Preparation of High-Consistency Diced Tomatoes by Immersion in Calcifying Solutions. A Pilot Plant Study

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A continuous process to improve the consistency of diced tomatoes based on product immersion in calcifying solutions was developed. The process efficacy was evaluated by a pilot plant built for this purpose. The diced tomatoes were immersed in a saline solution containing tomato serum, sodium, and calcium chloride. The pH of the calcifying solution was held constant through the process to a value close to neutrality by a device for the automatic addition of sodium hydroxide to the calcifying solution. The results showed a substantial consistency increase in the product obtained by immersion with respect to the product obtained by direct calcium addition. Moreover, the immersion product, consistency being equal, shows lower calcium content. This new technology was also employed for the preparation of diced tomatoes packaged aseptically. The results showed that the consistency increment was about 200% more with respect to the product obtained with the traditional technology of aseptic packaging, whereas the other analytical parameters were very similar.

Keywords: *Tomato; diced tomatoes; calcification; firmness*

INTRODUCTION

Many recent studies have pointed out that the softening of fruit and vegetables in the course of ripening and postharvest handling could be ascribed to the degradation of cell wall polysaccharides, primarily of pectic substances, in which several hydrolases, including polygalacturonase (PG) and pectin methylesterase (PME), are involved (Fisher and Bennet, 1991). Particularly important is the cleavage of the methyl ester groups from the pectin and the consequent calcium binding to carboxylate groups that form interionic calcium bridges between adjacent pectin chains (Carpita and Gibeaout, 1993). These hydrolytic activities bring about pectin solubilization also, as a consequence of pectin molecular weight decrease and charge increase (Smith et al., 1990), along with the loss of neutral sugar residues, such as arabinosyl and galactosyl, from pectin side chains (Gross and Wallner, 1979).

In the case of peeled and diced tomatoes, the product softening is mainly due to the thermal stabilization process. In the food industry, the reduction of this effect is obtained with the addition of calcium chloride to tomato industrial products. This process, known as calcification, is largely employed for tomato products (whole, pulp, diced, etc.). Generally, if the process is correctly performed, better textured products are obtained which show a higher drained weight than the untreated products (Lopez and Schoenemann, 1971; Bellucci et al., 1975). Moreover, this process accounts for a noticeable pH decrease because the organic acids normally present in the product dissociate more as a consequence of calcium addition. This effect makes high thermal treatments on the product unnecessary (Bellucci et al., 1972; Floros et al., 1992).

From a technological point of view, the main obstacle in the production of whole peeled tomato products with a good consistency is the choice of the variety, i.e., choice of fruits with suitable characteristics. Instead, for sliced tomato products, besides the fruit characteristics, also important are the procedures such as slicing, draining, mixing, and, last but not least, the thermal stabilization of the product. In fact, especially for the thermal treatment employed during the aseptic processing and packaging, problems arise between the conflicting necessity of maintaining the textural features of the product and the thermal treatments at temperatures high enough to assure an effective sterilization (Lee, 1991; Yang and Swartzel, 1991; Taeymans et al., 1985). In this case, in fact, it is difficult to correctly estimate the thermal treatment required, because of the very variable product conditions such as pH, initial temperature, dimension of dice pieces, thermal conductivity, initial microbial contamination, etc. Therefore, there is the tendency to perform harsh treatments in which the product reaches temperatures higher than 108 °C and comes out at temperatures of 100−102 °C after about 7−9 min of treatment. These conditions can be varied on the basis of the ratio of juice/diced product, pH, and product consistency. However, this treatment guarantees the product stability more than its quality, especially regarding piece consistency and integrity (Leoni, 1993).

Calcium addition to these products favors the maintenance of the tissue integrity, inasmuch as, according to the egg-box model proposed by Grant et al. (1973), the formation of calcium pectates increases the rigidity of the middle lamella and cell wall. In particular, the egg-box model has often been utilized by many researchers to explain the consistency variation of food products that received treatments changing the degree of pectin methylation (Klein et al., 1995; Lurie and Klein, 1992).

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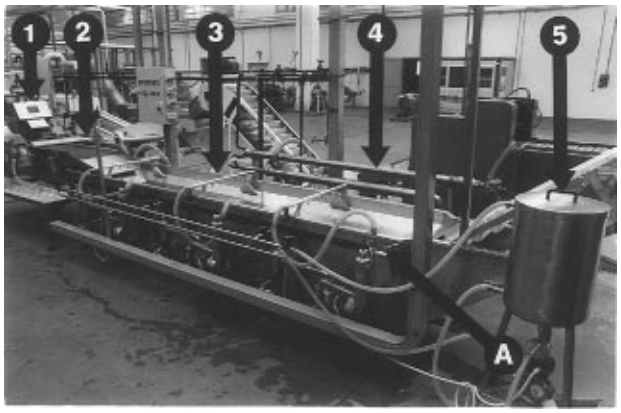

Figure 1. Partial view of the experimental plant employed for the continuous calcification process: (1) dicing unit; (2) drainage unit; (3) calcification pool; (4) thermal treatment unit, (5) sodium hydroxide dispenser unit, and (A) valve for the recirculation of calcifying solution through unit 4.

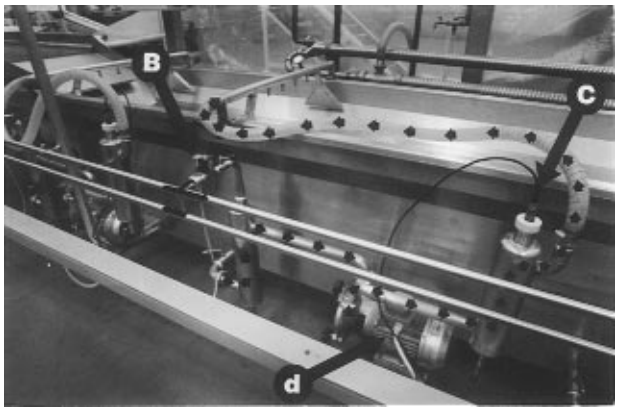

Figure 2. Partial view of the unit (5) for the dosage, distribution, and control of sodium hydroxide solution: (B) electric valve for the sodium hydroxide introduction into the pool, (C) pH probe, and (d) pump for the recirculation of calcifying solution. Thin forward arrows mark the sodium hydroxide flux direction and distribution; thick forward arrows mark the flux direction and distribution of calcifying solution in the pool (unit 3).

In this respect, particularly important is the activity of plant pectin methylesterase (PME) (Versteeg, 1979). This enzyme, in fact, attacks the pectin chain from the reducing end or close to free carboxyl groups and then proceeds linearly along the molecules. In this way, clusters of free carboxyl groups are formed which give to the pectin a high affinity for calcium ions (Krop and Pilnik, 1974; Kohn et al., 1983).

On the basis of these considerations, recently we explored the possibility of increasing the consistency of diced tomatoes, taking advantage of the deesterifying action of PME, endogenous and exogenous, on the pectic fractions of the product, in order to favor the cell wall structural rebuilding by the successive action of added calcium ions. The results showed that, by immersing diced tomatoes in calcifying solutions, at calcium ion concentrations of 200−800 mg/kg and at a pH close to neutrality, a noticeable increase of consistency occurred (Castaldo et al., 1995a). Moreover, the consistency increase was much more evident by adding to the calcifying solution tomato PME at a final concentration of 6−12 U/mL (Castaldo et al., 1995b). These results were explained mainly as a consequence of the synergic action of the endogenous and exogenous PME on the product calcification process, although this is certainly favored also by the calcium diffusion from the calcifying solution to the cell wall sites inside the product. The results relative to the calcium adsorbed to the products, as a consequence of the calcification process at a controlled pH, were surprising. These products, in fact, showed the same consistency but lower calcium content than diced tomatoes obtained with the traditional calcification process in which calcium was added directly. Therefore, we started a study to develop a continuous calcification process, performed at room temperature and a controlled pH, that can be utilized as an alternative to the traditional calcification procedure.

MATERIALS AND METHODS

Description of the Semi-Industrial Apparatus. A partial view of the plant employed for the studies on the continuous calcification process is depicted in Figure 1. The plant is essentially made of five units: the dicer (unit 1), two vibrating planes for the dice drainage (unit 2), a pool, with an augering device for the product transport, employed for the product calcification and three pumps for the solution recycling (unit 3), and a device for the thermal treatment of the solution in the pool (unit 4). This unit was composed of a tubular heat exchanger, of a system for the reduction of steam pressure, and of a successive plate heat exchanger (not shown in Figure 1) equipped with a glycolated water device for further solution cooling down to 25−28 °C. Finally, there was unit 5 for dosage, distribution, and control of sodium hydroxide solution. This unit was made of four electric valves, a 100 L reservoir, an electric pump (flow rate from 0 to 100 L/h), and three industrial process pH controllers (pH transmitter DO 9403T Delta Ohm) with preselected on/off switch function of the electric valves for the sodium hydroxide addition into the pool, equipped with three Hamilton (polylyte type) industrial electrodes. In Figure 2, the pH control units, the pH probes, and the electric valves of the hydroxide feeding circuit are shown.

The plant operations are based on batch trials previously made (Castaldo et al., 1995a,b). Briefly, the product (peeled tomatoes) was diced (unit 1), drained (unit 2), and then sent to the calcification pool (unit 3). Because of the product acidity (pH <4.6) and the residual PME activity that is still present on the product surface after the peeling treatment, the pH of the calcifying solution, set at 7.5, tends to become lower. The process conditions at this point are restored by the sodium hydroxide addition from unit 5. The product was in this way constantly maintained at the set pH value of 7.5 during the advancement in the pool by a mechanical system at constant speed. Afterward, the product was drained. Finally, part of the product was canned with addition of tomato juice at pH 3.9, and the other part was aseptically packaged in an industrial plant of the firm Doria SPA [Angri (SA), Italy].

Sample Preparations and Experimental Procedures. About 4 tons of tomatoes at full ripening stage were kindly supplied by the firms Doria SPA (Angri, Italy) and F.lli D'Acunzi SPA (Nocera sup., Italy).

Tomatoes were washed, sorted for integrity, steam-peeled, and then diced (1 × 1 × 1 cm) with a Bertuzzi California model dicer. Afterward, they were drained and processed. In all the experiments, the calcification pool was fed with diced tomatoes at a rate of 160 ± 10 kg/h. The dipping time was 5 min. At regular intervals of 1 h, 10 kg of product was withdrawn and canned in portions of 1 kg, for a total time of 8 h. Each can was prepared by adding 150 ± 3 g of juice with 5 ± 0.2 °Brix to 630 ± 3 g of canned product, . The juice was previously adjusted to pH 3.9 with 1 M citric acid. At the same time, 10 kg of diced and drained product not treated in the calcification pool was employed to prepare the reference samples. Part of the product was also employed to prepare samples with direct calcium addition utilizing as a reference the same product without calcium chloride addition. For the samples in which the calcium was added directly (220 mg of Ca^{2+}/kg), the quantity of juice to be added took into account the volume of added calcium chloride solution to maintain the same proportion between diced tomatoes and juice.

In order to verify the feasibility of the process, four series of experiments were performed.

In the first, the product, i.e., diced tomatoes, was dipped in the calcifying solution, at pH 7.5, made up with water in which calcium chloride, at a calcium ion concentration of 650 mg/L, and sodium chloride, at a sodium ion concentration of 50 mg/L, were dissolved. The sodium chloride was added inasmuch as PME is activated by sodium ions. The calcification process was conducted at room temperature (about 26 °C).

In the second experiment, the product was calcified in the same conditions as the first. The only difference was the continuous thermal treatment of the calcifying solution. This, in fact, was heated in a heat exchanger at 80 ± 3 °C. It was cooled in a successive step at about 45 °C, employing water as a cooling medium, and then in a plate exchanger at 26 ± 2 °C with a 50% glycol solution as the cooling medium.

In the third experiment, the calcifying solution was prepared using tomato serum instead of water. The solution was made by mixing tomato serum (obtained by centrifugation of tomato juice with a Pieralisi decanter) and water to a final optical refractometric residue of about 2.5 °Brix. To this solution were added calcium chloride and sodium chloride at the same concentration as above. The solution underwent the same thermal treatment of the second experiment. All the samples from the first three experiments were then canned and thermally stabilized in a water bath for 90 min at 100 °C. In the fourth experiment, the product was treated as in the third experiment, but instead of being canned, it was aseptically packaged and compared to the same product not calcified. The fourth experiment was made in the industrial plant of the Doria SPA firm at Angri (Salerno, Italy).

Analytical Determination. The analyses were made in duplicate after 45 days of storage. The following determinations were made on the canned product; pH, optical refractometric residue expressed as °Brix, drained weight, and reducing sugars with Fehling's method were determined according to the National Italian Standards (Ministero Dell'Agricoltura e delle Foreste, 1989), and molds were determined according to the HMC method (Howard, 1911). The calcium determination was performed after sulfonitric mineralization on 10 g of product with a Perkin-Elmer model 1100 atomic absorption spectrophotometer.

Texture Measurement. Texture modification of diced tomatoes was determined by measuring the products firmness with a universal traction−compression instrument (Instron model 4500) fitted with a Kramer cell. Three measurements were made on each preparation according to De Giorgi et al. (1994). The firmness is defined as the maximum force recorded during the compression.

Enzyme Activity Determination. Residual pectin methylesterase activity was determined according to Giovane et al. (1996). In brief, this highly sensitive method is based on an affinity chromatography technique which employs a resin-bound pectin methylesterase inhibitor, purified from kiwi (Balestrieri et al., 1990; Giovane et al., 1995), which selectively binds only that part of pectin methylesterase enzyme that could still be active after the stabilization thermal treatment. The active enzyme is eluted from the resin at alkaline pH and assayed with an automatic pH-stat (Crison model TT2050) in a thermostatted cell at 25 °C. Pectin (70% methylated) was used as a substrate in a 1% solution containing 0.15 M NaCl (pH 7.5), and 1−3 mL of PME sample in a final volume of 20 mL. The PME activity was expressed in units per milliliter of extract.

Product Color Determination. Color parameters *a*, *b*, *a*/*b*, and *L* were determined for the various samples after refining in a refiner with a hole diameter of 0.4 mm. The obtained puree was degassed, and the color was measured with a Tristimulus colorimeter model XL-805 from Gardner, reference tile ($L = 25.9$, $a = 28.5$, and $b = 13.1$).

Analyses on the Calcifying Solution. The analyses on the calcifying solution were: pH, optical refractometric residue, reducing sugars, mold and calcium. These analyses were performed with the same methods as above. D- and L-lactic acids were determined after concentration by lyophilization of 100 mL of calcifying solution. The residue was resuspended in 1 mL of water, and the lactic acids were determined with a kit from Boehringer, Mannheim. Ethanol was also determined with a kit from Boehringer, Mannheim.

RESULTS AND DISCUSSION

According to the egg-box model (Grant et al., 1973), the association between pectins with a low degree of methylation and calcium ions brings about the formation of polymeric structures with high reticulation. As a consequence, vegetable product containing pectins with a low degree of methylation, after treatments with calcium ions, shows higher consistency or, if it is fluid, a higher apparent viscosity (Van Buren, 1968, Van Buren, 1979; Guillou et al., 1992). It is possible in vegetable products to increase the content of low methylation pectins by acting on the factors that favor the deesterifying action of the PME. The most important of those factors is no doubt the pH. Many studies showed that the pH optimum of plant PME ranges between 7.5 and 9.0 (Giovane et al., 1990, 1994). However, in many vegetable products such as tomatoes, the pH value is consistently lower (3.5−5.0). Therefore, in these conditions, the endogenous PME does not work at the maximum speed. The immersion of the product in a solution at a pH close to neutrality presumably increases the efficacy of the PME action on the pectic fractions with the consequent formation of a higher production of free carboxylic groups which in the presence of calcium ions contribute to the structural reorganization of the pectic fractions.

Results obtained in a previous work (Castaldo et al., 1995a) showed that the immersion of diced tomatoes at pH 7.5 in solutions containing calcium ions at concentrations between 400 and 800 mg/L from 5 to 30 min gave an end product with high consistency and with a calcium content between 200 and 350 mg/kg of product (diced tomatoes and juice).

On the basis of these results and the above considerations, experiments were made in which the product contact time within the calcifying solution at pH 7.5 was 5 min and the calcium concentration of the calcifying solution 650 mg/L. This concentration value was chosen because the content of the calcium in the product after the immersion with a contact time of 5 min resulted in about 220−230 mg/kg, a value well below the law limits (Food and Drug Administration, 1991; European Union, 1986).

In Figure 3, which refers to experiment 1 (see Sample Preparations and Experimental Procedures), the mean values of calcium, °Brix, lactic acids, and ethanol determined on the solution employed for the diced tomato calcification during 8 h of process are reported. The results of Figure 3 show the values of the parameters most directly correlated with microbial growth during the process time, i.e., lactic acids and ethanol. Under the experimental conditions utilized, ethanol is produced at a rate of 0.62 mg L^{-1} h^{-1}. However, lactic acids are produced at a rate that is about twice that of ethanol (1.25 mg L^{-1} h^{-1}). As for mold content in the calcifying solution, it proved less than 4% during the whole process.

As for the soluble solids, a sharp increase in the calcifying solution, due to the strong osmotic exchange between the product and the calcifying solution, was obviously expected and, in fact, observed during the process. The soluble solids increased at a rate of about 0.1 °Brix h^{-1}. Lastly, as for the calcium concentration in the calcifying solution, it decreased during the process

Table 1. Changes of Analytical Parameters of Diced Tomatoes during the Calcifying Process According to the First Experiment[a]

	process time (h)									
analytical parameter	$t = 0$	$t = 1$	$t = 2$	$t = 3$	$t = 4$	$t = 5$	$t = 6$	$t = 7$	$t = 8$	mean values ± SD
	4.22	4.22	4.22	4.22	4.21	4.22	4.21	4.22	4.22	4.22 ± 0.01
pH	4.12	4.12	4.11	4.12	4.12	4.11	4.10	4.12	4.12	4.11 ± 0.01
		4.19	4.19	4.20	4.21	4.19	4.18	4.18	4.20	4.19 ± 0.01
	5.0	5.0	5.0	5.0	5.0	4.8	4.8	4.9	4.9	4.9 ± 0.2
soluble solids (°Brix)	5.0	5.0	5.0	5.0	4.9	5.0	4.9	4.9	4.9	4.9 ± 0.1
		4.3	4.3	4.4	4.3	4.3	4.3	4.3	4.3	4.3 ± 0.1
	5.34	5.36	5.34	5.45	5.49	5.49	5.38	5.39	5.38	5.40 ± 0.06
total solids (%)	5.43	5.44	5.45	5.35	5.36	5.44	5.42	5.40	5.45	5.41 ± 0.04
		4.68	4.68	4.69	4.72	4.70	4.72	4.69	4.70	4.70 ± 0.05
	2.48	2.40	2.34	2.34	2.30	2.40	2.38	2.38	2.40	2.38 ± 0.09
sugars (%)	2.34	2.32	2.27	2.27	2.23	2.30	2.34	2.33	2.38	2.31 ± 0.10
		1.96	1.96	1.95	1.90	1.94	2.05	2.0	1.94	1.96 ± 0.08
	0.39	0.42	0.41	0.42	0.42	0.41	0.42	0.42	0.41	0.41 ± 0.01
acidity (%)	0.41	0.42	0.41	0.41	0.42	0.43	0.41	0.41	0.42	0.41 ± 0.01
		0.32	0.32	0.34	0.32	0.34	0.34	0.32	0.33	0.33 ± 0.02
	46.4	44.8	43.8	42.9	41.9	43.7	44.2	44.1	44.6	44.0 ± 2.2
quozient sugars	43.8	42.6	41.6	42.4	41.4	42.3	43.2	43.1	43.7	42.7 ± 2.6
		43.3	41.9	41.6	40.2	41.3	43.4	42.6	41.3	41.9 ± 1.8
	7.3	7.8	7.7	7.7	7.6	7.5	7.8	7.8	7.6	7.6 ± 0.1
quozient acidity	7.5	7.7	7.5	7.6	7.8	7.9	7.6	7.6	7.7	7.6 ± 0.2
		6.8	6.8	7.2	6.8	7.2	7.2	6.8	7.0	7.0 ± 0.2
	149	153	167	155	174	188	170	176	180	168 ± 13
lactic acids (mg/kg)	155	164	170	157	170	185	174	172	188	170 ± 10
		160	168	146	136	178	189	184	201	170 ± 19
	2.01	1.99	1.99	1.99	1.99	2.04	2.01	2.01	1.99	2.00 ± 0.02
a/*b* (color parameter)	2.01	1.99	1.96	2.04	2.00	1.99	1.99	2.00	1.99	2.00 ± 0.02
		1.95	1.96	1.98	1.99	1.99	1.96	1.96	1.97	1.97 ± 0.02
	82.1	74.8	75.0	74.0	72.0	82.0	77.7	80.0	79.4	77.4 ± 3.8
drained weight (%)	82.8	77.8	82.7	80.3	73.2	83.2	79.8	81.2	80.3	80.1 ± 3.3
		90.1	91.8	85.1	88.5	87.2	81.0	87.8	91.6	87.9 ± 3.5
	28.2	29.3	27.4	23.2	31.3	34.4	32.3	34.3	35.6	30.7 ± 3.8
consistency	61.9	49.0	52.8	57.5	49.5	49.1	54.6	57.8	57.7	54.4 ± 4.7
		99.8	101.2	87.8	100.7	102.0	94.7	99.9	106.4	99.1 ± 5.1
	82	83	83	77	81	80	81	82	80	81 ± 2
Ca (mg/kg)	277	272	277	264	255	285	285	274	270	273 ± 10
		238	225	268	242	240	264	255	250	248 ± 15

[a] For each parameter, the first row refers to the product without calcium added, the second row to the product to which 220 mg/kg of calcium ions was added, the third row to the product obtained by immersion in the calcifying solution. The data are the mean values of three determinations.

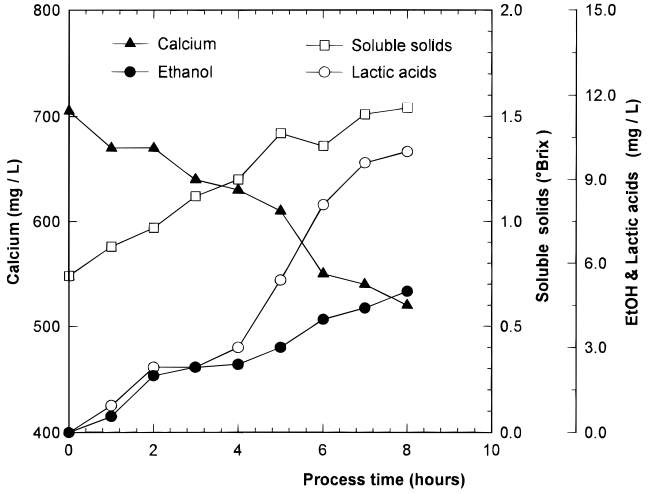

Figure 3. Evolution of some analytical parameters in the calcifying solution during the first experiment in which the calcifying solution was made up of an aqueous solution of 50 mM sodium chloride and 16.25 mM calcium chloride (650 mg/L calcium).

at a rate of 23.3 mg L^{-1} h^{-1}. However, the more interesting data are those regarding the canned product. On all the canned products (cans of 1 kg), determinations of residual PME activity according to Giovane et al. (1996) were made in order to evaluate one of the parameters more directly involved in texture modification during the storage. The results obtained confirmed for all the samples that the residual PME activity was very low, less than 1.0×10^{-4} u/g of product. These results clearly show that the stabilization thermal treatment employed (90 min in a water bath at 100 °C) was sufficient to inactivate PME in the product.

In Table 1, the analytical parameters and the consistency values found for the three kinds of canned products are reported. These are the products obtained without calcium addition, those with calcium added (220 mg/L), and the products obtained by immersion in the calcifying solution according to the first experiment. As for the pH, it was, in agreement with the values reported in a previous paper (Castaldo et al., 1995a), slightly higher for the products dipped in the calcifying solution at pH 7.5. Conversely, as reported by many authors, the direct calcium addition brings about a pH decrease in the product (Bellucci et al., 1972; Floros et al., 1992). In our case, the observed decrease with respect to products obtained without calcium addition was about 0.11 pH unit. The loss of soluble solids, mainly sugars and acids, was evident from the lower sugar and organic acid content of the packaged products (Table 1). In particular, sugars with the proposed treatment decrease by about 17%. Still higher was the percent decrease of the total acids for the products dipped in the calcifying solution, close to 20%.

To evaluate the marketability of the products, some commercial parameters normally utilized are reported in Table 1. They are essentially the mean values of the

Table 2. Changes of Analytical Parameters of Diced Tomatoes during the Calcifying Process According to the Third Experiment[a]

	process time (h)									
analytical parameter	$t = 0$	$t = 1$	$t = 2$	$t = 3$	$t = 4$	$t = 5$	$t = 6$	$t = 7$	$t = 8$	mean values ± SD
	4.29	4.28	4.28	4.29	4.30	4.28	4.29	4.28	4.29	4.29 ± 0.01
pH	4.19	4.20	4.19	4.18	4.20	4.20	4.21	4.18	4.19	4.19 ± 0.01
		4.37	4.36	4.36	4.35	4.35	4.36	4.34	4.37	4.35 ± 0.01
	4.4	4.5	4.5	4.4	4.4	4.5	4.4	4.4	4.4	4.4 ± 0.1
soluble solids (°Brix)	4.4	4.5	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4 ± 0.1
		4.2	4.2	4.3	4.2	4.2	4.2	4.3	4.3	4.2 ± 0.1
	4.77	4.87	4.80	4.87	4.87	4.80	4.87	4.77	4.77	4.82 ± 0.05
total solids (%)	4.78	4.84	4.76	4.79	4.83	4.76	4.84	4.78	4.77	4.79 ± 0.03
		4.47	4.55	4.56	4.59	4.55	4.56	4.55	4.55	4.54 ± 0.03
	2.33	2.15	2.27	2.15	2.15	2.27	2.15	2.30	2.30	2.23 ± 0.08
sugars (%)	2.30	2.10	2.27	2.09	2.09	2.26	2.12	2.30	2.30	2.20 ± 0.10
		2.03	2.21	2.10	2.07	2.18	2.05	2.22	2.20	2.11 ± 0.08
	0.34	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.34	0.35 ± 0.01
acidity (%)	0.35	0.35	0.34	0.36	0.36	0.34	0.34	0.35	0.33	0.35 ± 0.01
		0.31	0.31	0.32	0.31	0.30	0.32	0.30	0.31	0.31 ± 0.01
	48.8	44.1	47.3	44.1	44.1	47.3	44.1	48.2	48.2	46.2 ± 2.1
quozient sugars	48.1	43.4	47.7	43.6	43.3	47.5	43.8	48.1	48.2	46.0 ± 2.3
		45.4	48.6	46.0	45.1	47.9	44.9	48.8	48.3	46.4 ± 1.7
	7.1	7.2	7.3	7.2	7.2	7.3	7.2	7.3	7.1	7.2 ± 0.1
quozient acidity	7.3	7.2	7.1	7.5	7.4	7.1	7.0	7.3	6.9	7.2 ± 0.2
		6.9	6.8	7.0	6.7	6.6	7.0	6.6	6.8	6.8 ± 0.2
	85.8	82.4	80.8	81.2	73.9	77.7	78.4	73.4	83.2	79.6 ± 4.1
drained weight (%)	89.8	84.6	82.1	86.5	81.2	83.4	85.2	81.7	84.5	84.3 ± 2.7
		86.8	87.9	89.8	87.8	88.4	86.7	85.7	87.4	87.5 ± 1.2
	286	294	291	285	288	294	272	277	265	283 ± 10
lactic acids (mg/kg)	265	277	288	280	290	295	288	286	270	282 ± 10
		270	274	280	286	299	305	300	305	290 ± 14
	2.04	2.04	2.04	2.05	2.08	2.07	2.08	2.08	2.07	2.06 ± 0.02
a/*b*	2.03	2.04	2.04	2.06	2.03	2.03	2.02	2.07	2.03	2.04 ± 0.02
		2.04	2.03	2.01	2.01	2.01	2.02	2.01	2.01	2.02 ± 0.01
	77.5	78.6	79.4	81.3	78.2	77.4	79.6	82.5	79.0	79.3 ± 1.7
Ca (mg/kg)	267.5	272.7	284.6	278.5	284.0	298.6	295.3	278.5	281.0	282.3 ± 9.9
		253.4	248.6	205.4	228.0	233.4	198.7	231.5	254.0	231.6 ± 20.9

[a] For each parameter, the first row refers to the product without calcium added, the second row to the product to which 220 mg/kg of calcium ions was added, and the third row to the product obtained by immersion in the calcifying solution. The data are the mean values of three determinations. The consistence values are reported in Figure 6.

ratio of sugars/total solids (quozient sugars) and of the ratio of acidity/total solids (quozient acidity) evaluated during the process. The results reported in Table 2 paradoxically show that, notwithstanding the total sugars loss of about 17%, the sugar ratio remains close to that of the product not dipped in the calcifying solution, with a decrease of about 5%. Instead, the decrease of the acidity ratio for the dipped product is higher, about 8%.

As for lactic acids and ethanol, which are an index of microbial alteration, the results obtained on packaged products show that the content of these metabolites in the calcifying solution increases with the experiment time, but this does not seem to impair the practicability of the process. In fact, the analytical data found on the packaged product are close to those of commercial products. Similar considerations hold also for mold content, which was less than 4% for all the samples analyzed. As for the color (parameter *a*/*b*), the differences we found among the three kinds of products do not seem to depend on the particular process they underwent. More interesting are the data regarding the calcium content, the consistency, and the drained weight of the products. As for calcium content, for the products prepared without calcium addition, it was about 80 mg/kg, for the products prepared with direct calcium addition about 220 mg/kg, and for the product prepared by immersion about 250 mg/kg. The consistency values were about 40 kg for the products without calcium addition, about 57 kg for the products prepared by direct calcium addition, and about 104 kg (with an increase of 160%) for the products obtained with the described immersion process. The very high consistency values found for these last products were also paralleled by high drained weight values. In fact, it is well known that the lower the tendency of the juice to be squeezed out of the pulp during the thermal stabilized process, the higer the drained weight. This tendency is inversely correlated to the consistency.

As for the plant system, one of the main problems was the pH maintenance during the process close to the set condition at pH 7.5. The electric valves placed in the feeding circuit of sodium hydroxide, which is required for pH maintenance, were set in such a way that when the solution pH was lowered below 7.4 the NaOH solution flowed in the immersion pool until the pH reached the value of 7.5. At this pH value, the electric valves shut up, interrupting the hydroxide flow. Various experiments made with different NaOH concentrations showed that the hydroxide concentration of 5% gave the best result in terms of pH maintenance at the set conditions. In fact, pH oscillation of the calcifying solution, particularly in the first section of the immersion pool, where the acidity is higher, was very stable utilizing the 5% NaOH solution. Conversely, a higher NaOH concentration (Figure 4) caused a sharp pH increase as a consequence of addition and a long time to restore the set conditions. As for the successive sections of the immersion pool, they were less dependent of the concentration of hydroxide solution employed.

In order to reduce the microbial alteration in the calcifying solution during the process carried out at room temperature, the second experiment was performed with the calcifying solution undergoing a con-

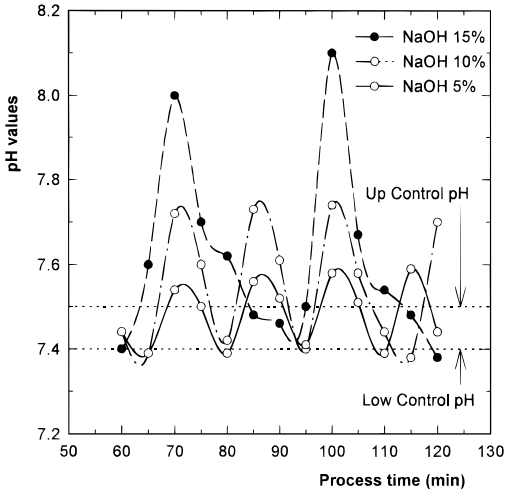

Figure 4. pH modifications of the calcification solution as a consequence of the addition of sodium hydroxide solution at different concentrations. The pH was measured in the first part of the immersion pool, soon after the introduction of the diced product.

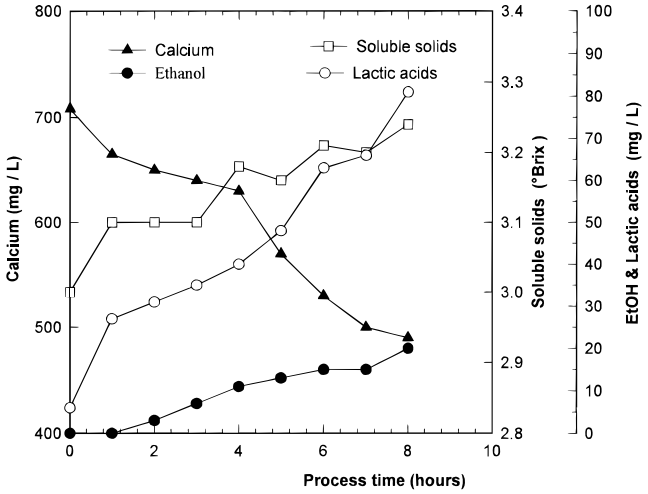

Figure 5. Evolution of some analytical parameters in the calcifying solution during the third experiment in which the calcifying solution was made up of tomato serum with sodium and calcium chloride at the same concentration as the first experiment.

tinuous pasteurization process. With this aim, we tried to find the most suitable recycling rate of the calcifying solution. Three different flow rates (150, 200, and 300 L/h) through the unit employed for the thermal treatment of the solution (Figure 1) were tested. The results show that the flow rates of 150 and 200 L/h do not substantially modify the content of ethanol and lactic acids. On the contrary, the flow rate of 300 L/h keeps the content of all those metabolites about 20% lower, with final values after 8 h below 6 mg/L for lactic acid and 4 mg/L for ethanol. The flow rate of 300 L/h was therefore chosen.

As for the consistency and analytical parameters of the products, they were very close to those of the first experiment. On the basis of these results, we did the third calcification experiments in a calcifying solution made up with tomato serum, in order to reduce the soluble solids loss from the product. For this purpose, 1500 L of tomato juice at a final residue of 4.5 °Brix was prepared by dilution of Hot-Break tomato concentrate at 28−30 °Brix. The diluted juice was centrifuged by a Pieralisi decanter. The serum was further diluted with water to a final residue of 2.5 °Brix and then added with calcium chloride and sodium chloride up to a concentration of calcium ions of 650 mg/L and sodium ions of 50 mg/L. The final solution showed an optic refractometric residue of 3. In Figure 5, the analytical data on the calcifying solution during the whole process are reported. The results show that the behavior of the analytical parameters is close to those of the previous experiments. However, the content of the alteration metabolites was higher during the whole experiment. This effect could be ascribed to the higher availability of nutrients for the microbial organisms. The production rates of microbial metabolites were, in fact, 2.46 mg L^{-1} h^{-1} for ethanol and 8.2 mg L^{-1} h^{-1} for lactic acids, with an increase with respect to the calcifying solution without serum of about 290 and about 600%, respectively.

As for the calcium consumption, it was similar to that found in the experiments made with the solution of calcium in water. Finally, as for soluble solids, the lower difference between diced tomatoes and the calcifying solution made with tomato serum decreases the loss of sugars and acids from the product. This is seen in Table 2 where the analytical data on the packaged

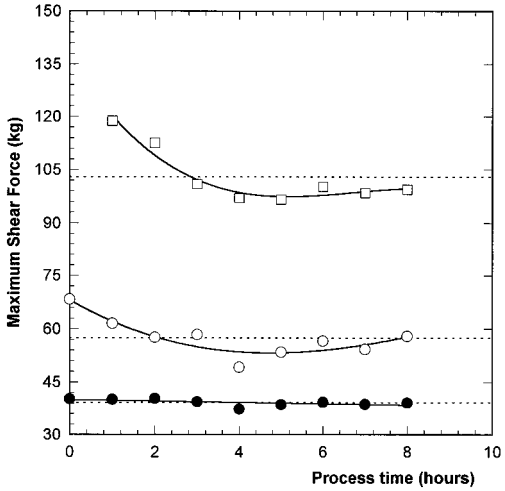

Figure 6. Comparison of the firmness observed during the process for diced and calcified tomato according to the third experiment (□), diced tomato obtained with direct calcium chloride addition (○) and with no treatment (●). The dotted lines represent the mean values.

product are reported. The results show that sugars and acids had a lower decrease, i.e., 5.5 and 11.5%, respectively, in comparison with the data of Table 1. Also, other parameters of commercial interest are close to those of traditional products. The sugar ratio remains almost constant, and the acidity ratio is lower by about 5.5%.

In Figure 6 the mean values of consistency found on the product in the course of the whole process are reported. The consistency value for the product without calcium addition was about 40 kg. The corresponding product with the calcium addition had value of about 57 kg. Instead, the product obtained by immersion showed a value of about 102 kg. For this last product, the consistency value does not seem to depend much on the calcium concentration in the calcifying solution. In fact, during the 8 h of the process, the calcium concentration decreased from 700 to 500 mg/L, but this fact did not influence the product consistency. From an industrial point of view, these data are very important inasmuch as the calcium concentration, not being very critical, could require a more simple automatic system

Table 3. Comparison between the Diced Tomatoes Obtained with Two Different Technologies[a]

analytical parameter	tomato diced (traditional procedure)	tomato diced (obtained by immersion in calcifying solution and aseptically packaged)
pH	4.42 ± 0.02	4.36 ± 0.03
soluble solids (°Brix)	4.7 ± 0.2	4.7 ± 0.2
total solids (%)	5.21 ± 0.06	5.19 ± 0.05
sugars (%)	2.19 ± 0.1	2.17 ± 0.2
acidity (%)	0.29 ± 0.01	0.32 ± 0.01
sugars ratio	42.0 ± 2.1	41.8 ± 1.9
acidity ratio	5.6 ± 0.2	6.2 ± 0.2
lactic acids (mg/kg)	533 ± 8	581 ± 9
Ca (mg/kg)	57 ± 7	230 ± 18
a (color parameters)	25.8 ± 0.1	24.6 ± 0.1
b (color parameters)	13.1 ± 0.1	13.7 ± 0.1
a/*b* (color parameters)	1.97 ± 0.02	1.80 ± 0.03
L (color parameters)	24.4 ± 0.2	25.5 ± 0.2
consistency (maximum shear force, kg)	38 ± 4	130 ± 11
residual PME activity range (u/g)	1.0×10^{-3} to $3.8 \times 10-3$	1.7×10^{-3} to $3.9 \times 10-3$

[a] The values are the mean of three determinations.

for the control and less accurate and expensive measurement devices.

In experiment 4, the behavior of the diced tomato, treated according to the experiment 3 but with aseptical packaging, was examined. Nine hundred kilograms of tomatoes was employed for the preparation of the diced product. One portion of the tomatoes was treated traditionally by peeling and then dicing the product. The remaining part, about 500 kg, was calcified according to experiment 3. Both were then employed to prepare the final products in a plant of the firm Doria SPA (Angri, Salerno, Italy). The diced product was first drained and then mixed in a tank, with tomato juice at an optic refractometric residue of 5. The product was pumped into a heat exchanger and maintained at the stabilization temperature of 110 °C for 10 min. Then it was cooled at 40 °C and packaged into aseptic bags in aliquots of 50 kg. For both samples, after a storage time of 60 days at room temperature, the analytical determinations and PME activity measurements reported in Table 3 were performed on bags chosen at random. The PME activity was about 10 times higher than the analogous product previously packaged in a can and stabilized for 90 min in a water bath at 100 °C. Fortunately, the residual PME activity was completely localized in the diced product and absent in the juice employed as the dispersing phase. In these conditions, very low consistency variations occur (Castaldo et al., 1996). The analytical data reported in Table 3 show the same characteristics for both products; including also the sugar and the acidity ratio. However, the noticeable difference of consistency reported in Table 3 indicates that the product prepared with the proposed calcification process maintains a consistency much higher than that of the reference product, notwithstanding the heavy thermal treatment of stabilization.

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