Journal of Food Engineering 89 (2008) 210–216

Contents lists available at ScienceDirect

Journal of Food Engineering

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

Modeling changes in health-related compounds of tomato juice treated by high-intensity pulsed electric fields

Isabel Odriozola-Serrano, Robert Soliva-Fortuny, Vicente Gimeno-Añó, Olga Martín-Belloso *

Department of Food Technology, UTPV-CeRTA, University of Lleida, Rovira Roure 191, 25198 Lleida, Spain

ARTICLE INFO

Article history:
Received 17 January 2008
Received in revised form 8 April 2008
Accepted 19 April 2008
Available online 28 April 2008

Keywords:
Modeling
High-intensity pulsed electric fields
Tomato juice
Health-related compounds
Antioxidant capacity

ABSTRACT

Changes in some health-related compounds (lycopene and vitamin C) and antioxidant capacity of tomato juice treated by high-intensity pulsed electric fields (HIPEF) were modeled as a function of the electric field strength and treatment time. Samples were subjected to electric field strengths from 20 to 35 kV/cm for up to 2000 μs using bipolar 1-μs pulses at 250 Hz. Weibull kinetic models predicted vitamin C and antioxidant capacity retention of HIPEF-treated tomato juice with good accuracy ($R^2_{adj} \geqslant 0.836$; $A_f = 1.001–1.010$). A model used to describe moisture sorption processes was the most accurate for describing lycopene changes through the HIPEF treatment time. The combined effect of treatment time and electric field strength on health-related compounds of tomato juice were successfully predicted ($R^2_{adj} > 0.948$; $A_f = 1.016–1.017$) through secondary expressions. Information from this study would be useful in determining optimal HIPEF-conditions to produce tomato juices with a high retention of bioactive compounds.

1. Introduction

Regular intake of tomatoes and tomato based products has been associated with lower incidence of various forms of cancer, in particular prostate cancer, and heart diseases (Arab and Steck, 2000). This beneficial effect is believed to be due, at least partially, to the action of antioxidant compounds, which reduce oxidative damage in the body. However, the nutritional value of tomato products depends on several factors such as processing and storage conditions (Willcox et al., 2003). Consumers demand high quality nutritious foods with fresh flavor, texture and color as well as with minimal or no addition of chemical preservatives (Bull et al., 2004). Consequently, emerging technologies for food processing and preservation, such as high-intensity pulsed electric fields (HIPEF), are being investigated (Deliza et al., 2003). HIPEF processing, as a non-thermal technology, has been shown to effectively inactivate microorganisms in tomato juice, thus leading to microbial inactivation levels similar to those achieved with heat pasteurization (Min et al., 2003). In addition, HIPEF treatments can achieve high rates of tomato juice peroxidase (POD), pectin methylesterase (PME) and polygalacturonase (PG) inactivation (Aguiló-Aguayo et al., 2007, 2008). Several authors have studied the evolution of quality parameters in tomato juice after HIPEF treatments and promising results have been obtained regarding the maintenance of health-related compounds and color attributes compared to heat treatments (Min et al., 2003; Odriozola-Serrano et al., 2008). Process parameters such as electric field strength and treatment time are important variables to be controlled in order to optimize the inactivation of microorganisms (Elez-Martínez et al., 2004, 2005) and enzymes (Giner et al., 2000; Elez-Martínez et al., 2006) by HIPEF. In addition, there are several works studying the effect of HIPEF treatment parameters on health-related compounds in juices. For instance, Cortés et al. (2006) reported that electric field strength and treatment time had a significant effect on HIPEF-treated orange juice carotenoids. In this way, Elez-Martínez and Martín-Belloso (2007) concluded that vitamin C retention and the antioxidant capacity in orange juice and "gazpacho" cold vegetable soup mostly depended on electric field strength and treatment time. On the other hand, several models have been used to describe the microbial destruction (Rodrigo et al., 2001; Elez-Martínez et al., 2004) and enzymatic inactivation (Giner et al., 2005; Elez-Martínez et al., 2006) as a function of the HIPEF critical parameters. Although retention of health-related compounds can be a limiting factor when defining process conditions, little information is available on modeling the content of antioxidant compounds as affected by HIPEF treatment parameters (Bendicho et al., 2002; Torregrosa et al., 2006). Therefore, the aim of this work was to propose mathematical models that properly relate changes in health-related compounds, namely lycopene and vitamin C, and antioxidant capacity of tomato juice to electric field strength and HIPEF treatment time.

* Corresponding author. Tel.: +34 973 702593; fax: +34 973 702596.
E-mail address: Omartin@tecal.udl.es (O. Martín-Belloso).

0260-8774/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jfoodeng.2008.04.019

2. Materials and methods

2.1. Tomato juices

Tomatoes (*Lycopersium esculentum* Mill. cultivar Bodar) at commercial maturity were bought from a local supermarket and kept at 4 °C before being processed. The fruits were chopped, crushed and then filtered through a 2-mm diameter steel sieve. Electric conductivity (Testo 240 conductivimeter; Testo GmBh & Co, Lenzkirch, germany), pH (crison 2001 pH-meter; Crison Instruments SA, Alella, Barcelona, Spain), soluble solids content (Atago RX-1000 refractometer; Atago Company Ltd., Japan) and color (Macbeth-Kollmorgen Institute Corp., Newburg, NY) of tomato juice were determined. The physico-chemical characteristics of just filtered tomato juice were: soluble solids = 4.1 ± 0.2°Brix, pH 4.32 ± 0.33, electric conductivity = 0.63 ± 0.21 S/m, and color L^* = 22.21 ± 0.53, a^* = 6.88 ± 0.33 and b^* = 5.14 ± 0.23.

2.2. Pulsed electric fields equipment

HIPEF treatments were carried out in a continuous flow bench scale system (OSU-4F, Ohio State University, Columbus, OH, USA). The treatment system consists of eight collinear chambers in series, each one with two stainless steel electrodes separated by a gap of 0.29 cm, thus defining a treatment volume of 0.012 cm^3. The flow rate of the process was adjusted to 60 mL/min and controlled with a variable speed pump (model 752210-25, Cole Palmer Instrument Company, Vermon Hills, IL, USA). Treated tomato juice was passed through a cooling coil was connected between each pair of chambers and submerged in an ice–water shaking bath. Thermocouples were attached to the surface of the stainless steel coils, 2.5 cm away from the HIPEF zones along the flow direction. The thermocouples were connected to temperature readers and isolated from the atmosphere with an insulation tape. The temperatures of the inlet and outlet of each pair of chambers were recorded every 0.1 s during HIPEF treatment and the samples never exceeded 40 °C. Samples of tomato juice were subjected to field strengths of 20, 25, 30 and 35 kV/cm during 100, 300, 600, 1000, 1500 and 2000 μs, using 1-μs square-wave bipolar pulses at 250 Hz. Treatment conditions were selected according to a previous study (Odriozola-Serrano et al., 2007a).

2.3. Bioactive compounds

2.3.1. Lycopene

Lycopene concentration in tomato juice was measured spectrophotometrically (CECIL CE 2021; Cecil Instruments Ltd., Cambridge, UK) following the method proposed by Davis et al. (2003). About 0.6 g of tomato juice was weighted and added to 5 mL of 0.05% (w/v) butylated hydroxytoluene in acetone, 5 mL of 95% USP grade methanol, and 10 mL of hexane. The homogenate was centrifuged at 320*g* for 15 min at 4 °C. Then, 3 mL of distilled water were added to each vial and the samples were shaken for 5 min at 4 °C. Afterwards, the vials were left at room temperature for 5 min to allow separation. The absorbance of the upper, hexane layer was measured in a 1-cm pathlength quartz cuvette at 503 nm blanked with hexane. The lycopene content of each sample was estimated according to Eq. (1):

$$\text{lycopene}(\text{mg/kg}) = \frac{A_{503} \times MW \times DF \times 1000}{\varepsilon \times L} \tag{1}$$

where MW is the molecular weight of lycopene (536.9 g/mol), DF is the dilution factor, L is the pathlength in cm and ε is the molar extinction coefficient for lycopene (172,000 L/mol cm).

Results were expressed as lycopene retention compared to the untreated sample.

2.3.2. Vitamin C

Vitamin C content of tomato juice was analyzed by HPLC. The extraction procedure was based on a method validated by Odriozola-Serrano et al. (2007b). A sample of 25 mL of tomato juice was mixed with 25 mL of a solution containing 45 g/L metaphosphoric acid and 7.2 g/L DL–1,4-dithiotreitol. The homogenate was centrifuged at 22,100*g* for 15 min at 4 °C (Centrifuge Avanti™ J-25, Beckman Instruments Inc., Fullerton, CA, USA). The supernatant was vacuum-filtered through Whatman No. 1 paper. Then, the samples were filtered with a Millipore 0.45 μm membrane. An aliquot of 20 μL was injected into the HPLC system consisting of a reverse-phase C18 Spherisorb® ODS2 (5 μm) stainless steel column (4.6 mm × 250 cm) and a 486 Absorbance Detector (Waters, Milford, MA). A 0.01% solution of sulphuric acid adjusted to pH 2.6 was used as eluent. The flow was isocratic at a rate of 1 mL/min at room temperature. Detection was performed at 245 nm. Identification of the ascorbic acid was carried out comparing the retention time and UV–visible absorption spectrum of the juice samples with those of the standards. Results were expressed as vitamin C retention related to the untreated sample.

2.4. Antioxidant capacity

The antioxidant capacity of tomato juice was studied through the evaluation of free radical-scavenging effect on 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical, according to the method described by Odriozola-Serrano et al. (2007a). Samples of tomato juice were centrifuged at 6000*g* for 15 min at 4 °C (Centrifuge Medigifer; Select, Barcelona, Spain) and aliquots of 0.01 mL of the supernatant were mixed with 3.9 mL of methanolic DPPH (0.025 g/L) and 0.090 mL of distilled water. The homogenate was shaken vigorously and kept in darkness for 30 min. Absorption of the samples was measured with a spectrophotometer at 515 nm against a blank of methanol without DPPH. Results were expressed as antioxidant capacity retention related to the untreated sample.

2.5. Data analysis

Each processing condition was assayed in duplicate and two replicate analyses were carried out in order to obtain the mean value. Several models such as first-order, first-order fractional conversion, Weibull distribution, Fermi and Hülsheger model have been used to describe the microbial destruction and enzymatic inactivation as a function of the HIPEF critical parameters. These different models were fitted to the experimental data and it was found that first-order model (Eq. (2)), Weibull distribution function (Eq. (3)) and a model proposed by Peleg (Eq. (5)), best relate the changes in antioxidant properties of tomato juices to HIPEF processing parameters.

First-order kinetics (Eq. (2)) are commonly used to fit the variation of health-related compounds in juices and nectars as a function of treatment time for heat processing (Vieira et al., 2000; Vikram et al., 2005; Wang and Xu, 2007). Bendicho et al. (2002) proposed a first-order model to describe the vitamin C changes in milk as affected by HIPEF treatment time.

$$\mathrm{RC} = \mathrm{RC}_0 \cdot \exp(-k_1 \cdot t) \tag{2}$$

where RC (%) is the relative content of health-related compounds or relative antioxidant capacity, RC_0 (%) is the intercept of the curve, k_1 is the first-order kinetic constant (μs^{-1}) and t is the treatment time (μs).

Weibull distribution Eq. (3) has been used to describe destruction of microorganisms (Rodrigo et al., 2001) and enzyme inactivation (Rodrigo et al., 2003; Giner et al., 2005; Soliva-Fortuny et al., 2006) under HIPEF. The use of Weibull distribution function to describe the retention of health-related compounds and antioxidant capacity has not been reported yet

$$RC = RC_0 \exp\left[-\left(\frac{t}{\alpha}\right)^{\gamma}\right] \quad (3)$$

where RC (%) is the relative content of health-related compounds or relative antioxidant capacity, RC_0 (%) is the intercept of the curve, t is the treatment time (μs), α is the scale factor (μs), and γ is the shape parameter that indicates concavity (tail-forming) or convexity (shoulder-forming) of the curve when it takes values below and above 1, respectively. Derived from the Weibull distribution function parameters (α, γ), $t_m$was defined as the mean processing time to achieve complete destruction/inactivation of the health-related compound or antioxidant capacity and can be used as a measurement of the resistance of these compounds to HIPEF treatments Eq. (4):

$$t_m = \alpha \cdot \Gamma\left(1 + \frac{1}{\gamma}\right) \quad (4)$$

where α and β are the parameters of the Weibull distribution and Γ is the gamma function.

Because of the shape similarity between solid-liquid extraction curves in sorption processes and the changes in lycopene retention, the fit of a model proposed by Peleg (1988) Eq. (5) to lycopene content as affected by HIPEF treatment time was evaluated. This model has been used to describe sorption processes in various foods (Turhan et al., 2002; Palou et al., 1994) and has been shown to properly fit the solid-liquid extraction kinetics of total polyphenols from grape seeds (Bucić-Kojić et al., 2007)

$$RC = RC_0 + \frac{t}{K_1 + K_2 \cdot t} \quad (5)$$

where RC (%) is the relative lycopene content, RC_0 (%) is the intercept of the curve, t is the treatment time (μs), K_1 (μs/%) is the Peleg rate constant indicating the lycopene formation rate at initial treatment time ($t = t_0$), and K_2 is the Peleg capacity constant, which is related to the steady value reached for prolonged treatment times Eq. (6):

$$RC_{\infty} = 100 + \frac{1}{K_2} \quad (6)$$

Additionally, kinetic rate constants obtained for each model were related, when possible, to the applied electric field strength through mathematical expressions. The combined effect of the electric field strength and treatment time on tomato juice antioxidant properties was described by rearranging these mathematical expressions into the best kinetic model for each compound.

The fit of the models to experimental data was evaluated by nonlinear regression procedures, using the Statgraphics Plus v.5.1 Windows package. Fitting accuracy of the models was evaluated through the analysis of the adjusted regression coefficients (R^2_{adj}), the accuracy factor (A_f) (Ross, 1996), the root mean square error (RMSE), the reduced Chi-square (χ^2) and mean bias error (MBE) (Hayaloglu et al., 2007). The higher the R^2_{adj} value as well as the lower the RMSE, χ^2 and MBE, the better the model fits experimental data.

3. Results and discussion

3.1. Lycopene

The effect of HIPEF treatments on the lycopene content of tomato juice is shown in Fig. 1. Fresh tomato juice had a lycopene content of 77 mg/L. Lycopene concentration was enhanced significantly after HIPEF processing from 3.8% to 37.7% compared to the untreated juice Our results agree with those of other studies reporting an enhancement in the carotenoids content of health-related compounds in HIPEF-processed juices (Torregrosa et al., 2005; Cortés et al., 2006). In addition, Odriozola-Serrano et al. (2008) reported a rise of 4.67% in tomato juice treated by heat at 90 °C for 60 s compared to the fresh juice. This rise in lycopene content might be attributed to the conversion of other carotenoids such as phytoene, phytofluene, ζ-carotene and neurosporene through desaturation, isomerization and cyclization into lycopene (Bramley et al., 1992). Further investigations are still needed to explain the mechanisms that mediate this HIPEF-induced conversion of carotenoids to lycopene.

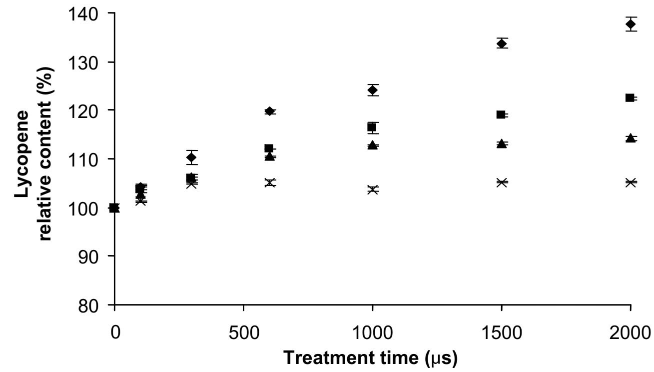

Fig. 1. Effect of treatment time and electric field strength on the lycopene retention of tomato juice (mean ± SD). Treatments were performed at 250 Hz and square bipolar pulses of 1-μs. Electric field strengths: (♦) 35 kV cm^{-1}, (■) 30 kV cm^{-1}, (▲) 25 kV cm^{-1}, and (×) 20 kV cm^{-1}.

Electric field strength and treatment time had a significant effect on tomato juice lycopene content (Fig. 1). The kinetic constants estimated by the models and determination coefficients for treatments of different electric field strength are shown in Table 1. The fitting performance of both the Weibull function and Peleg model was good irrespective of the electric field strength ($R^2_{adj} = 0.759 - 0.992$). Although A_f-values for the Weibull equations and Peleg approach were quite similar (1.007–1.032), the RMSE, MBE and χ^2 were lower using the latter model. Therefore, from a quantitative point of view, data were best described by the Peleg model Eq. (5), followed by Weibull function Eq. (3). Weibull distribution shape parameter (γ) and scale factor (α) were influenced by the electric field strength (Table 1). The higher the electric field strength, the greater the shape factor and the nearer the scale factor to 0 was. The γ took values from 2.3×10^{-1} to 5.8×10^{-1}.Values of the γ below 1 could be regarded as evidence that lycopene formation became increasingly lower over time. As can be seen in Table 1, the Peleg rate constant (K_1) was not linearly correlated by the applied electric field strength, thus indicating similar rates of lycopene formation at initial treatment time ($t = t_0$) irrespective of the intensity of the HIPEF treatments. In contrast, Peleg capacity constant (K_2), which is related to the steadily value reached for prolonged treatment time, increased as electric field strength rose, following an exponential trend that could be described with good accuracy by a first-order model ($R^2_{adj} = 0.988$, $A_f = 1.296$, RMSE = 0.147, MBE = 0.002, $\chi^2 = 6.8 \times 10^{-5}$) Eq. (7):

$$K_2 = (1.2 \cdot 10^1) \cdot \exp[-(2.1 \cdot 10^{-1})] \quad (7)$$

Lycopene content for prolonged treatment times (RC_{∞}), which was calculated from K_2 Eq. (6), took values from 105% to 169%. The greater the electric field strength, the higher the relative lycopene content after prolonged HIPEF treatment time. Consistently, Cortés et al. (2006) observed that the carotenoids content in HIPEF-treated orange juice increased significantly when the most intensive

Table 1
Kinetic constants of Weibull distribution function (Eq. (3)) and Peleg model (Eq. (5)) of lycopene content as a function of the pulsed electric field strengths

E	Weibull distribution function[a]						
	$\alpha \times 10^{-4}$ (μs)	$\gamma \times 10$	R^2_{adj}	A_f	RMSE	MBE	χ^2
35	−1.3 ± 0.2	5.8 ± 0.3	0.986	1.012	0.810	0.363	1.347
30	−3.5 ± 0.7	5.5 ± 0.3	0.985	1.007	0.589	0.078	0.424
25	−24.4 ± 15.6	4.1 ± 0.5	0.947	1.009	0.651	−0.046	0.674
20	−6203 ± 29,500	2.3 ± 0.8	0.759	1.032	1.197	1.434	6.298
	Peleg model[a]						
	$K_1 \times 10^{-1}$ (μs × %$^{-1}$)	$K_2 \times 10^2$ (%$^{-1}$)	R^2_{adj}	A_f	RMSE	MBE	χ^2
35	2.38 ± 0.16	1.45 ± 0.12	0.992	1.001	0.588	0.013	0.510
30	3.46 ± 0.25	2.79 ± 0.19	0.990	1.005	0.515	−0.022	0.246
25	2.73 ± 0.27	5.55 ± 0.27	0.984	1.004	0.452	0.023	0.128
20	2.69 ± 1.02	18.1 ± 1.66	0.835	1.006	0.528	0.013	0.319

E: Electric field strength (kV/cm).
R^2_{adj}: adjusted regression coefficients, A_f: accuracy factor, RMSE: root mean square error, MBE: mean bias error and χ^2: reduced chi-square.
[a] Mean values ± standard error.

treatments (35 or 40 kV/cm) were conducted. Carotenoids concentration rose as treatment time increased when HIPEF treatments at 25 or 30 kV/cm were applied to orange-carrot juice (Torregrosa et al., 2005).

The combined effect of treatment time and electric field strength on tomato juice lycopene content is described by Eq. (8), where the K_2 in the Peleg model Eq. (5) is replaced by Eq. (7), and K_1 is substituted by the mean value, calculated from those obtained for each electric field. The new model fitted well the experimental data and exhibited good accuracy ($R^2_{adj} = 0.976$, $A_f = 1.017$, RMSE = 1.004, MBE = 0.561 and $\chi^2 = 4.493$). Lycopene relative content estimated by the model Eq. (8) is compared with the experimental data in Fig. 2. The small deviation from the bisector in this plot is related to the good fitting accuracy of the model

$$\mathrm{RC} = 100 + \frac{t}{(2.82 \times 10^1) + ([1.2 \cdot 10^1] \cdot \exp(-[2.1 \cdot 10^{-1}] \cdot E) \cdot t)} \tag{8}$$

3.2. Vitamin C

Vitamin C content of untreated tomato juice was 130 mg/L. The effect of HIPEF processing parameters on the concentration of vitamin C in tomato juice is shown in Fig. 3. The results are in agreement with those obtained by Torregrosa et al. (2006), who reported vitamin C retentions between 87.5 and 97% in orange-carrot juice treated at different electric field strengths (25, 30, 35 and 40 kV/cm) for different treatment times (from 30 to 340 μs) using

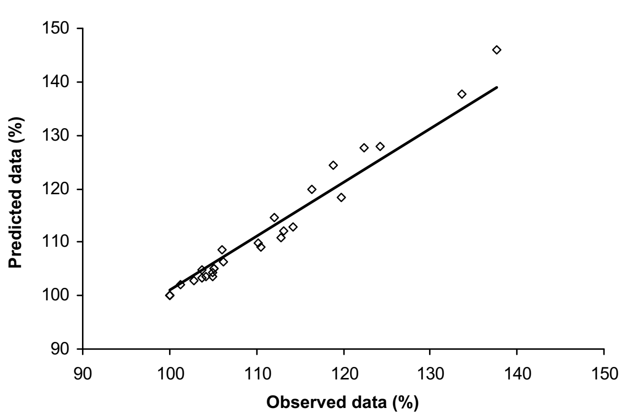

Fig. 2. Plot of the observed values of lycopene relative content after HIPEF treatments versus the predicted values by a secondary model (Eq. (8)).

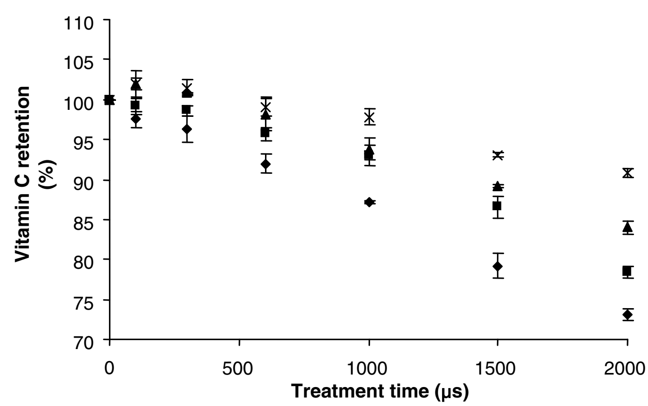

Fig. 3. Effect of treatment time and electric field strength on the vitamin C retention of tomato juice (mean ± SD). Treatments were performed at 250 Hz and square bipolar pulses of 1-μs. Electric field strengths: (♦) 35 kV cm^{-1}, (■) 30 kV cm^{-1}, (▲) 25 kV cm^{-1}, and (×) 20 kV cm^{-1}.

2.5-μs bipolar pulses. On the other hand, lower vitamin C retention just after treatment were obtained in heat-treated tomato juice at 90 °C for 30 or 60 s (79.2–80.4%) compared to the HIPEF-treated juices (Odriozola-Serrano et al., 2008). Vitamin C content significantly depended on the HIPEF treatment time and electric field strength applied during HIPEF-processing of the juice, so that the lower the treatment time and electric field strength, the greater the vitamin C retention (Fig. 2). Elez-Martínez and Martín-Belloso (2007) studied the variation of vitamin C content after applying different HIPEF treatments to "gazpacho", a cold vegetable soup where tomato is the major component, and obtained similar results to those found in the present study. Vitamin C is an unstable compound and under undesirable conditions it decomposes easily (Lee and Coates, 1999). Degradation of ascorbic acid depends upon many factors such as oxygen, light, processing temperature and time. In general, the milder the treatment, the better the vitamin C retention (Davey et al., 2000). Therefore, the high vitamin C destruction for prolonged intense HIPEF treatments may be explained through the instability of vitamin C to temperature and time.

The estimated parameters and the R^2_{adj}, A_f, RMSE, MBE and χ^2 of the models used to describe vitamin C variation at different electric field strengths are displayed in Table 2. Based on these coefficients, it can be concluded that both models fit well the data. However, it appears that the Weibull model is most suitable because have the highest R^2_{adj}, the lowest RMSE, MBE and χ^2 and the A_f values are the

Table 2
Kinetic constants of first-order (Eq. (1)) and Weibull distribution function (Eq. (3)) of vitamin C retention as a function of the pulsed electric field strengths

E	First-order model[a]					
	$k_1 \times 10^5$ (μs^{-1})	R^2_{adj}	A_f	RMSE	MBE	χ^2
35	15.2 ± 0.4	0.987	1.021	0.608	−0.239	0.462
30	10.2 ± 0.6	0.932	1.018	0.845	−0.266	1.760
25	7.5 ± 0.6	0.881	1.020	0.905	−0.501	2.165
20	4.1 ± 0.6	0.747	1.018	1.225	−0.435	8.007

E	Weibull distribution function[a]							
	$\alpha \times 10^{-4}$ (μs)	$\gamma \times 10$	t_m	R^2_{adj}	A_f	RMSE	MBE	χ^2
35	0.57 ± 0.04	11.0 ± 0.6	11,252	0.987	1.007	0.882	−0.659	1.854
30	0.48 ± 0.03	16.0 ± 0.3	7940	0.985	1.006	0.482	−0.079	0.167
25	0.55 ± 0.08	16.9 ± 0.4	8793	0.952	1.009	0.630	−0.227	0.624
20	0.66 ± 0.23	19.1 ± 1.5	10,028	0.836	1.010	0.808	−0.256	2.340

E: Electric field strength (kV/cm).
R^2_{adj}: adjusted regression coefficients, A_f: accuracy factor, RMSE: root mean square error, MBE: mean bias error and χ^2: reduced chi-square.
[a] Mean values ± standard error.

closest to 1 (Table 2). First-order rate constants were statistically influenced by the electric field strength and took values in the range of 4.1×10^{-5} to 1.52×10^{-4} μs^{-1}. The degradation of ascorbic acid studied by other authors was also fitted to first-order kinetics (Ariahu et al., 1997; Esteve et al., 1998). Bendicho et al. (2002) used a first-order model to describe the vitamin C depletion in HIPEF-treated milk. They obtained rate constants (k_1) ranging from 1.8×10^{-4} to 1.27×10^{-3} μs^{-1} using HIPEF treatments of up to 400 µs and electric field strengths from 18.3 to 27.1 kV/cm. Differences in the loss of vitamin C due to HIPEF treatments can be attributed not only to factors intrinsic to the food product, which can greatly condition the sensitivity of vitamin C to the applied treatments, but also to other factors such as HIPEF system, treatment chambers, pulse characteristics and electrical conditions. The scale parameter (α) and the shape parameter (γ) of the Weibull model were obtained by fitting Eq. (3) to the experimental data. The γ parameter, which ranged from 1.1 to 1.9, was inversely dependent on the electric field strength, suggesting that the higher the electric field strength the greater the effect of HIPEF treatment time. Values of γ parameter above 1 indicate that vitamin C became increasingly destroyed overtime. In contrast, α was independent from the electric field strength and took values from 5741 to 6587 µs. The values of mean time (t_m), which can be defined as the mean processing time to achieve complete destruction the vitamin C of tomato juice, were calculated from Eq. (4), and varied from 7939 to 11,252 µs. Because no references have been found reporting the use of Weibull equation to describe health-related compounds retention in HIPEF-treated products, the Weibull parameters were compared with those reported by Sampedro et al. (2006) for microorganisms and by Elez-Martínez et al. (2006) for enzymes. Considering the t_m parameter defined by the Weibull model, tomato juice vitamin C was more resistant to HIPEF treatments than *Lactobacillus plantarum* in orange juice-milk (15-40 kV/cm, up to 180 µs) but less than orange juice peroxidase treated at similar conditions to those used in the present work.

Although both tried models displayed good fit ($R^2_{adj} = 0.747 - -0.987$ and A_f = 1.006–1.021), the Weibull function was slightly more accurate in describing vitamin C changes as affected by HIPEF treatment time. First-order kinetics was adjusted to the γ estimated by the Weibull model for different electric field strength conditions. The model adequately fitted the shape constants, explaining 80.24% of the variability with good accuracy (A_f = 1.016, RMSE = 0.152, MBE = 0.001 and χ^2= 0.006) Eq. (9):

$$\gamma = (3.6) \cdot \exp[-(3.1 \cdot 10^{-2}) \cdot E] \tag{9}$$

Moreover, substitution of γ by Eq. (10) into the Weibull distribution Eq. (3) and replacing α by a mean constant value, calculated from those obtained for each electric field transforms the equation into a function dependent on both the electric field strength (E) and treatment time (t) Eq. (10). The model performed well under the whole range of applied conditions, with high determination coefficients ($R^2_{adj} = 0.941$) and good accuracy (A_f = 1.016, RMSE = 0.781, MBE = 0.042 and χ^2 = 1.202). The plot of the observed retention values versus the predicted data by Eq. (10) is shown in Fig. 4. Differences between the points of the graph and the line of equivalence are small and no local overestimation or underestimation of vitamin C retention is illustrated

$$\mathrm{RC} = \mathrm{RC}_0 \exp\left[-\left(\frac{t}{5.65 \cdot 10^3}\right)^{(3.6)\cdot\exp[-(3.1\cdot 10^{-2})\cdot E]}\right] \tag{10}$$

3.3. Antioxidant Capacity

Fig. 5 shows the antioxidant capacity of tomato juices treated under the studied experimental conditions. Antioxidant capacity significantly depended on electric field strength and treatment time (Fig. 5). HIPEF-treated tomato juice processed at 20 kV/cm had the highest antioxidant capacity, followed by that treated at 35 kV/cm. There was no statistical difference in the antioxidant capacity between tomato juices processed at 25 and 30 kV/cm. Changes in the antioxidant capacity of HIPEF-treated tomato juices are consistent with the variation in health-related compounds throughout processing. Vitamin C acts as a scavenging agent of

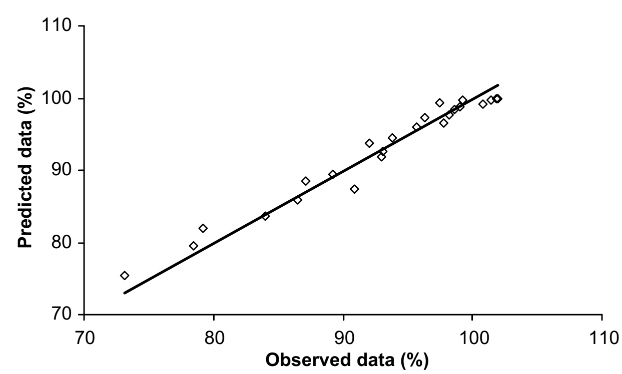

Fig. 4. Plot of the observed values of vitamin C retention after HIPEF treatments versus the predicted values by a secondary model (Eq. (10)).

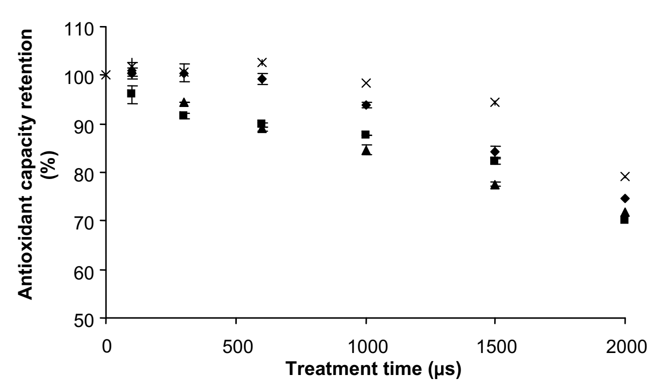

Fig. 5. Effect of treatment time and electric field strength on the antioxidant capacity of tomato juice (mean (SD). Treatments were performed at 250 Hz and square bipolar pulses of 1-µs. Electric field strengths: (♦) 35 kV cm^{-1}, (■) 30 kV cm^{-1}, (▲) 25 kV cm^{-1}, and (×) 20 kV cm^{-1}.

Table 3
Kinetic constants of first-order (Eq. (1)) and Weibull distribution function (Eq. (2)) of antioxidant capacity retention as a function of the pulsed electric field strengths

E	First-order model[a]					
	$k_1 \times 10^5$ (μs^{-1})	R^2_{adj}	A_f	RMSE	MBE	χ^2
35	11.3 ± 1.2	0.836	1.039	1.227	−0.718	7.500
30	15.8 ± 0.8	0.916	1.031	0.446	0.326	3.560
25	16.9 ± 0.4	0.984	1.010	0.185	−0.088	0.792
20	6.7 ± 1.6	0.592	1.053	0.775	−0.850	12.661

E	Weibull distribution function[a]							
	$\alpha \times 10^{-4}$ (μs)	$\gamma \times 10$	t_m	R^2_{adj}	A_f	RMSE	MBE	χ^2
35	0.34 ± 0.02	22.1 ± 1.6	5004	0.984	1.008	0.561	−0.157	0.355
30	0.7 ± 0.2	8.9 ± 1.3	15,971	0.912	1.003	0.501	0.185	3.541
25	0.62 ± 0.06	9.7 ± 0.6	12,512	0.983	1.009	0.135	−0.121	0.842
20	0.27 ± 0.01	47.9 ± 6.2	3271	0.967	1.001	0.034	−0.311	0.913

E: Electric field strength (kV/cm).
R^2_{adj}: adjusted regression coefficients, A_f: accuracy factor, RMSE: root mean square error, MBE: mean bias error and χ^2: reduced chi-square.

reactive oxygen species before they participate in oxidative reactions (Carr and Frei, 1999). In this way, vitamin C reduction as a result of HIPEF treatments, was reflected in a depletion of antioxidant capacity in tomato juice (Figs. 3 and 5). On the other hand, it has been reported that also lycopene accounts for the changes in antioxidant capacity of tomato products (Gahler et al., 2003). In this study, the extent of the changes in antioxidant capacity could be also associated with the variation in lycopene relative content. As can be seen in Fig. 1 and Fig. 5, tomato juice having the greatest lycopene concentration, had the second highest antioxidant capacity. Therefore, these results suggest that changes in antioxidant capacity of the juices might be due to vitamin C concentrations, rather than lycopene content.

In order to adequately relate changes in antioxidant capacity to treatment time, first-order Eq. (2) and Weibull functions Eq. (3) were fitted to the experimental data. Estimated first-order rates, Weibull parameters and regression coefficients for both models, obtained for different electric field strength, are shown in Table 3. The fitting performance of the first-order kinetic model was high for treatments with an electric field strength between 25 and 35 kV/cm but dramatically decreased for 20 kV/cm treatments ($R^2_{adj} = 0.592 - 0.984$). In contrast, adequacy of Weibull distribution seemed to be consistently good regardless of the applied electric field strength ($R^2_{adj} = 0.912 - 0.984$) (Table 3). As can be seen in Table 3, α and γ varied upon electric field strength. However, changes in Weibull parameters could not be well fitted by any model, provided that no clear influence of the electric field strength on α and γ were observed.

Values of mean time to achieve complete loss of antioxidant capacity (t_m) were calculated according to Eq. (4). The results ranged from 3271 to 15,970 μs. Elez-Martínez et al. (2006) used the Weibull model to describe the inactivation of peroxidase by HIPEF treatments of up to 35 kV/cm for 1500 μs and they reported t_m ranging from 100 to 43,000 μs. Rodrigo et al. (2001) reported t_m values of 0.71–72 μs for *L. plantarum* and *Byssochlamys fulva* in orange-carrot juice treated at electric field strength within 15-40 kV/cm. Therefore, in a first approach, according to Weibull model, tomato juice antioxidant capacity was shown to be less sensitive to HIPEF treatments than microorganisms, but more than enzymes.

On the other hand, Aguiló-Aguayo et al. (2007) reported that treatments carried out at 35 kV/cm for 1500 μs, supplying an energy density of 8269 kJ/L, achieved 5 log reductions for *Lactobacillus brevis*, whereas an inhibition of 97% peroxidase, 82% pectin methylesterase and 50% polygalacturonase activity in tomato juice compared to the untreated juice was observed. In addition, Mosqueda-Melgar (2007) observed that the naturally-occurring microbial population in tomato juice was maintained below 1 $\log_{10}$ for at least 28 days of storage at 5 °C when applying a HIPEF treatment of 35 kV/cm for 1000 μs. Microbial counts of 10^7 CFU/mL were reached after 50 days of storage. Therefore, the most intensive conditions applied in this study led to safe and stable tomato juices, with minimal changes in their health-promoting properties. HIPEF-treated (35 kV/cm for 1500 μs with 1-μs bipolar pulses at 250 Hz, energy input of 8269 kJ/L) tomato juice exhibited higher lycopene content (133%) and slightly lower vitamin C concentration (87%) compared to the fresh juice.

4. Conclusions

The evaluation of the effects of HIPEF critical parameters on the antioxidant potential of tomato juice contributes to determine the optimal processing conditions in order to obtain tomato juices with high nutritional quality. Retention of health-related compounds and antioxidant capacity depend on the HIPEF processing parameters. Generally, the greater the electric field strength and treatment time, the lower the vitamin C and the higher lycopene contents. The model based on Weibull distribution function is likely to be a useful tool for describing vitamin C and antioxidant capacity changes in tomato juice treated by HIPEF treatments. The Peleg model most accurately described kinetics of lycopene in HIPEF treated tomato juice. The proposed mathematical models may help to predict the variation of the antioxidant potential of tomato juice as affected by key parameters involved in HIPEF treatments.

Acknowledgements

This study has been carried out with financial support from the Commission of the European Communities, Framework 6, Priority 5 'Food Quality and Safety', Integrated Project NovelQ FP6-CT-2006-015710. This work was also supported by the Interministerial Commission for Science and Technology (CICYT) of the Ministerio de Educación y Ciencia (Spain) through the Project ALI 2005-05768. Isabel Odriozola-Serrano thanks the Agència de Gestió d'Ajuts Universitaris i de Recerca of the Generalitat de Catalunya (Spain) and the European Social Fund for the predoctoral grant.

References

Aguiló-Aguayo, I., Soliva-Fortuny, R., Martín-Belloso, O., 2007. Effects of pulsed electric field or heat treatments on pectin methylesterase and polygalacturonase activities and viscosity during storage of tomato juice. In: IFT Annual Meeting, Chicago, IL. Institute of Food Technologists.

Aguiló-Aguayo, I., Odriozola-Serrano, I., Quintão-Teixeira, L.J., Martín-Belloso, O., 2008. Inactivation of tomato juice peroxidase by high-intensity pulsed electric field as affected by process conditions. Food Chemistry 107, 949–955.

Arab, L., Steck, S., 2000. Lycopene and cardiovascular disease. American Journal of Clinical Nutrition 71 (6), 1691S–1695S.

Ariahu, C.C., Adekunle, D.E., Nkpa, N., 1997. Kinetics of heat/enzymatic degradation of ascorbic acid in fluted pumpkin (*Telfairia occidentalis*) leaves. Journal of Food Processing and Preservation 21, 21–32.

Bendicho, S., Espachs, E., Arántegui, J., Martín, O., 2002. Effect of high intensity pulsed electric fields and heat treatments on vitamins of milk. Journal of Dairy Research 69, 116–123.

Bramley, P., Teulieres, C., Blain, I., Bird, C., Schuch, W., 1992. Biochemical characterization of transgenic tomato plants in which carotenoids synthesis has been inhibited through the expression of antisense RNA to p TOM5. Plant Journal 2, 343–349.

Bucić-Kojić, A., Planinić, M., Tomas, S., Bilić, M., Velić, D., 2007. Study of solid–liquid extraction kinetics of total polyphenols from grape seeds. Journal of Food Engineering 81, 236–242.

Bull, M.K., Zerdin, K., Howe, E., Goicoechea, D., Paramanandhan, P., Stockman, R., Sellahewa, J., Szabo, E.A., Johnson, R.L., Steward, C.M., 2004. The effect of high-pressure processing on the microbial, physical, and chemical properties of Valencia and Navel orange juice. Innovative Food Science and Emerging Technologies 5, 135–149.

Carr, A., Frei, B., 1999. Does vitamin C act as a pro-oxidant under physiological conditions? FASEB Journal 13, 1007–1024.

Cortés, C., Esteve, M.J., Rodrigo, F., Torregrosa, F., Frígola, A., 2006. Changes of colour and carotenoids contents during high-intensity pulsed electric field treatment in orange juices. Food and Chemical Toxicology 44 (11), 1932–1939.

Davey, M.W., Van Montagu, M., Inze, D., Sanmartin, M., Kanellis, A., Smirnoff, N., Benzie, I.J.J., Strain, J.J., Favell, D., Fletcher, J., 2000. Plant L-ascorbic: chemistry, function, metabolism, bioavailable and effects of processing. Journal of the Science of Food and Agriculture 80, 825–860.

Davis, A.R., Fish, W.W., Perkins-Veazie, P., 2003. A rapid spectrophotometric method for analyzing lycopene content in tomato and tomato products. Postharvest Biology and Technology 28 (3), 425–430.

Deliza, R., Rosenthal, A., Silva, A.L.S., 2003. Consumer attitude towards information on non conventional technology. Trends in Food Science and Technology 14 (1–S2), 43–49.

Elez-Martínez, P., Martín-Belloso, O., 2007. Effects of high intensity pulsed electric field processing conditions on vitamin C and antioxidant capacity of orange juice and gazpacho, a cold vegetable soup. Food Chemistry 102 (1), 201–209.

Elez-Martínez, P., Escolà-Hernández, J., Soliva-Fortuny, R.C., Martín-Belloso, O., 2004. Inactivation of *Saccharomyces cerevisiae* suspended in orange juice using high-intensity pulsed electric fields. Journal of Food Protection 67, 2596–2602.

Elez-Martínez, P., Escolà-Hernández, J., Soliva-Fortuny, R.C., Martín-Belloso, O., 2005. Inactivation of *Lactobacillus brevis* in orange juice by high-intensity pulsed electric fields. Food Microbiology 22, 311–319.

Elez-Martínez, P., Aguiló-Aguayo, I., Martín-Belloso, O., 2006. Inactivation of orange juice peroxidase by high-intensity pulsed electric fields as influenced by process parameters. Journal of Agricultural and Food Chemistry 86, 71–81.

Esteve, M.J., Frígola, A., Martorell, L., Rodrigo, C., 1998. Kinetics of ascorbic acid degradation in green asparagus during heat processing. Journal of Food Protection 61, 1518–1521.

Gahler, S., Otto, K., Böhm, V., 2003. Alterations of vitamin C, total phenolics, and antioxidant capacity as affected by processing tomatoes to different products. Journal of Agricultural and Food Chemistry 51, 7962–7968.

Giner, J., Gimeno, V., Espachs, A., Elez, P., Barbosa-Cánovas, G.V., Martín, O., 2000. Inhibition of tomato (*Licopersicon esculentum* Mill.) pectin methylesterase by pulsed electric fields. Innovative Food Science and Emerging Technologies 1, 57–67.

Giner, J., Grouberman, P., Gimeno, V., Martín, O., 2005. Reduction of pectinesterase activity in a commercial enzyme preparation by pulsed electric fields: comparison of inactivation kinetic models. Journal of the Science of Food Agriculture 85, 1613–1621.

Hayaloglu, A.A., Karabulut, I., Alpaslan, M., Kelbaliyev, G., 2007. Mathematical modeling of drying characteristics of strained yoghurt in a convective type tray-dryer. Journal of Food Engineering 78, 109–117.

Lee, H.S., Coates, G.A., 1999. Vitamin C in frozen, fresh squeezed, unpasteurized, polyethylene-bottled orange juice: a storage study. Food Chemistry 65, 165–168.

Min, S., Jin, Z.T., Zhang, Q.H., 2003. Commercial scale pulsed electric field processing of tomato juice. Journal of Agricultural and Food Chemistry 51 (11), 3338–3344.

Mosqueda-Melgar, J., 2007. Aplicación de pulsos eléctricos de alta intensidad de campo en combinación con sustancias antimicrobinas para garantizar la calidad e inocuidad microbiológica de zumos de frutas. Doctoral thesis. University of Lleida, Spain.

Odriozola-Serrano, I., Aguiló-Aguayo, I., Soliva-Fortuny, R., Gimeno-Añó, V., Martín-Belloso, O., 2007a. Lycopene, vitamin C, and antioxidant capacity of tomato juice as affected by high-intensity pulsed electric fields critical parameters. Journal of Agricultural and Food Chemistry 55, 9036–9042.

Odriozola-Serrano, I., Hernández-Jover, T., Martín-Belloso, O., 2007b. Comparative evaluation of UV–HPLC methods and reducing agents to determine Vitamin C in fruits. Food Chemistry 105, 1151–1158.

Odriozola-Serrano, I., Soliva-Fortuny, R., Martín-Belloso, O., 2008. Changes of health-related compounds throughout cold storage of tomato juice stabilized by thermal or high intensity pulsed electric field treatments. Innovative Food Science and Emerging Technologies. doi:10.1016/j.ifset.2007.07.009.

Palou, E., Lopezmalo, A., Argaiz, A., Welti, J., 1994. The use of Pelegs equation to model osmotic concentration of papaya. Drying Technology 12, 965–978.

Peleg, M., 1988. An empirical model for the description of moisture sorption curves. Journal of Food Science 53, 1216–1219.

Rodrigo, D., Martínez, A., Harte, F., Barbosa-Cánovas, G.V., Rodrigo, M., 2001. Study of inactivation *Lactobacillus plantarum* in orange-carrot juice by means of pulsed electric fields. Journal of Food Protection 64, 259–263.

Rodrigo, D., Barbosa-Cánovas, G.V., Martínez, A., Rodrigo, M., 2003. Pectin methyl esterase and natural microflora of fresh mixed orange and carrot juice treated with pulsed electric fields. Journal of Food Protection 66, 2336–2342.

Ross, T., 1996. Indices for performance evaluation of predictive models in food microbiology. Journal of Applied Bacteriology 81, 501–508.

Sampedro, F., Rivas, A., Rodrigo, D., Martínez, A., Rodrigo, M., 2006. Effect of temperature and substrate on Pef inactivation of *Lactobacillus plantarum* in an orange juice–milk beverage. European Food Research and Technology 223, 30–34.

Soliva-Fortuny, R., Bendicho-Porta, S., Martín-Belloso, O., 2006. Modeling high-intensity pulsed electric fields inactivation of a lipase from *Pseudomonas fluoresecens*. Journal of Dairy Science 89, 4096–4104.

Torregrosa, F., Cortés, C., Esteve, M.J., Frígola, A., 2005. Effect of high-intensity pulsed electric fields processing and conventional heat treatment on orange-carrot juice carotenoids. Journal of Agricultural and Food Chemistry 53, 9519–9525.

Torregrosa, F., Esteve, M.J., Frígola, A., Cortés, C., 2006. Ascorbic acid stability during refrigerated storage of orange-carrot juice treated by high pulsed electric field and comparison with pasteurized juice. Journal of Food Engineering 73, 339–345.

Turhan, M., Sayar, S., Gunasekaran, S., 2002. Application of Peleg model to study water absorption in chickpea during soaking. Journal of Food Engineering 53, 153–159.

Vieira, M.C., Teixeira, A.A., Silva, C.L.M., 2000. Mathematical modeling of the thermal degradation kinetics of vitamin C in cupuaçu (*Theobroma grandiflorum*) nectar. Journal of Food Engineering 43, 1–7.

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.D., Xu, S.Y., 2007. Degradation kinetics of anthocyanins in blackberry juice and concentrate. Journal of Food Engineering 82, 271–275.

Willcox, J.K., Catignani, G.L., Lazarus, S., 2003. Tomatoes and cardiovascular health. Critical Reviews in Food Science and Nutrition 43, 1–18.