

Kinetic modelling of the degradation of quality of osmo-dehydrofrozen tomatoes during storage

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Received 15 August 2005; accepted 26 May 2006

Abstract

Tomato slices were submitted to osmotic pretreatment in a high DE maltodextrin syrup and were subsequently frozen. The objective was to evaluate the quality stabilisation of the osmo-dehydrofrozen samples during their frozen storage over a wide temperature range from -5 to -20 °C. Colour change, total lycopene content and vitamin C (L-ascorbic acid) loss were kinetically studied, and their temperature dependence was modelled by the Arrhenius equation. Dehydrofrozen samples exhibited significantly improved stability, with the rates of colour change, total lycopene and L-ascorbic acid loss being reduced by up to 64% for osmotically pretreated tomatoes, compared to the untreated samples.

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Keywords: Osmotic dehydration; Freezing; Tomatoes; Colour; Lycopene; Vitamin C

1. Introduction

Tomato is a popular vegetable with an exceptional healthy image as a primary source of vitamins and antioxidant components. It is consumed fresh in many forms but is not suitable for traditional freezing, due to considerable texture degradation, colour alteration and nutritional loss during the process and subsequent frozen storage (Abushita, Hebshi, Daood, & Biacs, 1997).

A prefreezing treatment can help to reduce the rate of quality loss, improving product stability during transport, handling and storage. Osmotic removal of water without phase change (Barbanti, Mastrocola, & Severini, 1994) can be an effective pretreatment in combined preservation techniques (Bolin & Huxsoll, 1993; Crowe, Clegg, & Crowe, 1998; Torreggiani, 1995; Torreggiani & Bertolo, 2001). As the cell wall of fruits and vegetables is not completely selective, the water flow outside the cell is accompa-

nied by the simultaneous counter-diffusion of solutes from the concentrated solution into the tissue (Kowalska & Lenart, 2001). The reduction in water content during osmotic treatment reduces the amount of water to be frozen (Li & Sun, 2002), lowers the freezing point, minimising the refrigeration load during freezing (Huxsoll, 1982), and the cost of subsequent packaging, distribution and storage. The tissue modification owing to water reduction and solids uptake leads to an increase in the value of the glass transition temperature (Brake & Fennema, 1999; Del Valle, Aranquiz, & Leon, 1998; Forni, Sormani, Scalise, & Torreggiani, 1997; Torreggiani et al., 1999) and could stabilise the frozen food quality, especially when correct temperatures are applied.

Several parameters, such as the cultivar used, the temperature of the process, the composition and the concentration of the osmotic agents in the osmotic solution, the specific characteristics of the food and the mixing parameters, influence significantly the osmotic dehydration process. A number of publications have described the role of these factors not only on mass exchange (Beristain,

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Azuara, Cortes, & Garcia, 1990; Conway, Castaigne, Picard, & Vovan, 1983; Cunha, Oliveira, Aboim, Frias, & Pinheiro-Torres, 2001; Kaymak-Ertekin & Cakaloz, 1996; Lazarides, Gekas, & Mavroudis, 1997; Rastogi & Raghavarao, 1994), but also on the quality of the final, dehydro-frozen products (Chiralt et al., 2001; Forni et al., 1997; Torreggiani et al., 1999; Tregunno & Goff, 1996). The quality of products, in most cases, is assessed at controlled, low temperatures, representative of nominal frozen conditions (e.g. at -18 , -20 and -30 °C) and at distinct storage periods (e.g., at the beginning, middle and end of their commercial shelf-life), not allowing for a complete kinetic analysis, across the whole freezing range of practical interest. There is need for a more systematic kinetic modelling approach of product quality degradation, using characteristic indices such as vitamin C, colour, chlorophyll content, and selected sensory parameters (Giannakourou & Taoukis, 2003).

Among these parameters, vitamin C, a valuable nutrient and antioxidant, is a well-established measure of frozen products degradation. During processing, distribution, and storage of frozen vegetables, ascorbic acid oxidizes to dehydroascorbic acid, which is irreversibly hydrolysed to 2,3-diketogulonic acid, which possesses no vitamin C activity. This oxidation is enhanced by temperature increases during frozen storage. The retention of ascorbic acid in frozen products is thus strongly dependent on their temperature history (Favell, 1998).

Colour is an important quality index for the food industry, and specifically for the tomato industry. Chlorophyll and carotenoids are responsible for the colour of tomatoes. In the early stages of development the chlorophyll imparts a green colour, and when the tomato starts the ripening process, the chlorophyll is degraded and carotenoids are synthesized (Hobson & Davies, 1971). Colour changes during frozen storage have been reported in some high-carotenoid foods, including tomato and its products. The typical colour change during storage was characterised as a decrease of the red character, an increase of the yellow character, and simultaneous lightening of the colour (Urbanyi & Horti, 1989).

Lycopene, the principal pigment in tomatoes, also acts as an antioxidant, by quenching free radicals during normal metabolism and may deactivate DNA chain-breaking agents that are implicated in some cancers (Sies & Stahl, 1998). A number of epidemiological studies have suggested the positive health benefits of lycopene (Omoni & Aluko, 2005). Lycopene can be considered a valuable quality index for tomato products. Being highly unsaturated, it is susceptible to oxidation and other chemical changes during processing and storage. The quantities of carotenoids, and lycopene, are diminished as a function of frozen storage time.

The objective of this work was the systematic kinetic study of the quality loss of frozen tomatoes, untreated (unblanched and blanched) and pretreated with an osmotic agent. Quality deterioration over the whole temperature

range of practical interest (-5 to -20 °C) was measured. The aim was to study the effect of the osmotic pretreatment on the shelf life of frozen tomato.

2. Materials and methods

2.1. Materials

Fresh tomatoes, grown in Crete for industrial use (hybrid: Noa), were obtained directly from a selected grower and transported to the laboratory within 24 h of harvesting. Tomatoes were sorted and sliced (to an average thickness of 6 mm) and each slice was longitudinally cut into halves. Part of the tomatoes was blanched by direct immersion of samples in hot water at 80 °C for 80 s, to ensure enzyme inactivation.

2.2. Osmotic pretreatment

Tomatoes were osmodehydrated in 56.5% (w/w) syrup of a high dextrose equivalent (DE) maltodextrin (Glucidex® (IT47, Lestrem, France; HDEM). The selection of HDEM was based on a previous comparative study of osmotic agents (Dermesonlouglou, Giannakourou, & Taoukis, 2003, 2004). HDEM led to the optimum mass exchange (water loss and solids gain) and sensory characteristics of the final product. The high concentration of osmotic solution followed similar practice reported in the literature (Gianotti, Sacchetti, Guerzoni, & Dalla Rosa, 2001; Kaymak-Ertekin & Cakaloz, 1996; Lenart & Flink, 1984; Lerici, Pinnavaia, Dalla Rosa, & Bartolucci, 1985; Tregunno & Goff, 1996). NaCl (3.5% w/w) and CaCl₂ (1.5% w/w) were also added for texture reinforcement purposes. Small additions of NaCl to the osmotic solution have been shown to increase the driving force of the process and also attenuate the sweetness of fruit (Adambounou, Castaigne, & Dillon, 1983; Lerici et al., 1985). Calcium chloride is used to minimise tissue damage during processing by interaction with pectins and other cellular wall components, which reinforces the mechanical properties of the plant cellular matrix (Gras, Vidal, Betoret, Chiralt, & Fito, 2003; Izumi & Wtada, 1995). Osmodehydration was conducted at 35 °C for 1 h, conditions selected after preliminary tests. The tomato to syrup ratio was 1:5 (w/w).

Water loss (WL) and solids gain (SG) after time t of each osmotic process, were calculated according to the following equations (Panagiotou, Karathanos, & Maroulis, 1999):

$$WL = \frac{(M_0 - m_0) - (M - m)}{m_0} \quad (1)$$

$$SG = \frac{m - m_0}{m_0} \quad (2)$$

where M_0 is the initial mass of tomatoes before osmotic treatment, M is the mass of tomatoes after time t of osmotic treatment, m is the dry mass of tomatoes after time t of

osmotic treatment and m_0 is the dry mass of tomatoes before osmotic treatment.

2.3. Freezing

Osmodehydrated tomatoes, as well as untreated (unblanched and blanched) products, were rapidly frozen at $-40\text{ }^\circ\text{C}$ for 24 h (Sanyo MIR 553, Sanyo Electric Co., Ora-Gun, Gunma, Japan), packed in a laminate film of 20 μm bio-oriented polypropylene (BOPP)/48 μm polyethylene (PE) (with a water vapour transmission rate (WVTR) $< 6\text{ g/m}^2$ per day), and kept at $-40\text{ }^\circ\text{C}$ for a short period of time before being distributed to temperature controlled cabinets.

2.4. Shelf life kinetic study

Packages of untreated (unblanched and blanched) samples and samples pretreated with the osmotic agent were stored in temperature controlled cabinets (Sanyo MIR 153, 253 and 553, Sanyo Electric Co., Japan) at constant temperatures (from -5 to $-20\text{ }^\circ\text{C}$), constantly monitored by type T thermocouples and a multichannel data logger (CR10X, Campbell Scientific, Leicestershire, UK). Samples were obtained at appropriate time intervals for each storage temperature, based on ASLT (Accelerated Shelf Life Testing) methodology (Taoukis, Labuza, & Saguy, 1997), and a rough estimate of expected temperature dependence of L-ascorbic acid loss and colour change rate, based on previous studies (Dermesonlouoglou et al., 2003, Dermesonlouoglou, Giannakourou, & Taoukis, 2004). Measurements of the quality indices of all products, were conducted at appropriate time intervals, in order to kinetically model their rate of change.

Moisture content, water activity (a_w) and pH of the osmodehydrofrozen and conventionally frozen samples were measured. Moisture content was determined by drying at $110\text{ }^\circ\text{C}$ for 24 h (WTB Binder 7200, Type E53, Tuttlingen, Germany). Sample water activity was determined using a hygroscope (Rotronic AG, AM3+AwVD, Bassersdorf, Switzerland) at $25\text{ }^\circ\text{C}$. Soluble solids content ($^\circ\text{Brix}$) was measured with an Atago hand refractometer (Atago Co., Osaka, Japan).

2.5. Physicochemical analyses

2.5.1. Colour measurement

Quantification of the colour change was based on measurement of CIELab values (CIE, 1978) with a CR-200 Minolta Chromameter[®] (Minolta Co., Chuo-Ku, Osaka, Japan) with an 8 mm measuring area. A standard white plate (Calibration plate CR-200, $L = 97.50$, $a = -0.31$, $b = -3.83$) was used to standardise the instrument under “C” illuminant condition, according to the CIE (Commission International de l’Eclairage). At pre-determined times of isothermal storage, according to

the experimental design, measurements were conducted on the same internal part of ten tomato samples, in order to obtain consistent information. Tomatoes were coded (from 1 to 10), placed in appropriately designed sealed packages and three replicates of each measurement were conducted.

2.5.2. Lycopene determination

Lycopene was determined using a high performance liquid chromatography method (HPLC) proposed by Sadler, Davis, & Dezman (1990). A 5 g sample of homogenised tomato was accurately weighed into a 125-ml flask. Flasks were tightly and thoroughly wrapped in aluminum foil to exclude light. Hexane–acetone–ethanol (2:1:1, 100 ml) was added to the flask, which was stoppered and mechanically agitated. Double distilled water (15 ml) was added, followed by another 5 min agitation. The solution subsequently separated into distinct polar (65 ml) and non-polar (50 ml) layers. The lycopene-bearing upper hexane layer was filtered through a 0.22 μm filter (Chromafil PET-20/25, Macherey–Nagel, Diiren, Germany) and then injected into the chromatographic column. An HP Series 1100 HPLC (quaternary pump, vacuum degasser, a Rheodyne 20 μl injection loop and a Diode Array Detector, controlled by HPChemStation software; Hewlett-Packard); was used with a Hypersil ODS column (250 \times 4.6 mm) of particle size 5 μm . The mobile phase was methanol:tetrahydrofuran:water (Merck, Darmstadt, Germany) (67:27:6) at a flow rate of 2 ml/min with detection at 472 nm, calibrated by external standard method. All measurements were conducted in duplicate.

2.5.3. Texture measurement

Texture measurements were conducted by means of a texture analyser (TA-XT2i; Stable Microsystems, Godalming, Surrey, UK), and a TPA (texture profile analysis) test was carried out. Using a blade, samples were cut at a fixed rate and depth (3 mm). Texture characteristics such as firmness, elasticity, chewiness and cohesiveness were calculated.

2.5.4. L-Ascorbic acid determination

L-Ascorbic acid (Vitamin C) was determined by HPLC (Giannakourou & Taoukis, 2002). Homogenate (5 g) were mechanically stirred in 15 ml of a 4.5% solution of metaphosphoric acid for 15 min. The mixture was vacuum filtered and diluted with HPLC grade water the total final volume was measured and an aliquot was filtered through a 0.45 μm filter (Chromafil PVDF-45/25, Macherey–Nagel, Germany), prior to injection into the chromatographic column. The same HPLC instrument as in the lycopene analysis was used. The mobile phase was HPLC grade water with metaphosphoric acid (pH 2.2) at a flow rate of 0.5 ml/min with detection at 245 nm, calibrated by external standard method. All measurements were conducted in duplicate.

2.5.5. Sensory evaluation tests

Sensory evaluation was carried out by a panel of five trained testers. The panel directly evaluated the samples based on a 9-point scale of preference grading.

2.6. Data analysis

The results of quality measurements were plotted *versus* time for all temperatures studied. The temperature dependence of deterioration rate k was then modelled using the Arrhenius equation (Eq. (3)):

$$\ln k = \ln k_{\text{ref}} - \left(\frac{E_A}{R}\right) \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right) \quad (3)$$

where k_{ref} is the rate constant of the degradation of the respective quality index at the reference temperature, T_{ref} , E_A is the activation energy of the studied action and R is the universal gas constant.

2.7. Statistical analysis

Analysis of variance (ANOVA) and Tukey multiple range tests ($\alpha = 0.05$) were used to determine statistically significant differences (STATISTICA®, StatSoft, Tulsa, OK) between the different storage temperatures and treatments, concerning the rates of colour change, total lycopene loss and L-ascorbic loss.

3. Results and discussion

3.1. Osmotic pretreatment

The water (WC), total solids (TS) and total soluble solids (TSS) contents determined in untreated tomatoes and tomatoes treated in the osmotic solution are shown in Table 1. Total solids and soluble solids content increased after pretreatment, with a corresponding decrease in the moisture content. Application of a blanching pretreatment caused an increase of water and loss of solids, due to heat-induced chemical reactions, leading to degradation of cell constituents (Del Valle et al., 1998). The osmotically pretreated samples exhibited 8% water loss and 2% solids gain.

Table 1 shows that osmotic pretreatment substantially lowered the water activity of tomato samples. The osmotic dehydration allowed a reduction of the water activity down to a level of 0.97, reducing lower moisture giving less sensitive products with sensorial characteristics very similar

to those of the fresh product, maintaining colour, texture and aroma.

The freezing and storage of frozen tomato samples at the temperatures studied did not significantly change the level of dry matter, soluble solids, pH or water activity. Statistically significant changes were observed in the contents of lycopene, vitamin C, colour and texture, and sensory properties.

3.2. Colour change

For frozen tomatoes, the chroma change, expressed as shown in Eq. (4) was found to be adequately modelled by a pseudo zero-order reaction.

$$DC = k_{\text{col}} * t = \sqrt{(a - a_0)^2 + (b - b_0)^2} \quad (4)$$

where DC is the chroma change, a , a_0 and b , b_0 the values of a and b colour parameters at storage times t and t_0 , k_{col} is the reaction rate which is an Arrhenius function of temperature. Colour change for untreated (unblanched and blanched) and pretreated tomatoes at two temperatures studied (-5 and -15 °C) is shown in Fig. 1a and b.

From the plots of DC versus time (Fig. 1a and b), the corresponding degradation rates (k_{col}) were calculated, showing the protection provided by the application of the osmotic procedure prior to freezing. For instance, the rate of chroma change for untreated, blanched and pretreated with HDEM tomato samples at -15 °C were 0.102, 0.151 and 0.076 per day, respectively.

Temperature dependence of the rates of colour degradation was adequately described by Arrhenius kinetics across the whole temperature range studied (Fig. 2), and the values of the activation energies were calculated in (kJ/mol) as 45.22 ($R^2 = 0.994$), 23.56 ($R^2 = 0.949$) and 37.47 ($R^2 = 0.931$) for the untreated, blanched and pretreated with the HDEM syrup tomato samples, respectively.

Statistical analysis (ANOVA), as well as the Tukey HSD test ($p = 0.05$) were conducted to assess the impact of different storage temperatures and treatments on colour degradation rate. Based on the results, both have a significant effect on the rate of tomato colour degradation.

3.3. Lycopene loss

During subsequent frozen storage, the average retention of total lycopene content was systematically measured across the whole temperature range of the experimental

Table 1
Water content (WC: g water/g initial sample weight), total solid content (TS: g solids/g initial sample weight), total soluble solids (TSS: °Brix), pH, water loss (WL), solid gain (SG) and water activity (a_w) of tomato samples before and after blanching and osmotic pretreatment (mean of three readings \pm standard deviation)

	WC	TS	TSS	pH	WL	SG	a_w
Untreated samples	0.949 \pm 0.007	0.051 \pm 0.007	4.67 \pm 0.40	4.13 \pm 0.097	–	–	0.990 \pm 0.006
After blanching	0.963 \pm 0.007	0.037 \pm 0.007	5.00 \pm 0.50	3.97 \pm 0.090	–	–	0.987 \pm 0.009
After osmotic treatment	0.857 \pm 0.008	0.143 \pm 0.008	11.00 \pm 0.75	3.88 \pm 0.080	8.42 \pm 0.284	1.80 \pm 0.110	0.973 \pm 0.006

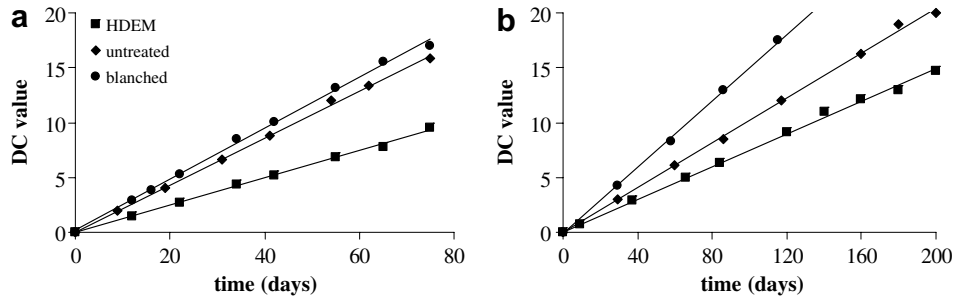


Fig. 1. Chroma change in frozen tomatoes, untreated, blanched and osmotically pretreated at storage temperatures: (a) $-5\text{ }^{\circ}\text{C}$ and (b) $-15\text{ }^{\circ}\text{C}$.

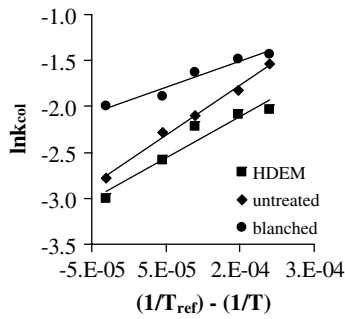


Fig. 2. Arrhenius plot of the chroma change for all samples ($T_{\text{ref}} = -18\text{ }^{\circ}\text{C}$, $k_{\text{ref,untreated}} = 0.075\text{ day}^{-1}$, $k_{\text{ref,blanching}} = 0.144\text{ day}^{-1}$, $k_{\text{ref,HDEM}} = 0.062\text{ day}^{-1}$).

design, and was expressed relative to [lyc] to the concentration of lycopene at the beginning of the experiment (in mg per 100 g of sample). Lycopene loss was adequately described by an apparent first order reaction (Eq. (5)), as is representatively shown in Fig. 3a and b, for untreated (unblanched and blanched) conventionally frozen tomatoes, and for tomatoes pretreated in the HDEM syrup, at $35\text{ }^{\circ}\text{C}$ for 1 h, and stored at two temperatures, -5 and $-15\text{ }^{\circ}\text{C}$:

$$\frac{C_{\text{lyc}}}{C_{\text{lyc}_0}} = \exp(-k_{\text{lyc}}t) \quad \ln\left[\frac{C_{\text{lyc}}}{C_{\text{lyc}_0}}\right] = -k_{\text{lyc}}t \quad (5)$$

where k_{lyc} is the apparent reaction rate of lycopene, estimated by a least squares regression. For all pretreated samples the estimated rate of lycopene loss (k_{lyc}) had lower values, compared to the corresponding rates for the untreated and blanched samples.

It is generally proposed that freezing does not prevent the degradation of carotenoids. According to Biacs & Wissgott (1997) the losses are above all due to the activity of enzymes, particularly in an oxygen-containing environment. In the present study, after 12 months of storage at $-20\text{ }^{\circ}\text{C}$, losses of lycopene reached 59%. In the literature lower losses, of about 48%, were reported (Lisiewska & Kmiecik, 2000). The natural occurrence of enzymes such as peroxidase, catalase and lipase in the tomato contribute to a decrease in its sensory properties and loss of nutrients (Begliomini, Montedoro, Servili, Petruccioli, & Federici, 1995; Hemeda & Klein, 1990; Williams, Lim, Chen, Pangborn, & Whitaker, 1986). Peroxidase especially was classified among the most important enzymes in tomato processing (Bizzari, Andreotti, & Massini, 1981), although it was observed that the biochemical activities of enzymes rapidly declined in tomato fruits. Moreover, Prestamo & Manzano (1993) determined an inhibitory effect of ascorbic acid on peroxidase activity in the tomato.

The reduction of the total lycopene content was more pronounced for the blanched frozen tomato samples. For instance, the rate of total lycopene loss (in mg per 100 g of sample) for blanched samples at $-15\text{ }^{\circ}\text{C}$ was 0.250 per day compared to 0.182 per day for the pretreated samples. A possible explanation is that heat treatment during blanching disintegrates the plant tissue and destroys cellular compartments, increasing decomposition (Mayer-Miebach & Spieß, 2003).

Processing conditions such as high temperature, long processing time, light and oxygen have been shown to have effects on lycopene degradation. According to Shi, Le Maguer, Kakuda, Liptay, & Niekamp (1999), in the

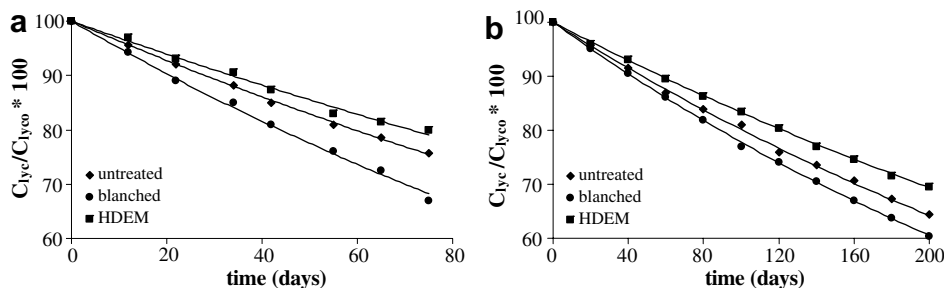


Fig. 3. Total lycopene loss in frozen tomatoes, untreated, blanched and osmotically pretreated at storage temperatures: (a) $-5\text{ }^{\circ}\text{C}$ and (b) $-15\text{ }^{\circ}\text{C}$.

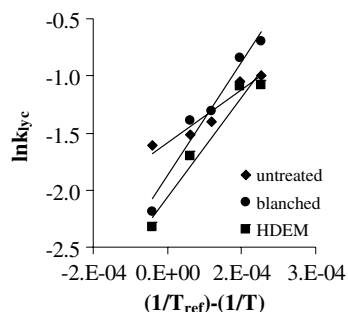


Fig. 4. Arrhenius plot of total lycopene loss for all samples ($T_{\text{ref}} = -18\text{ }^{\circ}\text{C}$, $k_{\text{ref,untreated}} = 0.205\text{ day}^{-1}$, $k_{\text{ref,blanched}} = 0.155\text{ day}^{-1}$, $k_{\text{ref,HDEM}} = 0.127\text{ day}^{-1}$).

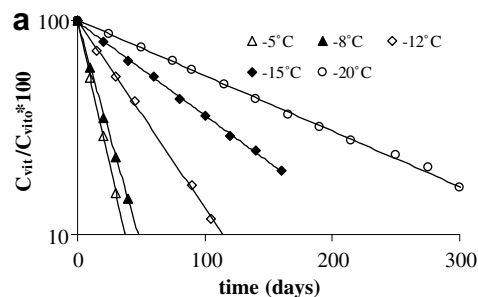
osmotic treatment, the predominating mechanism is isomerisation of lycopene. A possible explanation of this result is that sugar enters the tomato matrix and strengthens the binding force of lycopene in the tomato matrix. Osmotic solution (sugar) remaining on the surface layer of the tomato retards oxygen penetration and oxidation of lycopene. The osmotic treatment reduced lycopene losses in comparison to the other freezing methods, from 5% to 35%, approximately.

Temperature dependence of the rates of total lycopene loss was adequately described by Arrhenius kinetics over the whole temperature range studied (Fig. 4), and the values of the activation energies in the different systems were calculated in kJ/mol as 25.55 ($R^2 = 0.918$), 54.85 ($R^2 = 0.959$) and 48.49 ($R^2 = 0.960$), for the untreated, blanched and pretreated samples, respectively.

3.4. Texture alteration

Texture measurements could not be modelled. Parameters such as firmness and cohesiveness of all osmotically pretreated samples were from 39% to 67% higher than the respective untreated samples when measured thawed. Chewiness and elasticity did not differ significantly between treatments. No consistent time-temperature correlation was obtainable for the texture parameters during storage.

In literature, it was reported that freezing and frozen storage caused deterioration of the texture of tomatoes.



Textural properties are intimately associated with the cellular structure and pectic composition. Fuchigami, Miyazaki, & Hyakumoto (1995) observed that the inferior texture of frozen tomatoes was accompanied by a decrease in the content of pectic compounds. Lisiewska & Kmiecik (2000) also reported that the level of protopectins and pectins were significantly reduced by the freezing process itself and during subsequent frozen storage of tomato tissue. It is known that the desirability of the tomato is mainly attributed to its unique texture and palatability, which can easily be damaged during processing (Barrett, Garcia, & Wayne, 1998).

3.5. L-Ascorbic acid loss

L-Ascorbic loss was adequately described by an apparent first order reaction (Eq. (6)), as is representatively shown in Fig. 5a and b, for untreated samples and samples pretreated with syrup, at 35 °C for 1 h:

$$\frac{[\text{asc}]}{[\text{asc}]_{t_0}} = e^{-k_{\text{asc}} t} \quad (6)$$

where k_{asc} is the apparent reaction rate of L-ascorbic loss, estimated by a least square regression, and $[\text{asc}]$ is the concentration of L-ascorbic acid in 100 g of product (untreated, blanched or osmotically pretreated). For all pretreated samples, the estimated rate of L-ascorbic loss

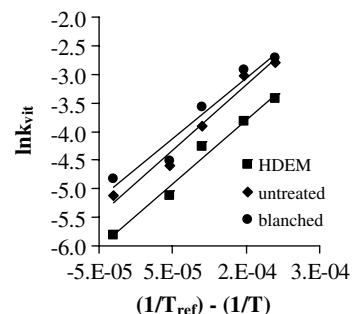


Fig. 6. Arrhenius plot of vitamin C loss for all samples ($T_{\text{ref}} = -18\text{ }^{\circ}\text{C}$, $k_{\text{ref,untreated}} = 0.008\text{ day}^{-1}$, $k_{\text{ref,blanched}} = 0.010\text{ day}^{-1}$, $k_{\text{ref,HDEM}} = 0.004\text{ day}^{-1}$).

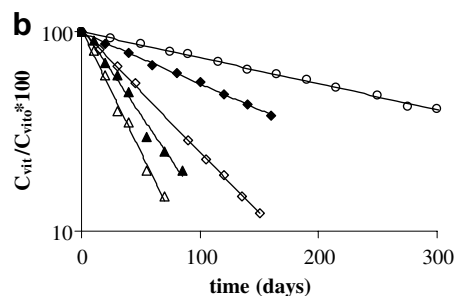


Fig. 5. Change of ascorbic acid content of frozen tomatoes stored at different temperatures: (a) untreated and (b) osmotically pretreated samples with HDEM.

Table 2

Results of sensory evaluation of thawed tomato samples, untreated (UT), blanched (BL) and pretreated with HDEM (OT), stored for 0, 3, 6 and 12 months at -20°C , on a 9-point hedonic scale (mean values)

Quality factor	Before freezing	After freezing		Storage time in months									
				3			6			12			
				UT	BL	OT	UT	BL	OT	UT	BL	OT	
Colour, NS	9.0	6.1	6.9	7.0	4.9	4.3	6.5	4.8	4.5	4.8	3.5	3.5	3.8
Texture, NS	9.0	6.1	6.0	7.0	4.3	3.0	7.3	2.5	2.3	4.0	2.5	2.0	3.5
Taste, NS	9.0	5.5	5.4	7.5	3.3	3.9	5.8	2.8	2.5	4.0	2.5	2.0	3.2
Overall acceptance, NS	9.0	5.9	6.1	7.2	4.1	3.7	6.5	3.3	3.1	4.3	3.0	2.5	3.8

The effect of storage time (0, 3, 6 and 12 months) for all treatments was significant, $F > F_{\text{crit}}$. The effect of treatment (UT, blanching and osmotic treatment) for each storage time was also significant, $F > F_{\text{crit}}$. The effect of storage time and treatment on quality factors (colour, texture, taste and overall acceptance) was not significant, $F < F_{\text{crit}}$.

had lower values, compared to the corresponding rates for the untreated samples.

For all different storage temperatures, L-ascorbic acid is significantly more stable in the modified matrix of pretreated samples compared to that of untreated and blanched samples. Temperature dependence of the rates of L-ascorbic acid loss was adequately described by Arrhenius kinetics over the whole temperature range studied (Fig. 6), and the values of the activation energies in the different systems were calculated (in kJ/mol) as 94.22 ($R^2 = 0.971$), 87.61 ($R^2 = 0.946$), 92.59 ($R^2 = 0.982$), for the untreated, blanched and pretreated samples, respectively. The activation energy values calculated by the Arrhenius equation give a useful measure of temperature dependence comparable to the ample information existing from kinetic modelling of frozen and unfrozen foods (Giannakourou & Taoukis, 2003).

The empirical application of the Arrhenius model can be of significant practical value for shelf life modelling and predictions. Despite questions regarding the theoretical validity of the Arrhenius equation in specific frozen ranges of interest, cautious application serves as a useful practical tool for shelf life calculations and predictions. For instance, if the shelf life calculation referred merely to nutritional (50% loss of vitamin C) degradation, the values of shelf life for untreated and osmotically pretreated frozen tomato are calculated as 126 and 231 days at -20°C . Vitamin C is an important quality index, but the fact that commercial and consumer acceptability are mainly based on sensory quality criteria, such as colour, texture, taste and flavour should not be overlooked.

3.6. Sensory evaluation tests

Sensory evaluation tests showed that colour, texture, taste and overall acceptance of all osmo-dehydrofrozen tomatoes were significantly improved, when compared to the respective quality features of conventionally frozen, both blanched and unblanched samples (Table 2). Directly, after the freezing process, at zero time of storage at -20°C , statistical differentiation was observed in the organoleptic quality of the frozen tomatoes (Table 2). This confirmed

the initial observation that colour and tissue integrity are well-retained in osmotically pretreated samples. During frozen storage, untreated samples suffered from texture and taste deterioration. For pretreated samples, taste was in most cases judged as 'pleasant and acceptable' despite differing from the traditional "tomato" organoleptic perception. In Table 2, scores for colour, texture (consistency), taste and overall acceptance (which includes the appearance, consistency, taste and flavour) are demonstrated for all of the tomato samples, stored for 0, 3, 6 and 12 months at -20°C . Statistical analysis did not show significant differences between different quality attributes (Table 2).

4. Conclusions

The objective of this work was to evaluate the effect of pretreatment with the selected osmotic agent on the quality and sensory characteristics of frozen tomatoes. Pretreated frozen tomatoes were found to have improved quality stability during subsequent frozen storage. Colour, total lycopene and L-ascorbic acid showed a significantly increased retention in the dehydrofrozen samples, compared to the untreated (unblanched and blanched), conventionally frozen ones, over the whole temperature range of potential frozen storage studied. For example, after 12 months of storage at -20°C , the dehydrofrozen tomatoes, compared with the conventional frozen samples, unblanched and blanched, contained 20–28% more vitamin C, and 14–35% more lycopene. Colour differences were perceptible between untreated and pretreated samples. The osmotic pretreatment led to thawed tomato samples with the most desirable sensory characteristics, such as attractive appearance (bright red colour, preservation of shape), good texture (firm, not soft), and pleasant taste. The temperature dependence of colour change, lycopene loss and vitamin C loss was modelled with the Arrhenius equation. The activation energy calculated by the equation could be applied in the prediction of shelf life of frozen tomato tissue. The pretreated samples could be used as food ingredients in products such as pizzas and ready to eat frozen meals. The use of osmodehydrated tomatoes in vegetable salads is also possible.

Acknowledgement

Work co-funded by national funds (General Secretariat of Research & Technology) and the European Commission/European Social Fund (Project PENED2003-03ED834).

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