 μL, compounds were detected at a wavelength of 520 nm, and the temperature and flow rate were maintained at 30 °C and 1 mL min^{-1}, respectively. Gradient elution was performed according to the method of Durst and Wrolstad (2001). The mobile phases comprised eluents A (acetonitrile) and B (10 mL/100 mL acetic acid, 5 mL/100 mL acetonitrile and 1 mL/100 mL phosphoric acid). A linear gradient of 5–20 mL/100 mL A over 20 min was used, and 1 min elapsed before the next injection.

Anthocyanidins were identified by comparing the HPLC retention times for the sample and for the standards. A chromatogram of the blueberry pulp with solids content of 16 g/100 g prior to heating is presented in Fig. 2. In this figure, peaks identified as delphinidin (1), cyanidin (2), petunidin (3), peonidin (4) and malvidin (5) can be observed. The anthocyanidin levels were quantified using the calibration curves constructed with the corresponding anthocyanidin standards. The standard deviation of the concentration of anthocyanins was calculated using the least squares method and the results were expressed as grams of anthocyanidin per kilogram of fresh matter. All analyses were performed in duplicate.

The percentage of degradation was calculated using Equation (3), where the total anthocyanin content ([Acy]) pre and post the heating processes, ohmic or conventional, is taken into consideration.

$$\text{Anthocyanin degradation}(\%) = \left(1 - \frac{[\text{Acy}]\text{post heating}}{[\text{Acy}]\text{pre heating}}\right) \times 100 \qquad (3)$$

3. Results and discussion

The magnitude and duration of the heating process exerts strong influence in anthocyanin stability. Several studies have been carried out in order to evaluate and quantify this influence (Khanal,

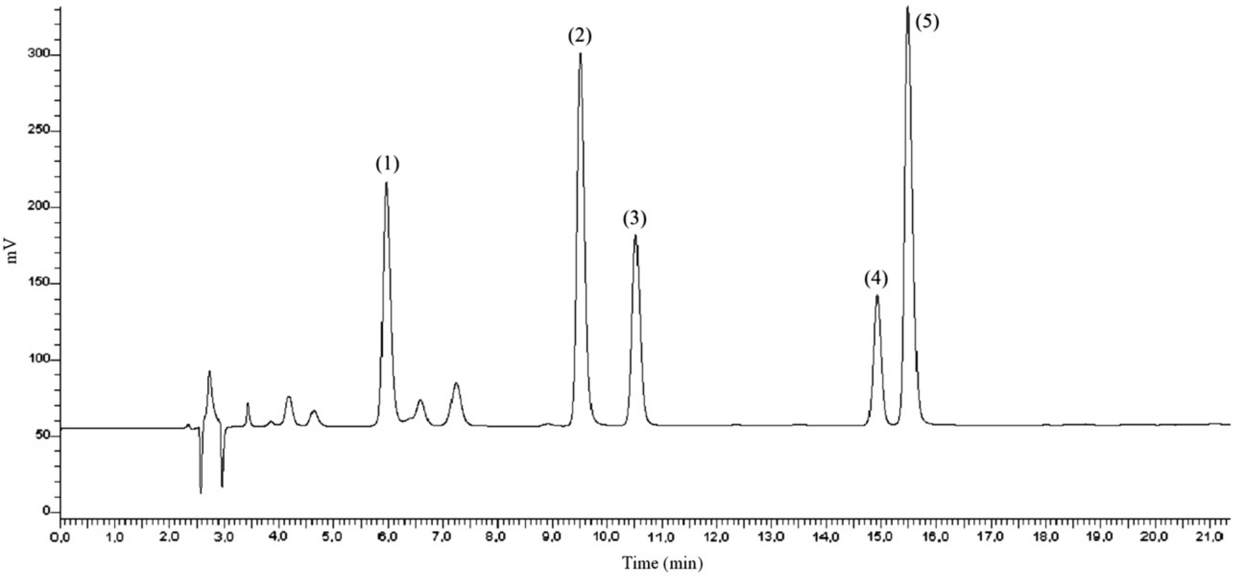

Fig. 2. Chromatogram of the blueberry pulp with solids content of 16 g/100 g prior to heating. Peak assignment: (1) delphinidin, (2) cyanidin, (3) petunidin, (4) peonidin and (5) malvidin.

Howard, & Prior, 2010; Oliveira et al., 2010; Queiroz et al., 2009; Rossi et al., 2003). The present work considered the effect of two variables over anthocyanin degradation: voltage and solids content; these parameters were chosen because they have influence on the heating time. Both high applied voltage and the use of pulp with high solids content result in faster heating, and less degradation is expected with faster processes.

Ohmic and conventional heating experiments were performed effectively, allowing the pulp to be kept at the desired temperature during the entire treatment period. Fig. 3 shows the temperature profiles during heating (25–90 °C), treatment period (90 °C), and cooling (90–10 °C) of the blueberry pulp with 10 g/100 g solids content during ohmic heating with three different voltages 160, 200 and 240 V and during conventional heating. Since little temperature differences were observed within the ohmic cell, the profiles were plotted for the average temperature between the two different locations inside the ohmic cell where this variable was monitored. As expected, the experiments performed with higher voltages or using pulp containing higher amounts of solids exhibited the shortest heating times. Overall, considering all the experiments performed, the heating period varied from 1.9 to 5.7 min, for ohmic heating and the heating period was of 4.0 min for conventional heating. The cooling time from 90 to 10 °C for the experiments performed was between 4.4 and 6.3 min. The results for the ohmic heating will be presented next, followed by the results for conventional heating and a comparison of the two technologies.

3.1. Ohmic heating

All experiments were performed as expected: the voltage was kept constant, varying ±1 V from the target value; the maximum temperature difference inside the cell ranged between 0.9 and

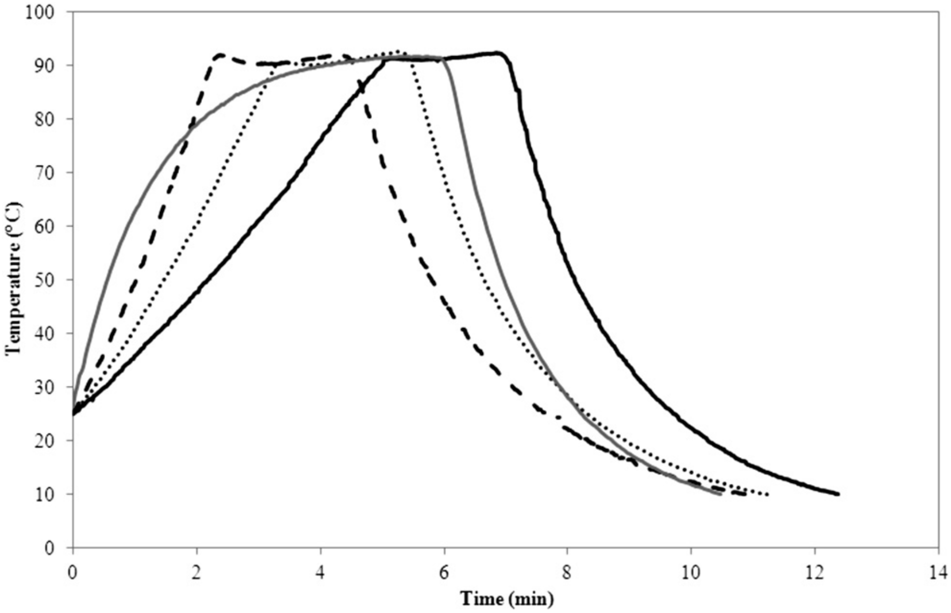

Fig. 3. Temperature profile inside the cells during ohmic heating using 160 (—), 200 (······) and 240 V (- -) and conventional heating (——).

Table 3
Analysis of variance (ANOVA) and regression coefficients of the second-order polynomial equation for the percentage of anthocyanin degradation.

Regression coefficients		
Intercept	β_0	11.8
Linear	β_1	2.8
	β_2	0.6
Quadratic	β_{11}	−0.7
	β_{22}	–
Interaction	β_{12}	−0.8

3.8 °C; and the average pasteurization temperature varied from 90.0 to 91.2 °C. The greatest temperature differences inside the cell occurred in the experiments with faster heating. This behavior was expected since when heating is faster, there is less time for the heat to be conducted. Additionally, the manual voltage regulation could be responsible for the minor system instabilities. Nonetheless, these parameters were considered satisfactory.

The percent degradation of anthocyanins (response variable Y) obtained from all experiments, as well as the anthocyanin content prior to and after processing, are presented in Table 2. The error between the percentages of anthocyanin degradation of the three central points was 4.5%, showing an acceptable difference between independent experiments. The total anthocyanin content ([Acy]) was determined by adding the contents of delphinidin and malvidin. Pelargonidin was not identified in the sample, and the other anthocyanidins were present at levels below the quantification level for the diluted pulp. Because the samples were not completely homogeneous, the total anthocyanin content prior to ohmic heating, presented in Table 2, varied among samples with the same solids content. Anthocyanin degradation varied between 5.7 and 14.7% in the voltage and solids content ranges analyzed.

The experimental data were used to calculate the coefficients of the second-order polynomial equation. Table 3 summarizes the model parameters and determination coefficient. The model obtained considered only the influences of significant factors ($p < 0.05$); thus, the insignificant quadratic effect of the solids content is absent in the regression equation. The average error between the predicted values and the experimental values (calculated using Equation (2)) was 4.3%. The error could most likely be reduced if a more homogeneous product was used, as anthocyanins are not distributed homogeneously inside the fruit.

The model obtained (a second-order polynomial equation) adequately represented the experimental data with a coefficient of determination (R^2) of 0.969. This value indicates that approximately 97% of the anthocyanin degradation can be predicted by the suggested model. To verify the significance of the model, analysis of variance (ANOVA) was conducted, and the results indicated that the model was significant with no lack of fit ($p = 0.445$), suggesting that the model adequately represented the relationship between the response and the factors.

Voltage has linear and quadratic positive effects, and the solids content exerts a linear positive effect. These results differ from the expected results because low anthocyanin degradation was associated with low voltages and not necessarily with faster heating. The effects of voltage on anthocyanin degradation will be further discussed in Section 3.3. The positive effect of the solids content, i.e., the increase in anthocyanin degradation with an increase in solids content, was observed in studies involving strawberries and sour cherries (Cemeroglu, Velioglu, & Isik, 1994; Garzón & Wrolstad, 2002). This influence of the solids content could be related to the greater proximity of the reacting molecules in juices with higher soluble solids contents (Nielsen, Marcy, & Sadler, 1993). Inter- and intramolecular co-pigmentation with other moieties and other anthocyanins provides greater stability against temperature changes, as well as pH and light variations (Francis, 1992).

Table 4 shows the results for delphinidin and malvidin separately; the pre- and post-ohmic heating anthocyanin content and percentage of degradation are presented. Data demonstrates that, with the exception of runs 4, 5 and 9, delphinidin was the most unstable compound. The high level of degradation of this anthocyanidin can be related to its high content of hydroxyl substituents, which are more susceptible to degradation reactions. The same behavior was observed by Lee, Durst, and Wrolstad (2002) and Skrede et al. (2000).

3.2. Conventional heating

The conventional heating experiment had a heating time of 4 min, and the average pasteurization temperature was 91.2 °C. This heating time was in between the values obtained for ohmic heating. The percentage of anthocyanin degradation was calculated by adding the delphinidin and malvidin contents, as described for ohmic heating, and the obtained value was 7.2%.

3.3. Comparison of ohmic and conventional processing

Comparing ohmic and conventional heating processes for the blueberry pulp with 10 g/100 g solids content it is possible to observe that for high voltages, 200 and 240 V, the degradation is higher when ohmic heating is applied, but for a lower voltage, 160 V, the degradation is lower than the observed during conventional heating.

Clearly, the literature values for anthocyanin degradation in fruits products vary considerably. Studies demonstrated that its stability is influenced by the intrinsic properties of the product and the process characteristics causing these differences to occur. Brownmiller, Howard, and Prior (2008), Lee et al. (2002), and

Table 4
Delphinidin and malvidin contents pre- and post-ohmic heating (OH) and experimental results for anthocyanin degradation.

Run	Delphinidin			Malvidin		
	[Acy] pre OH (mg/100 g)	[Acy] post OH (mg/100 g)	Degradation (%)	[Acy] pre OH (mg/100 g)	[Acy] post OH (mg/100 g)	Degradation (%)
1	35.7 ± 0.4	32.8 ± 0.4	8.1	26.9 ± 0.4	25.3 ± 0.5	6.1
2	69.7 ± 0.4	61.2 ± 0.4	12.2	44.4 ± 0.4	41.3 ± 0.5	7.1
3	35.7 ± 0.4	29.5 ± 0.5	17.3	26.9 ± 0.4	24.6 ± 0.5	8.7
4	58.9 ± 0.4	51.5 ± 0.4	12.7	40.5 ± 0.5	34.6 ± 0.5	14.4
5	51.3 ± 0.4	48.8 ± 0.3	5.03	35.6 ± 0.4	33.3 ± 0.2	6.7
6	55.1 ± 0.5	45.3 ± 0.6	17.7	37.6 ± 0.5	33.7 ± 0.5	10.3
7	32.9 ± 0.5	29.3 ± 0.4	10.7	27.7 ± 0.4	24.8 ± 0.5	10.6
8	80.8 ± 0.4	69.2 ± 0.4	14.4	49.7 ± 0.4	45.5 ± 0.5	8.5
9	52.8 ± 0.6	47.2 ± 0.4	10.7	36.3 ± 0.4	31.8 ± 0.5	12.3
10	51.3 ± 0.4	44.2 ± 0.4	13.9	35.6 ± 0.4	32.3 ± 0.5	9.4
11	51.3 ± 0.4	44.4 ± 0.5	13.5	35.6 ± 0.4	31.8 ± 0.6	10.8

Skrede et al. (2000) carried out experiments to determinate the anthocyanin degradation levels in blueberries using time/temperature conditions similar to those used in this study, and they found lower levels of degradation than those obtained in this work. In contrast, Volden et al. (2008) found a considerably higher level of anthocyanin degradation of 59% in red cabbage after 3 min of processing at 95 °C. Moreover, in studies in which anthocyanins were exposed to high temperatures for longer periods of time, the level of degradation reached 55% (Queiroz et al., 2009).

According to Patras et al. (2010), given the currently available data, it is not possible to predict the exact effect of thermal treatment on anthocyanin retention, and it is necessary to evaluate each case individually until a consensus is reached. In this work, anthocyanin degradation showed a significant relation to the applied heating voltage. Although a direct comparison is not possible due to lack of work evaluating anthocyanin degradation in the presence of an electric field, some studies evaluated the influence of ohmic heating on ascorbic acid and/or vitamin C degradation and compared conventional and ohmic techniques. A recently published studies performed in our laboratory using the same ohmic heating equipment evaluated the effects of voltage and solids content on vitamin C and ascorbic acid degradation in acerola pulp. The results obtained by Mercali, Jaeschke, Tessaro, and Marczak (2012) were similar to the results obtained for anthocyanins in this work: higher voltages caused higher degradation levels, being an indicative of the similarity of the chemical reactions undergone by these compounds.

The research of Lima, Heskitt, Burianek, Nokes, and Sastry (1999) determined whether the presence of an electric field altered the rate of degradation of ascorbic acid. They compared ohmic and conventional heating and found very similar kinetic parameters for both treatments. Their study also evaluated the effect of electrolysis on ascorbic acid degradation, and they observed gas production when stainless electrodes were used but not with titanium-coated electrodes. In both cases, electrolysis did not affect the ascorbic acid concentration. Nevertheless, a different study (Assiry, Sastry, & Samaranayake, 2003) yielded results similar to those obtained in this work. The authors found a higher level of degradation of vitamin C during ohmic heating using high voltages relative to conventional heating. They concluded that during ohmic heating, in addition to the degradation caused by heat, there is also electrochemical degradation due to a number of reactions, including electrode reactions and electrolysis of the solution; in addition, reactions between the electrode materials and the electrolysis products may influence the degradation reaction mechanisms and the kinetic parameters.

As described by Assiry et al. (2003) one of the main reactions influencing degradation is the electrolysis of water, which yields hydrogen at the cathode and oxygen at the anode. Since alternating current is used in the system both reactions occur at each electrode.

$$\text{Cathode}:\ 2H^{+}(aq) + 2e^{-} \rightarrow H_2(g) \tag{4}$$

$$\text{Anode}:\ 2H_2O(l) \rightarrow O_2(g) + 4H^{+}(aq) + 4e^{-} \tag{5}$$

$$\text{Overall}:\ 2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \tag{6}$$

According to the authors, the molecular oxygen generated by water electrolysis causes additional oxidation of the ascorbic acid. The presence of molecular oxygen in the system presented in this work could be related to the observed anthocyanin degradation. Another important reaction, also described by Assiry et al. (2003), is electrode corrosion. These reactions may happen in the ohmic heating systems either by direct metal oxidation or by electrochemical generation of corroding chemicals. The direct metal oxidations yields hydrogen and metal ions, these ions migrate into the medium and can be oxidized and undergo other secondary reactions.

In an agitated system, like the apparatus used in this work, the products of the previously described reactions could have dispersed in the pulp, where further reactions may have occurred, enhancing degradation. The frequency of electrochemical reactions is greater when higher voltages are used, as observed in the experiments of Içier and Ilicali (2005), Palaniappan and Sastry (1991) and Qihua, Jindal, and Van Winden (1993). In the last mentioned work, bubbles were produced during the ohmic heating of orange juice as a result of electrochemical reactions. Like ascorbic acid, anthocyanins are effective antioxidants and therefore oxidize easily (Skrede et al., 2000). The unsaturated nature of anthocyanins makes them prone to attack by molecular oxygen; consequently, anthocyanins are likely to undergo similar chemical reactions, and these reactions may explain the observed behavior.

When metallic electrodes are used, electrochemical reactions must always be taken into account when frequencies between 50 and 60 Hz are used (Ruan et al., 2002). In the present study, it was possible to observe the deposition of black materials on the electrodes during the use of the experimental apparatus, and the Pt-100 m lost their black color due to the dissociation of the nickel–phosphorous alloy coating. According to the literature, the use of inert materials for the electrodes and the use of high frequencies are able to prevent electrochemical reactions (Içier & Ilicali, 2005). These effects can be observed in the study of Jun, Sastry, and Samaranayake (2007), who showed that retort pouches used with stainless steel electrodes and high frequencies can minimize bubble formation. Moreover, tests carried out using commercial equipment with frequencies above 100 kHz did not yield any sign of metallic dissolution (Ruan et al., 2002).

Further research must be carried out in order to elucidate the mechanisms of anthocyanin degradation during ohmic heating and confirm the hypothesis suggested in this work; future experiments should be conducted using lower voltages. A new system is being currently developed in our laboratory, which will allow us to evaluate lower voltages combined with different frequency ranges.

4. Conclusions

This article presents a study concerning anthocyanin degradation during the thermal treatment of blueberry pulp using ohmic and conventional heating. For the ohmic heating experiments, the effects of the voltage and the solids content were evaluated. Most of the independent variables – quadratic and linear voltage variables, the linear solids content variable and the interaction variable – had significant effects on the response values, the exception being the quadratic effect of the solids content. A second-order polynomial model was obtained, and the equation shows that anthocyanin degradation increases as both parameters analyzed increases. The level of degradation varied from 5.7 to 14.7% for the ohmic heating experiments, and for the conventional heating experiment, the level of degradation was 7.2%.

The percentage of anthocyanin degradation was similar or even lower than those obtained with conventional heating when the ohmic heating process was used with low voltage gradients. When higher voltage gradients were applied, the levels of degradation were greater for the ohmic-heated pulp. These results might be explained by electrochemical reactions that are catalyzed by high voltages. The results emphasize the importance of the use of inert materials in electrodes and electrode coatings or the use of high frequency power to limit electrochemical reactions.

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