EFFECTS OF HEAT TREATMENTS ON QUALITY PARAMETERS AND THE NATURAL ANTIOXIDANTS OF TRIPLE CONCENTRATED TOMATO PASTE

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Abstract
Transformation processes involve one or more heat treatments may affect the biochemical, technological and nutritional quality of finished products. It was determined the microbial load of tomato juice to calculating the sterilizing value. Validation of sterilization schedules was performed using the standard computation software by CTCPA (Technical Centre for the Conservation of Agricultural Products-France). It was established 108°C/3min and 102°C/2min 53s. The triple concentrated tomato paste was produced by the continuous technological process by the method of cold break. The influence of the two scales of sterilization on Brix, pH, acidity, chlorides, reducing sugars, protein, viscosity, lycopene, ascorbic acid and α-tocopherol determined by standard methods was evaluated. The analysis of variance ANOVA showed the existence of highly significant differences between the effect of 108°C/3min and the 102°C/2min 53s on acid contents with (+1.19%) at 102°C ($p \leq 0.001$), chlorides with (+7.24%) at 102°C ($p \leq 0.001$), reducing sugars with (-2.45%) at 108°C and (-1.37%) at 102°C ($p \leq 0.01$), proteins with (-1.48%) at 108°C and (-0.60%) at 102°C ($p \leq 0.001$), and ascorbic acid with (-19.67%) at 108°C and (-17.77%) at 102°C ($p < 0.05$). Tests of correlation and principal component analysis helped to highlight the relationship between the studied parameters and temperature changes. Brix rate is correlated with those of reducing sugars (R=0.71), acids (R=0.70) and proteins (R=0.53). The results revealed an improved bioavailability of lycopene (+4.56%) at 108°C and (+2.30%) at 102°C. There was a stable α-tocopherol and viscosity. Reducing rates of sterilization without effect on safety improves the final quality of triple concentrated tomato paste.

Keywords: triple concentrated tomato paste, scales of sterilization, quality parameters, natural antioxidants, PCA.

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1. INTRODUCTION

Nowadays, the processing industry of fruit and vegetables has continued to seek to diversify and evolve its products. However, the development of this transformation process is confronted with a limit which is the basis of its existence: the heat treatment. This physical phenomenon responsible for the total elimination of micro-organisms leads nevertheless a number of damage to the quality of the product itself. Destruction of microorganisms by heat is often at the expense of nutritional and organoleptic qualities of the product. Will present canner's is towards reduction sterilization schedules to improve the quality of their final products, while ensuring the microbiological safety (Couvert, 2002).
Tomato *Lycopersicon esculentum*, is one of the most important international cultures. It is known for its nutritional benefits. It is the main source of antioxidants such as carotenoids (lycopene and β-carotene) and vitamins (ascorbic acid and α-tocopherol) (Feudo Lo et al., 2011). Technological treatments applied in processing industries of tomato cause sometimes physical, chemical and biological changes. They can cause the modification of the nutritional value (Consonni and al., 2009).
The aim of our study is the demonstration of sterilization schedules without compromising the safety of the product and assessing their effects on quality parameters and natural antioxidants of triple concentrated tomato paste. For this, the pH, viscosity and levels of Brix, chlorides, acids, proteins, reducing sugars, ascorbic acid, lycopene and α-tocopherol were determined.

2. MATERIALS AND METHODS

2.1. Preparation of samples

For the calculation of the sterilizing value, the first step is the determination of the total microbial load of tomato juice by the

enumeration of micro-organisms (AFNOR, 1993).
- Aerobic germs at 30 °C/72 h (NF V 08-011).
- Aerobic germs at 55 °C/72 h (NF V 08-011).
- Enterobacteriaceae 37 °C/24 h (NF V 08-025).
- Yeasts and molds at 25 °C/5 days (NF V 08-022).
- Stability Test incubation at 30 °C/21 days (NF V 08-402).

Samples collected under sterile conditions are:
- Tomato juice (Brix 6-7 %), (02) sample units of juice.
- Finished product (sample bag of triple tomato paste, (Brix 36-38 %), (03) sample units of finished product.

The second step is the design and validation of sterilization schedules, using the standard computation software CTCPA (Technical Centre for the Conservation of Agricultural Products-France). It has been established:
- Sterilization at 108 °C for 3 min.
- Sterilization at 102 °C for 2 min 53 s.

Gradual cooling to 37 °C is used to limit the over-cooking and losses in the organoleptic and nutritional qualities of the product. The triple concentrated tomato paste was produced by the continuous technological process by the method of cold break and aseptic packaging. The concentrate thus obtained has a dry soluble residue between 36-38 %.

Microbiological data of tomato juice and the finished product as well as the parameters of the two scales of sterilization used in the technological process are shown in table 1 and table 2.

Table 1: Microbiological data of tomato juice and finished product

Analysis methods	Tomato Juice	Finished product
Total germs at 30 °C	$2.4\ 10^5$ UFC/g	Absence
Total germs at 55 °C	Absence	Absence
Enterobacteriaceae at 37 °C	Absence	Absence
Yeast	Absence	Absence
Mold	1 Mold	Absence
Stability test /pH		Stable $pH_T = 4.19$ pH = 4.19

pH_T: pH indicator, pH: pH of the sample.

Table 2: Parameters of the two scales of sterilization used in the technological process

Sterilization schedules	S_1 108 °C /3 min	S_2 102 °C /2 min 53 s
Output	8833 (L/h)	10500 (L/h)
Capacity chambering	442 (L)	442 (L)
Z (value characterizing the slope of the mortality curve of the microbial population considered)	13 (°C)	13 (°C)
T* Reference	94 (°C)	94 (°C)
P (sterilizing value)	65	21
P° (sterilizing value specific to canned tomatoes)	> 10	> 10
Cooling	37 (°C)	37 (°C)

2.2. Distribution of batches

A control: No heat treatment of the sample in the evaporator after concentration and before sterilization.

A batch sample S1: Heat treatment at 108 °C for 3 min.

A batch sample S2: Heat treatment at 102 °C for 2 min 53s. The samples were numbered and stored in a refrigerator at 5 °C (± 0.1 °C).

2.3. Determination of quality parameters and the natural antioxidants of triple concentrated tomato paste:

Soluble solids or Brix

This is the concentration of sucrose in an aqueous solution having the same refractive index as the product analyzed. This concentration measured by the refractive index is then expressed as a percentage, is measured using a refractometer Abbe (CEE 1764/86) (NA 5669).

This parameter represents a very important commercially quality and is subject to strict regulation. Classification of the product is based on its refractive index expressed as a percentage of Brix. The triple concentrated tomato paste must have a rate between 36-38%.

Potential Hydrogen

Potential Hydrogen expresses the acidity of the product. It is a very important concept for determining the aggressiveness of the tomato.

It also defines the membership of the various product categories classified according preserves the pH is pH < 4.5 or pH ≥ 4.5 (JORA, 1998). The pH of triple concentrated tomato paste (Cold Break) should be between 4.20 and 4.50. The pH determination was conducted using a pH meter (NF V 08-406).

Acidity

The aim is to measure the total content of natural acids. The assay was performed by titration with NaOH 0.1N using phenolphthalein. Titratable acidity is expressed as citric acid monohydrate per 100g of product: 1ml NaOH N/10 = 0.07 g of citric acid monohydrate (NA 691) (NF V05-101).

Rate of chlorides

Chlorides express the salinity of the product. The addition of salt as a conservative increases the Brix. Thus, the existing natural salt content is fixed at 2 % of the dry matter content. Beyond these values, measured chlorides are considered additional salts. The assay is done by titration of the excess of a standard solution of silver nitrate used in the precipitation of chloride by a standard solution of potassium thiocyanate in the presence of ferric ammonium alum (CEE 1764/86) (CACQE No.08.96.13). The chloride content is expressed as percentage by mass of sodium chloride (%).

Protein content: Kjeldahl method

Protein components are present in most fruits and vegetables. However, they are of paramount importance, as enzymes involved in the metabolism of fruit during growth. Protein is expressed in tomato-based products from the determination of total nitrogen (NF V03-050). Proteins contain an average of 16 % nitrogen, it is recognized by convention as: protein in g= 6.25 g × N. The results are expressed in mg of protein per 100 g of product.

Reducing sugar content: Lane-Eynon method

Sugars up to 65 % of the dry matter of tomato derivatives and are mostly reducing sugars, mainly glucose and fructose in roughly equal proportions (CEE 1764/86). The amount of sucrose existing naturally in tomatoes is negligible. The determination of reducing sugars that occur naturally in the product is made by the Lane-Eynon method without inversion using Fehling's solution. The results are expressed as a percentage of invert sugar per 100 g of soluble solids (%).

Viscosity

Viscosity is one of the most important technological factors in the quality of tomato paste. It is related to the content of fruit in alcohol-insoluble substances such as protein, pectin and polysaccharides (Gallais and al., 1992). It is the combined effect of the liquid, soluble and insoluble material in suspension, pectin, which contribute to the general consistency of tomato paste (Hawbecker, 1995).

The importance of the study of viscosity on the one hand provides information on how to use technological treatments (flow properties of the material, ability to condensation flow during processing treatments, thermal conductivity, density ...) and secondly the characteristics of nutritional and sensory quality for consumers. It is done through a viscometer. It is calculated the distance in the measuring apparatus, the sample diluted to 12.5 % Brix for 30 s. The values are expressed in cm Bostwick (Codex STAN, 1981).

Lycopene

The carotenoid mainly found in red tomatoes, is (E)-lycopene. The latter is the most stable form of the thermodynamic point of view. It is their main pigment (Chanforan, 2010). The majority of lycopene found in the skin and pulp. It is responsible for the red color of tomatoes. With these 11 conjugated double bonds and two unconjugated lycopene is 100 times more effective than α-tocopherol as an antioxidant (Basuny and al., 2009). Lycopene is determined by spectrophotometry at 502 nm (LAB Maselli LC-01) after dilution of the sample with 50 % distilled water. The concentrations are expressed in mg/100 g of product.

Ascorbic acid

Levels of total vitamin C in tomatoes vary depending on the variety and growing conditions. They are generally between 7 and 30 mg/100 g of fresh matter. They can reach 70

mg/100 g in cherry tomatoes (Raffo and al., 2006). The proportions of ascorbic acid (AA) and dehydroascorbic acid (DHAA) also vary depending on the cultivar and environmental conditions. The oxidized form may represent 0 to 85% of the total vitamin C (Toor and al., 2006). These variations are due to changes in environmental conditions may induce a change in the redox state of the system AA / DHAA. Its antioxidant power is related to the reversible interconversion between the oxidized and reduced form (Guil-Guerrero and al., 2009).

The method used for the determination of vitamin C is a standardized volumetric 2,6-dichloro-phenol indophenol (CACQE No. 08.97.22). Ascorbic acid is readily oxidized, especially in an alkaline medium, to dehydroascorbic acid. The reducing action of ascorbic acid is the basis for the determination of chemical compound. At acidic pH, ascorbic acid discolors 2,6-dichlorophenol indophenol reaction is quantitative and allows a determination of ascorbemy (Boumendjel and Boutebba, 2003a; Pascaud, 1998). It is expressed in mg/100 g of product.

α-Tocopherol

The α-tocopherol is form of vitamin E found mainly in fresh tomatoes. Levels vary greatly depending on the variety and harvest dates (Dumas and al., 2003). In the fruit, it is distributed in various tissues but it is in the seeds than highest concentrations are encountered (Pinela, and al., 2012). It is the third antioxidant of tomato after lycopene and ascorbic acid. It is involved in protecting the body against several diseases (Hazewindus and al., 2012). Vitamin E is measured in a spectrophotometer at 510nm after extraction with petroleum ether. It is expressed in mg/100 g of product (Rougereau, 1981).

2.4. Statistical analysis

For statistical analysis software Minitab (v.15) and STATISTICA (v.6) were used. It has been used in the analysis of variance (ANOVA), the Student t test and the principal component analysis (PCA). The results are presented as mean ± standard deviation of three replicates. Statistical tests were performed at a significance level of $\alpha = 0.05$.

3. RESULTS AND DISCUSSION

The results of the quality parameters and natural antioxidants of triple concentrated tomato paste obtained are shown in Table 3.

Table 3: Quality Parameters and natural antioxidants of triple concentrated tomato paste

Parameters	Control	S_1	S_2
Brix (%)	38,417 ± 0,176	37,905 ± 0,252	38,126 ± 0,295
Reducing sugars (%)	52,992 ± 0,601	51,692 ± 0,196	52,266 ± 0,579
pH	4,190 ± 0,080	4,080 ± 0,073	4,054 ± 0,035
Acidity (%)	6,565 ± 0,090	6,565 ± 0,090	6,735 ± 0,090
Chlorides (%)	0,442 ± 0,013	0,442 ± 0,013	0,474 ± 0,014
Viscosity (cm Bw)	9,250 ± 0,264	9,100 ± 0,516	9,000 ± 0,000
Proteins (mg/100g)	6,770 ± 0,022	6,670 ± 0,017	6,730 ± 0,017
Lycopene (mg/100g)	59,240 ± 1,866	61,940 ± 2,594	60,600 ± 2,582
Vitamin C (mg/100g)	14,776 ± 0,393	11,870 ± 0,253	12,150 ± 0,276
Vitamin E (mg/100g)	1,313 ± 0,035	1,307 ± 0,035	1,307 ± 0,035

3.1. Brix - pH - Acidity – Chlorides

Levels of natural acids and chlorides are strongly influenced by the heat treatment ($p \leq 0.001$). They are inversely proportional to the increase in the sterilization temperature. The percentage of acid is below 10 %. The rates of Brix and pH were not affected by temperature changes ($p < 0.05$). The rate of soluble solids undergoes no significant change.

Tests of correlation and principal component analysis PCA (Fig.1 and Fig.4) lead to the following hypotheses: the changes in the rate of Brix dependent longer of the variations in the rate of reducing sugars (R=0.71), the acidity (R=0.70) and protein (R=0.53) than those of chlorides. The variation of the protein did not affect the quality of the product. It has an effect on the overall expression of brix.

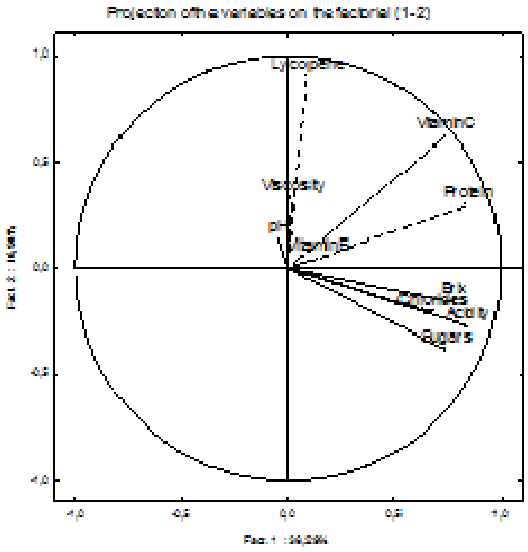

Fig. 1 Correlation circle axis (1-2)

3.2. Proteins - reducing sugars

Sterilization decreases very significantly the protein ($p \leq 0.001$) and reducing sugars ($p \leq 0.01$) levels. The t-test confirms the difference between sterilization at 108 °C/3 min and 102 °C/2 min 53 s. This is explained by deployment and into reaction of proteins with other molecules at high temperature induces their denaturation (Boumendjel and Boutebba, 2003b; Anthon and al., 2011). Sugars present in tomatoes are 95% reducing sugars. A positive correlation was observed between the protein and the rate of ascorbic acid (R=0.83). In acidic and hot medium, the conditions are favorable to the process of non-enzymatic browning, therefore, generates reducing the nutritional value of tomatoes by degrading the essential amino acids and vitamin C (Guil-Guerrero and al., 2009). This is due to the difference between the two physical treatments employed.

3.3. Viscosity

The t-test shows no significant difference in viscosity between sterilization at 108 °C/3 min and 102 °C/2 min 53 s ($p<0.05$). Tests of correlation and principal component analysis, lead to the following hypotheses: on the axes (1-3) and (2-3) of PCA (Fig.2 and Fig.3), the viscosity measurements are inversely correlated with those of pH and acidity. It is assumed that the viscosity of tomato depends on several parameters. The preheating temperature can inactivate or not, pectinolytic enzymes. The duration of the heat treatment process during a hot break can degrade pectin by β-elimination or acid hydrolysis (Tehrani and Gandhi, 2007).

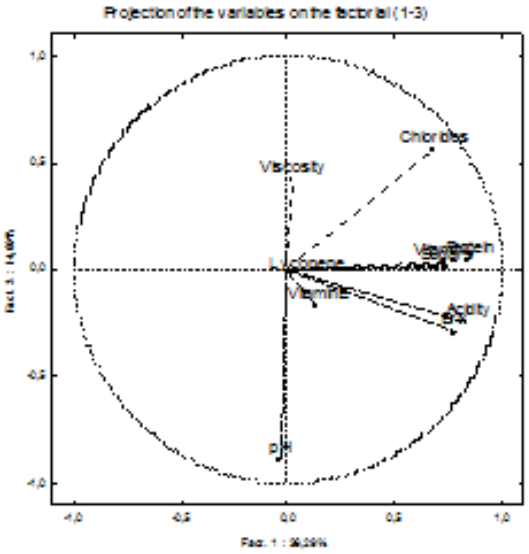

Fig. 2 Correlation circle axis (1-3)

The degradation of pectic compounds by pectinolytic biocatalysts and the release of galacturonic acid contribute greatly to accelerate the breakdown of cells (Bayod, and al., 2008). The viscosity of tomato decreases considerably. There is no difference between the effects of two treatments applied on the consistency of the product. The content of soluble and insoluble and their distribution within the product will influence the rheological properties (Chanforan, 2010). The viscosity has been extensively studied because consistency is with the color and flavor, a parameter that characterizes the quality of the product (Krebbers, and al., 2003; Magerramov, and al., 2007).

3.4. Lycopene

Figures 1 and 3 on the axes (1-2) and (2-3), it was appears that the rates of lycopene are correlated with those of ascorbic acid (R=0.62). A defense mechanism against oxidation from dietary compounds such as vitamin C, vitamin

E, selenium and carotenoids substances probably may exist (George and al., 2011).

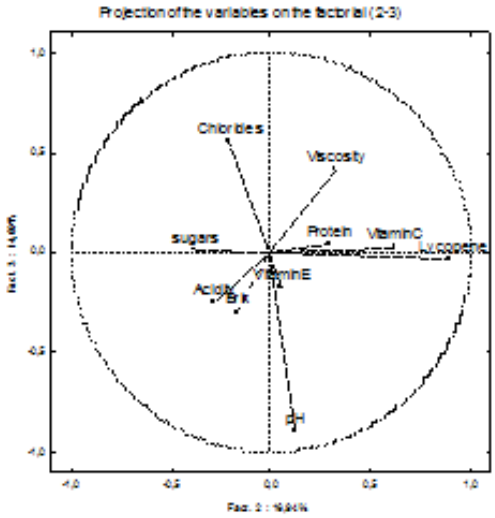

Fig. 3 Correlation circle axis (2-3)

It was observed an increase in lycopene levels when the heat increases (+4.56 %) at 108 °C/3 min and (+2.30 %) at 102 °C/2 min 53 s (Fig.5). The content of (E)-lycopene increases during the manufacture of that product, which could be explained by a better extractability of lycopene in dosage, phenomenon due to the release of lycopene from the plant matrix in during heating (Pérez-Conesa and al., 2009; Xianquan and al., 2005). It showed the stability of this antioxidant against heat.

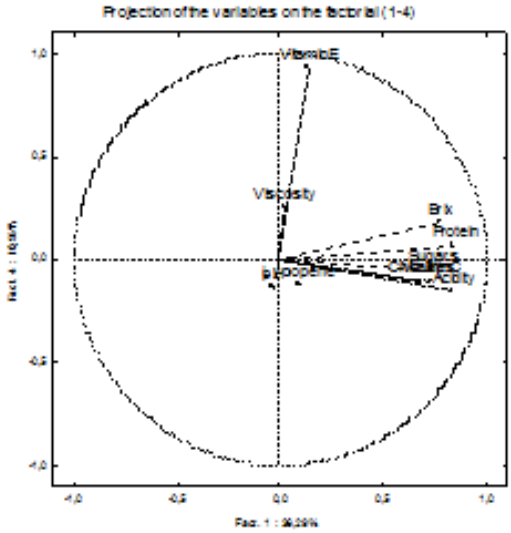

Fig 4 Correlation circle axis (1-4)

3.5. Ascorbic acid and α-tocopherol

From Figure 5, the sterilization acts strongly on the concentrations of ascorbic acid by decreasing significantly (p<0.05) with (-19.67 %) at 108 °C/3 min and (-17.77 %) at 102 °C/2 min 53 s. Because of its high sensitivity to heat and light, vitamin C is systematically degraded by processing methods. Under the conditions used, the losses are more or less important. Temperature, pH, and the duration of treatment are the principal parameters affecting the degradation of this compound (Rajchl and al., 2010). Unlike vitamin C, for tocopherol levels, the Student's t-test revealed no significant difference at p<0.05 after the two heat treatments used. This is explained by the stability of tocopherols against thermal treatments. According to Capanoglu and al., 2008, the total tocopherol (sum of forms α, β, γ and δ) is not significantly affected by treatment during the industrial preparation of a concentrate from fresh tomatoes. Because of its relatively low level in fresh tomatoes, vitamin E has been much less studied than vitamin C in tomato-based products. Publications regarding evolution are rare and contradictory. As the rate of degradation of the lycopene, β-carotene, vitamin E, vitamin C and certain polyphenols is linked to synergistic effects that exist between them (Hazewindus, and al., 2012).

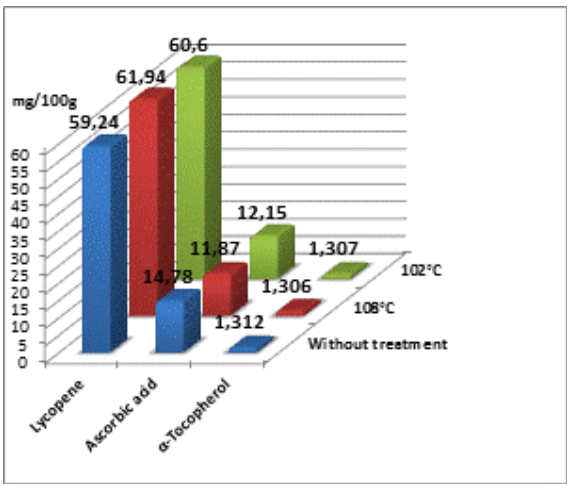

Fig 5. Variations in the rates of natural antioxidants as a function of heat treatments applied

4. CONCLUSIONS

Sterilization schedules optimized and applied influenced the biochemical, technological and nutritional quality of triple concentrated tomato paste product according to the method of cold break. The rate of Brix most depends on changes in acidity than chlorides. They are inversely proportional to the temperature increase during the determined time.

Sterilization at 108 °C/3 min caused the decrease in protein and reducing sugars contents compared to that at 102 °C/2 min 53 s. The viscosity is inversely correlated with pH and acidity. There are no differences between the effects of the two treatments applied on the consistency of the product.

The rate of lycopene increased depending on the sterilization schedules employees. There is a better bioavailability of the antioxidant. It is correlated with that of ascorbic acid. The latter has been degraded during the manufacture of the concentrated product. It is sensitive to heat. The α-tocopherol is stable against the defined physical conditions.

Reducing the rates of sterilization without effect on safety improves the final quality of triple concentrated tomato paste.

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