# Heat Damage Evaluation during Tomato Products Processing

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To evaluate the efficiency of furosine as a heat damage index in tomato products, its content was determined in each step of tomato pulp (9% dry matter) and tomato paste (31% dry matter) processing. Furosine levels (mg/100 g protein) increased linearly as a function of heat treatment severity, although the slopes of the two products differed because of the different dry matter contents. The standardization of furosine values on the basis of dry matter content [mg furosine/(g protein·g dry matter)] highlighted an identical linear increase of furosine for both products. Hence, furosine appears to be a good heat damage index of tomato products, allowing the evaluation of both product quality and processing technology. Furosine was also determined on several tomato products collected from the Italian market, detecting values from 43 to 140 for tomato pulp, from 93 to 132 for tomato sauce, and from 220 to 468 mg/100 g protein for tomato paste.

**Keywords:** *Furosine; heat damage; tomato products*

## INTRODUCTION

Heat treatments during tomato processing cause chemical and physical changes which can affect the nutritional and sensorial quality of the final products.

The level of 5-(hydroxymethyl)-2-furfural (HMF) and the optical density of tomato serums have been used to measure the heat damage during production (Luh et al., 1964) and storage of tomato paste (Luh et al., 1958; Luh et al., 1964) and to study the browning mechanisms in tomato products using model systems (Miki, 1974; Porretta, 1991). Even though HMF is the parameter that is at present normally used by the tomato industry to evaluate heat damage, it shows a low sensitivity. For example, from the data of Porretta and Sandei (1991) about a study for the evaluation of two HMF analysis methods, it is possible to observe that HMF presented only a slight variation (that is, between 13 and 38 ppm) among samples with a soluble solids contents between 8 and 30 °Brix (a wide range of heat treatment conditions), while it presented high values (ca. 185 ppm) only in samples of 38–40 °Brix.

The quantification of several Amadori compounds, the first stable products of Maillard reaction, has been used by Shräder and Eichner (1996) to evaluate heat damage in tomato products. The authors observed significant Amadori compound levels only in tomato concentrates with dry matter content above 45%, increasing as a function of dry matter content of the product.

Furosine, $\epsilon$-*N*-(2-furoylmethyl-L-lysine), produced by acid hydrolysis of the Amadori compounds, successfully used for the evaluation of heat treatment intensity in several food products (Erbersdobler et al., 1987; Resmini et al., 1990a; Pompei and Spagnolello, 1997) and for the quality assessment of pasteurized milk (Resmini et al., 1992) and Mozzarella cheese (Pellegrino et al., 1994), has also been proposed as a freshness parameter of shell eggs (Hidalgo et al., 1995).

The high sensitivity and versatility of furosine suggest it as a good method to measure tomato products heat damage and should fulfill an important need of the tomato industry. The aim of this study is to evaluate the thermal history of tomato pulp and tomato paste production through the measurement of furosine content in each process step in order to verify furosine efficiency as a heat damage index in tomato products.

## MATERIALS AND METHODS

From two industrial food plants processing tomato pulp and tomato paste, for each processing step (Figure 1) a sample of 2000 mL was collected, stored in plastic bottles, and immediately frozen. The samples were kept in a freezer ($-25$ °C) until analysis. To calculate the holding times needed for the construction of the time–temperature profiles of the processes (see Figure 2), product temperatures, flow rates, volumes, and percentages of soluble solids (as determined by refractometer) were determined. The sampling and the measurements were repeated in two different days for each product.

In the laboratory, the following analyses were twice performed on the thawed and homogenized samples: dry matter content (g per 100 g of product), following the AOAC official gravimetric method n. 964.22 (AOAC International, 1995a); protein content (g per 100 g of product), using the Kjeldahl method (n. 920.152 AOAC International, 1995b); furosine content (mg per 100 g of proteins), following the HPLC method as proposed for milk by Resmini et al. (1990b). Furosine analytical method was adapted to tomato products as follows: to 0.5 g of tomato product with °Brix>12° (B7···B9 from Figure 1) plus 1.5 g of distilled water or 2 g of tomato product with °Brix<12° (A1···A10, B1···B6 from Figure 1) accurately weighted in 10 mL screw-cap Pyrex vials was added 6 mL of 10.6 N HCl. After nitrogen was bubbled for 1 min, the vials were sealed and kept at 110 °C for 23 h. Afterward, the sample was filtered through a 0.22 $\mu$m Millipore GS membrane (Millipore, Bedford, MA). A volume of 0.5 mL of filtrate underwent solid-phase extraction in a Sep-Pak $C_{18}$ Millipore cartridge, prewetted with methanol and water. Furosine was eluted from the cartridge using 3 mL of 3 N HCl, and 20 $\mu$L of the eluate was injected in a liquid chromatography apparatus consisting of two 510 HPLC pumps, a 680 automated gradient controller, and a 490 programmable multiwavelength detector, all from Millipore Waters (Milford, MA). The instrument was connected to a D-2500 chromato-integrator (Merck-Hitachi, Darmstadt, Germany). Operative conditions of the HPLC

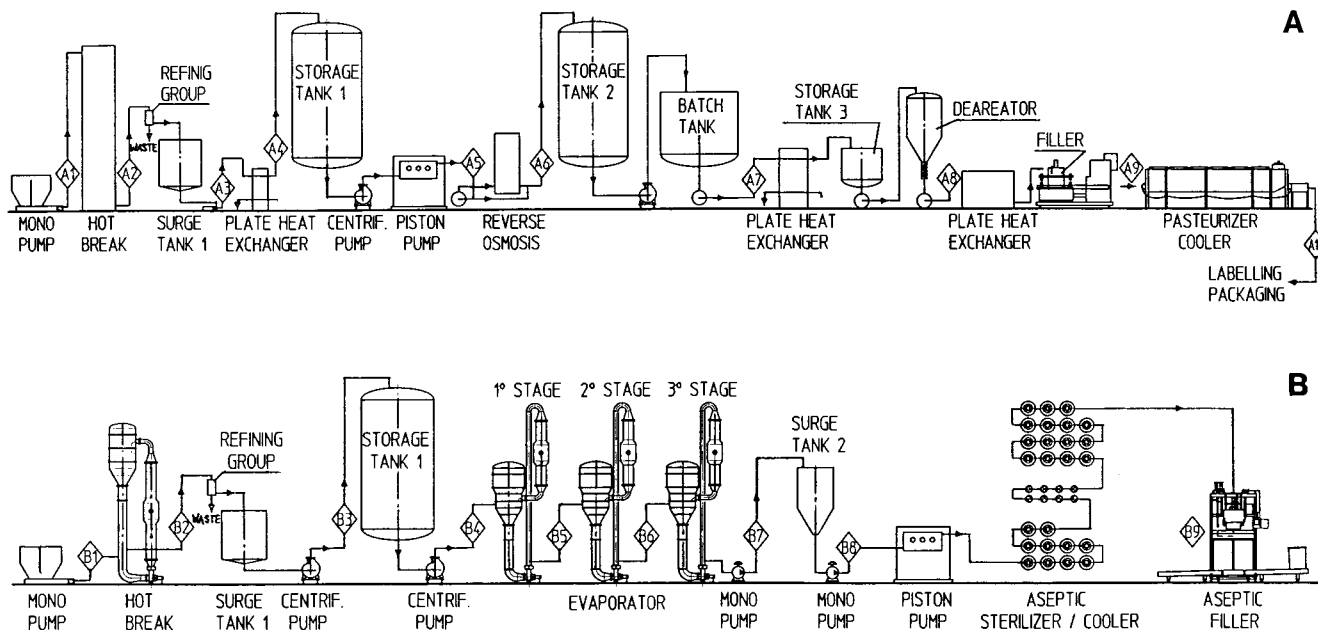**4388** *J. Agric. Food Chem.,* Vol. 46, No. 10, 1998

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**Figure 1.** Tomato pulp (A) and tomato paste (B) processing lines. A1···A10 and B1···B9 are the sampling points.
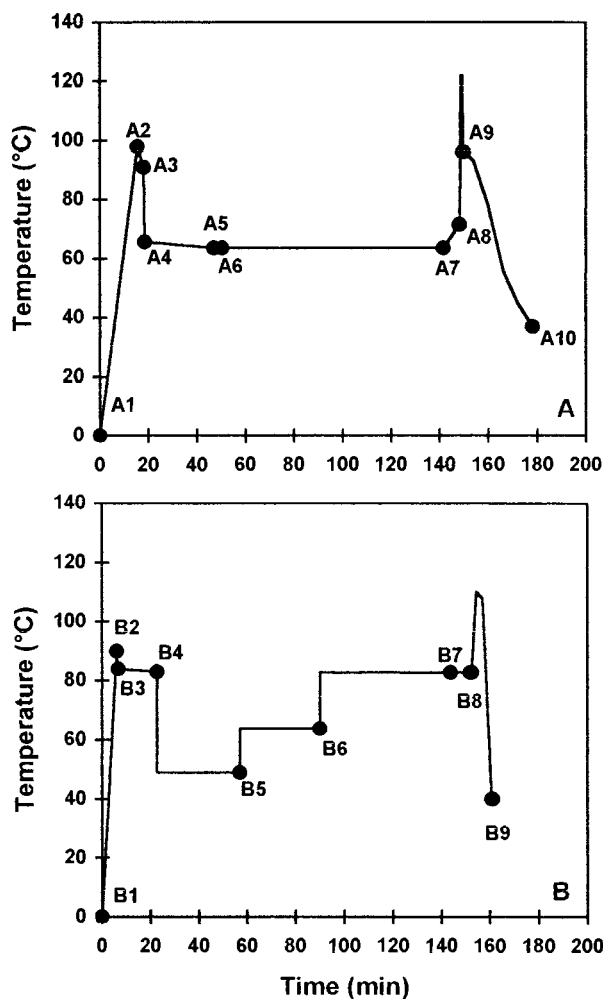


**Figure 2.** Time−temperature profiles of tomato pulp (A) and tomato paste (B) production processes. A1···A10 and B1···B9 are the sampling points.

analysis of furosine were as follows: a $C_8$ furosine-dedicated column (250 × 4.6 mm, Alltech Italia S.R.L., Milan, Italy); column temperature, 35 °C; detection multiwavelength 280 nm; mobile phase (A) 0.4% acetic acid in water, (B) 0.3%

potassium chloride in solvent A; flow rate, 1.2 mL/min. The elution gradient, expressed as proportion of eluent B, was as follows: initial condition, 2% for 13.5 min; from 2 to 50% in 7 min, 50% for 1 min; from 50 to 2% in 1.5 min, 2% for 10 min.

A calibration curve was built, using 28 different concentrations (between 0.06 and 9.36 $\mu$mol/L) of hydrated furosine·2HCl (Neosystem Laboratoire, Strasbourg, France) in 3 N HCl. Based on the calibration curve, the limit of detection was calculated as the intercept value of the regression line plus three times the standard error of the estimate (Miller and Miller, 1988).

The repeatability of the furosine analytical method in tomato pulp and tomato paste was assessed by performing, in each case, 10 replicate measurements on the same commercial sample. The results were expressed in terms of standard deviation (SD) and of coefficient of variation (CV).

To evaluate the heat damage severity, Co value was computed using the following equation

$$\text{Co} = \int_0^t \mathrm{d}t/10^{(T^* - T)/z}$$

where Co is expressed as time at the reference temperature ($T^* = 80$ °C), $t$ is the time of the treatment, $T$ is the actual temperature of the treatment (°C), and $z$ represents the increase in temperature that causes a 10-fold increase in the reaction rate, chosen in this case as 25 °C.

Finally, as a comparison, 12 tomato pulp, 6 tomato sauce, and 9 tomato paste samples from the Italian market were also analyzed following the same analytical methods formerly mentioned.

## RESULTS AND DISCUSSION

**Furosine Calibration Curve and Repeatability Test.** The furosine calibration curve was linear in the range 0.06−9.36 $\mu$mol/L ($r^2 = 0.999$), showing a detection limit of 0.15 $\mu$mol/L for the standard solution. The repeatability of the furosine analytical method, expressed in terms of mean ± SD and CV, was 140.2 ± 10.3 (CV = 7.3%) in tomato pulp and 432.3 ± 26.9 mg/100 g protein (CV = 6.2%) in tomato paste. On the basis of the CV values, method repeatability in these two products was acceptable (Horwitz, 1983).

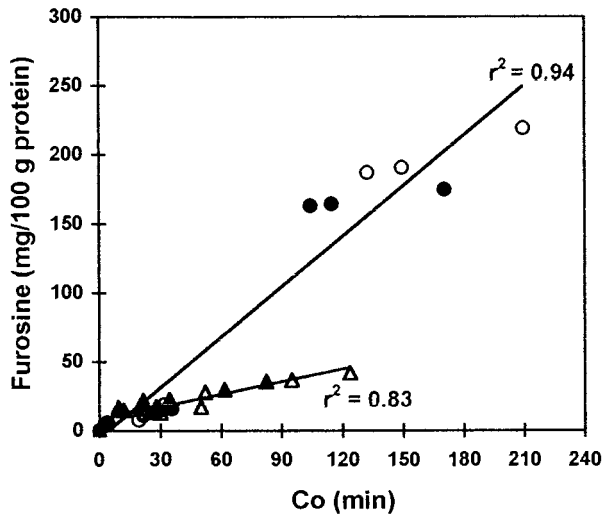**Furosine Evolution during Processing.** The time−temperature profiles of only one sampling day for

**Figure 3.** Furosine content as a function of Co value (equivalent time at a reference temperature of 80 °C) during the production process of tomato pulp (▲, △) and tomato paste (●, ○) in two different days.



**Figure 4.** Standardized furosine as a function of Co (equivalent time at a reference temperature of 80 °C) during the production process of tomato pulp (▲, △) and tomato paste (●, ○) in two different days.

each product are presented, as example, in Figure 2. To evaluate heat treatments severity the Co values were calculated at a reference temperature of 80 °C using a theoretical $z$ value of 25 °C hypothesized on the basis of the $z$ values reported by other authors for heat damage reactions in other food products (Kessler, 1981; Pompei and Rossi, 1994; Pompei and Spagnolello, 1997). At present a research is conducted to study furosine formation kinetics in tomato products.

Figure 3 reports furosine content evolution during tomato pulp and tomato paste processing, along with the regression lines considering the data of the two sampling days. For both processing lines, the final Co values are different in the two sampling days: for tomato pulp because of the different time passed in the storage and batch tanks (from A6 to A7) and for tomato paste because of the different holding time in the third evaporator stage (from B6 to B7); these slight changes lead to different Co value in the sampling points (Figure 3). Furosine level increased linearly ($p \leq 0.001$) as a function of the heat treatment severity (Co) along the processes [$r^2 = 0.83$ ($n = 20$) for the pulp and $r^2 = 0.94$ ($n = 18$) for the paste] and showed different slopes for both products.

The sudden increase of furosine in the third stage of evaporation (from B6 to B7) seems to be caused not only by the heat treatment intensity but also by the higher dry matter contents reached (from ca. 12 to ca. 31%): under these conditions, the reactant chemical availability is higher. This hypothesis is confirmed by Figure 4, that shows the standardized furosine values [mg furosine/(g protein·g dry matter)] obtained dividing the furosine levels (mg/100 g protein) by the dry matter percentage. This standardization highlights a linear increase ($r^2 = 0.84$) of furosine as a function of Co, independently from the product type.

**Furosine in Tomato Products Collected from the Market.** The furosine levels of several samples collected from the Italian market of tomato pulp, tomato sauce, and tomato paste identified by their dry matter content are presented in Figure 5A. There is a great variation in quality, as expressed by furosine content, among the samples of each product, suggesting a high variability of the processing conditions adopted by the
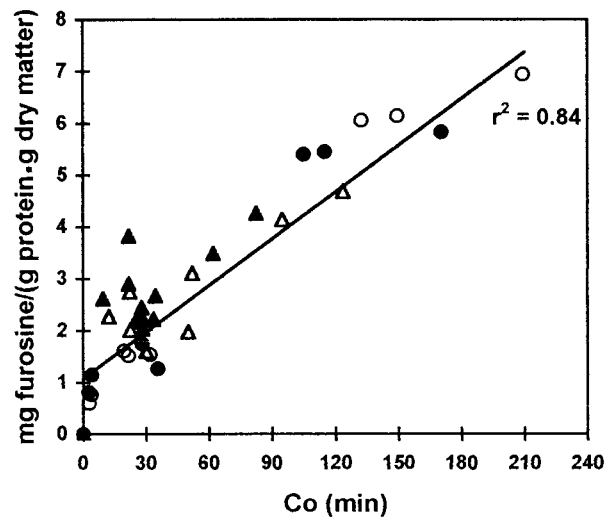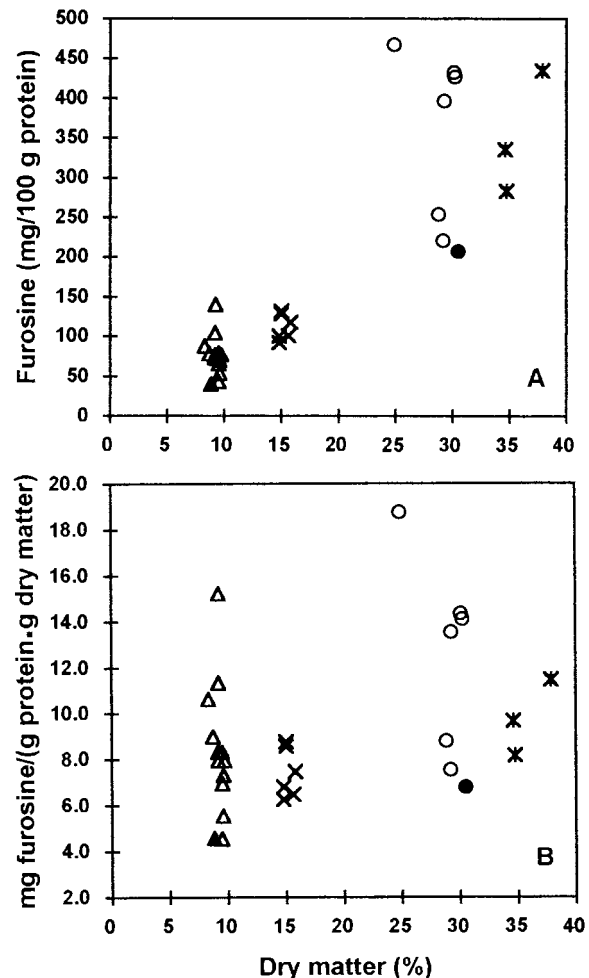


**Figure 5.** Furosine (A) and standardized furosine (B) as a function of dry matter content of different tomato products sampled in the Italian market: tomato pulp (△), tomato sauce (×), tomato paste (○, *). Solid symbols (▲ and ●) represent the two end product samples studied in this research (A10 and B9).

different producers. Figure 5B presents the standardized furosine values of these commercial samples: the difference in data suggests that, independently from the

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product type, the various processing plants adopt technologies that cause very different thermal damages to the end product.

Hence, the results presented in this study show that furosine is a very good index of heat damage even in the initial steps of the Maillard reaction; furthermore, it differentiates sharply between processing technologies and allows discrimination among the products available on the market.

## ABBREVIATIONS USED

Co, defined for a given heat treatment as the time required to get, at the reference temperature, the same chemical effect of the heat treatment, with reference to a well-defined reaction; CV, coefficient of variation; HMF, 5-(hydrodymethyl)-2-furfural; HPLC, high-performance liquid chromatography; *p*, probability; $r^2$, determination coefficient; SD, standard deviation; $T^*$, reference temperature (°C); *T*, temperature (°C); *t*, time (s); *z*, increase in temperature that causes a 10-fold increase in the reaction rate (°C).

## ACKNOWLEDGMENT

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