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Degradation kinetic (D_{100}) of lycopene during the thermal treatment of concentrated tomato paste

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ABSTRACT

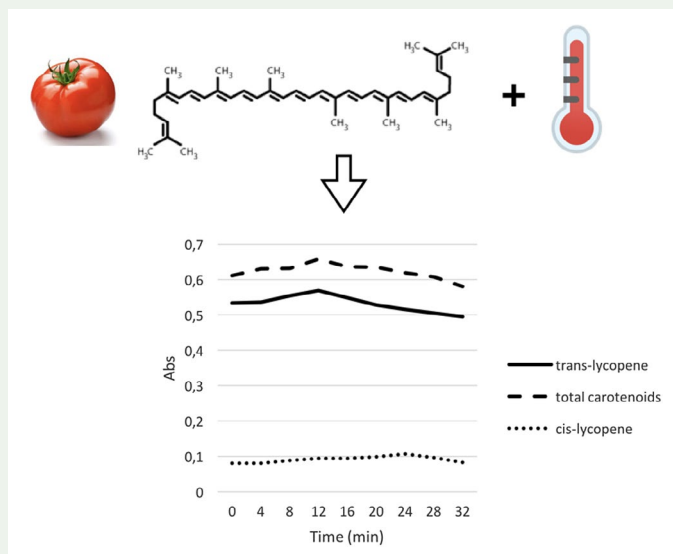
Heat treatments can cause degradation in tomatoes of lycopene which has important antioxidant effects. No information about decimal reduction time (D_{100}) of lycopene is available. D -value is the time required at a given temperature to reduce 90% of the molecule. This study for the first time determine the kinetic of lycopene thermal degradation. The content was measured at regular intervals of pasteurization using canned tomato paste to determinate D value. Microbiological analysis was carried out to verify product stability after packaging. Yeasts, molds and lactic acid bacteria were determined. The pasteurization time allowed to observe a loss of the red color. Lycopene content, after an increase at 8 min, decreased at 32 min of pasteurization. D_{100} value was calculated at 75 min; a diminution of 90% in lycopene content in the concentrated tomato paste was observed. Microbiological analysis confirmed the stability of products after 8 min of pasteurization.

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1. Introduction

Tomatoes and their derivatives are an important source for the food industry. Italy is the European leader in tomato transformation with about 5200 metric tons of tomatoes addressed to become processed products by the food industry (Tomato World Processing Council 2017). Tomatoes health beneficial effects have been linked to the presence of lycopene in fresh and processed tomatoes (Gama et al. 2006), and this stimulated studies on recovery of lycopene from vegetal sources and processing by products (Naviglio et al. 2008a, 2008b) which can be an valuable raw material for other industrial uses (Baaka et al. 2016). Epidemiological studies have shown that the intake of tomatoes and tomato-based products may reduce the risk of different types of cancer and this has been associated with lycopene content of tomato (Marti et al. 2016; Bacanli et al. 2017) and cardiovascular diseases (Costa-Rodrigues et al. 2018). Lycopene is a carotenoid, responsible for the red colour of tomatoes as well as for other vegetals, e.g. guava, rosehip, watermelon, and pink grapefruit (Alda et al. 2009). Among the other carotenoids contained in tomatoes, such as β -carotene, ζ -carotene, phytofluene, phytoene, α -carotene, and lutein, lycopene is the most abundant, being present in a range from 6 to 540 mg/kg, depending on several factors related to the cultural practices, variety and maturity (Odriozola-Serrano et al. 2008). The concentration of secondary metabolites present in tomatoes depends on many factors, and recently multi-variate analysis has been coupled to High Resolution Magic Angle Spinning Nuclear Magnetic Resonance to allow to discriminate between different origin samples of tomatoes allowing also to assess the lycopene content (Mallamace et al. 2014). This is, in fact, a complex effect, which impact on the phytonutrients (e.g. abscisic acid, abiotic and biotic stress, etc.). The characteristic pigmentation of red ripe tomato fruit is the result of the *de novo* synthesis of carotenoids, e.g. lycopene and β -carotene, which are associated with the change in fruit colour from green to red as chloroplasts are transformed to chromoplasts. The genetic background of tomato variety influence their content, but this does not exclude that environmental factors also strongly affect it, e.g. lycopene content and colour of ripening tomatoes are affected by environmental conditions (Brandt et al. 2003, 2006). Among the relevant aspects to be considered when dealing with this vegetal, it must be mentioned the beneficial effect of using on field natural herbicides environmental friendly (Cimmino et al. 2012) since bioactive compounds content could be affected, as well as the possible contamination of this vegetal due to the presence of *Fusarium* spp. microfungi and their secondary metabolites affecting the beneficial compounds content of the vegetal matrix (Mikušová et al. 2013). Lycopene, molecular formula is $C_{40}H_{56}$, is an acyclic open-chain polyene with 13 double bonds. Because of its highly unsaturated structure, it has good antioxidant properties with ability of quenching singlet oxygen and free radicals (Gharbi et al. 2016; Mueller et al. 2016). Lycopene is present in fresh vegetables in the all-trans form, which is the most thermodynamically stable one. During processing and storage, isomerisation from all-trans to mono-cis or poly-cis forms and oxidation can occur (Shi et al. 2008). Cis isomers of lycopene have different physical and chemical properties: lower melting points; decreased color intensity; lower extinction coefficient; a displacement of λ_{max} to shorter wavelength and a reduction in vibrational fine structure. Oxidative degradation of carotenoids, including lycopene, is due to the exposure to oxygen, high temperature, exposure to light and extreme pH conditions. Processing of tomatoes determines some changes, in particular improves the bio-availability and bioaccessibility of lycopene for absorption by the gut, particularly if processed

in the presence of lipids (Page et al. 2012; Palmero et al. 2014; Martinez-Hernandez et al. 2016; Cilla et al. 2018). During concentrated tomato paste processing, the product is packed in tinplate boxes at about 90 °C and, after crumbling, the boxes are subjected to heat treatment in a hot water bath at 100 °C for 3 min. Typically for small sizes, this thermal treatment is carried out to ensure the total sterility after boxing and crunching.

In this study, the lycopene content and changes in the colour during thermal treatment of concentrated tomato were evaluated. The pasteurization was prolonged until 32 min to observe the effect of the heating on lycopene content and to estimate the decimal reduction time (D_{100}) of this important substance. At the best of our knowledge, no data in the scientific literature are currently available.

2. Results and discussion

Samples treated for different times showed comparable values of pH, acidity, optical residue and reducing sugar. Results are reported in Table 1. No significant differences were detected with the increase in thermal treatment time. Brightness (L), red saturation index ('a'), yellow saturation index ('b'), and delta E values obtained during heat treatment are reported in Figure 1. During pasteurization, a general reduction of brightness (L) was observed. In particular, after 16 min of treatment, a significant decrease of 1.72% was observed respect to the control samples (tomato paste at time 0).

The parameters 'a' and 'b' also showed a decreasing trend with prolonging of treatment. In particular, significant differences after 16 min of treatment were observed in both cases, with a reduction of 1.54% and 1.41% for 'a' and 'b' respectively. As a consequence, hunter a/b ratio showed significant reduction after 28 min of treatment (2.45%). Colour differences increased with time of treatment. As can be observed in the Figure 1, up to 16 min, Delta E values were between 0.2 and 0.5 and, therefore, colour differences were not distinguishable. Instead, Delta E values of the samples collected from 16 to 32 min increased progressively until reaching values between 2 and 2.5 corresponding to very distinct colour differences. The reduction of colour parameters confirmed that the excessive heat treatment can reduce the colour of concentrate paste. Isomerization of carotenoids, formation of brown pigments (Maillard-derived compounds), changes in physical state of lycopene are reported as possible causes of these variations (Shi et al. 2008). These results were confirmed by serum color analysis as shown in Figure 1, where absorbance at 420 nm showed an increase during the heat treatment that could be due to non-enzymatic browning reactions and increase of the oxidation products.

Together with carotenoids, tomato is known as good source of phenols (Patras et al. 2009). TP in control sample was 211.2 mg / 100 g dry matter (dm), within the range normally reported in scientific literature (140–250 mg/100 g dm) (Capanoglu et al. 2008; Vallverdu-Queral et al. 2012). Significant differences were observed for samples treated for 28 min, showing a reduction of 10%. Major differences were observed in the sample treated for 32 min, where TP were reduced of 17% respect to the untreated sample, showing a value of 175.2 mg/100 g dm.

Figure 1 reports the analysis of carotenoids and show that all-*trans*-lycopene is the principal pigment present in the tomato concentrate. Xianquan et al. (2005) indicated temperatures above 100 °C as ideal for the formation of lycopene cis isomers. Other authors (Sharma and Le Maguer 1996) indicated, instead, no formation of cis isomers since the reaction is so



Table 1. Basic parameters (pH, optical residual, acidity, NaCl, reducing sugars) of samples collected at different pasteurization times and lycopene content in samples treated at different time and temperature (°C).

	Time (min)									
	0	4	8	12	16	20	24	28	32	
pH	4.32 ± 0.01	4.33 ± 0.01	4.32 ± 0.02	4.32 ± 0.02	4.32 ± 0.01	4.33 ± 0.01	4.32 ± 0.02	4.32 ± 0.02	4.32 ± 0.01	4.32 ± 0.01
Bx	18.55 ± 0.16	18.66 ± 0.13	18.73 ± 0.03	18.71 ± 0.05	18.55 ± 0.16	18.66 ± 0.13	18.73 ± 0.03	18.73 ± 0.03	18.71 ± 0.05	18.71 ± 0.05
Acidity (g/100 g)	1.14 ± 0.01	1.11 ± 0.03	1.11 ± 0.05	1.14 ± 0.05	1.14 ± 0.03	1.11 ± 0.01	1.11 ± 0.03	1.11 ± 0.03	1.14 ± 0.02	1.14 ± 0.01
NaCl (g/100 g)	0.48 ± 0.01	0.49 ± 0.02	0.46 ± 0.01	0.45 ± 0.03	0.48 ± 0.02	0.49 ± 0.02	0.46 ± 0.03	0.46 ± 0.03	0.45 ± 0.02	0.45 ± 0.03
Reducing sugars (%)	9.82 ± 0.12	9.87 ± 0.11	9.86 ± 0.09	9.85 ± 0.32	9.82 ± 0.12	9.87 ± 0.11	9.86 ± 0.09	9.86 ± 0.09	9.85 ± 0.32	9.85 ± 0.32
Dry matter (%)	19.97 ± 0.10	20.04 ± 0.31	20.09 ± 0.07	20.02 ± 0.07	20.05 ± 0.06	20.03 ± 0.10	20.05 ± 0.05	20.05 ± 0.05	20.06 ± 0.06	20.09 ± 0.08
Lycopene (mg/100 g dm)	180.91 ^b ± 0.67 (<i>T</i> = 88.6)	208.63 ^a ± 2.35 (<i>T</i> = 90.0)	216.00 ^b ± 3.10 (<i>T</i> = 91.3)	188.24 ^b ± 3.14 (<i>T</i> = 93.2)	176.6 ^b ± 2.01 (<i>T</i> = 94.6)	181.27 ^b ± 0.88 (<i>T</i> = 96.6)	183.82 ^b ± 0.79 (<i>T</i> = 97.7)	189.14 ^b ± 0.22 (<i>T</i> = 98.5)	150.37 ^c ± 0.32 (<i>T</i> = 98.7)	

Note: Different letters correspond to statistical significant differences ($p < 0.05$).

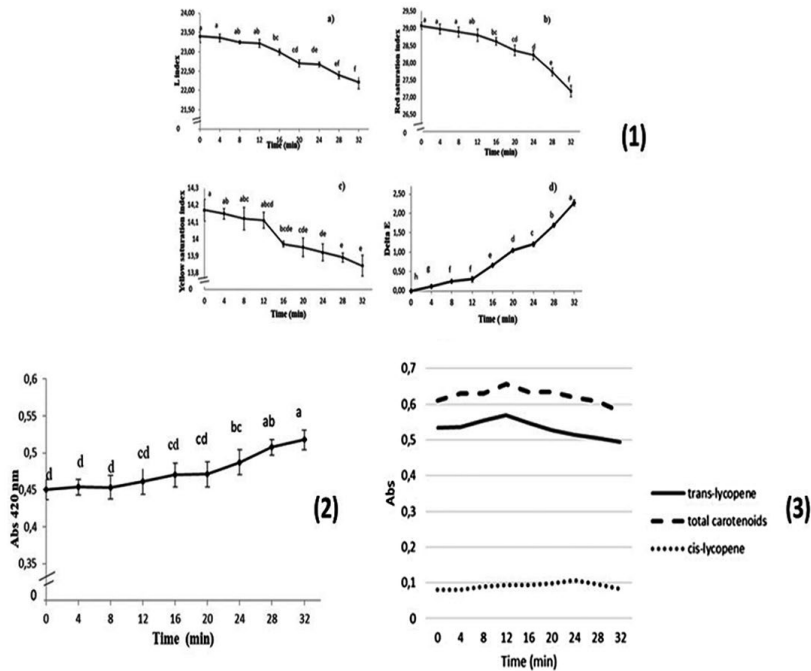


Figure 1. Trends of color scale values (L,a,b and Delta E) during heat treatment.

Notes: Different letters for the same parameter correspond to statistical significant differences ($p < 0.05$) (1); trend of serum absorbance at 420 nm during treatment. Different letters correspond to statistical significant differences ($p < 0.05$) (2); total carotenoids, trans and cis-lycopen absorbance of tested samples during pasteurization (3).

fast that they are immediately degraded. In our case, the absorbance of the *cis* isomers remained constant respect to the control sample during the experimental treatment.

In Table 1 the lycopene content found for different time-temperature conditions is reported. Lycopene increased during the first 8 min of treatment when temperature was 91.3 °C. The higher lycopene content (216 mg/100 g dm) could be attributed to a better extractability of carotenoids due to disintegration of chromoplasts and melting of carotenoid crystals (Patras et al. 2009). It is known that several factors can affect lycopene content during thermal treatment, such as degradation, isomerization from trans to cis form and efficiency of extraction from the matrix (Shi et al. 2008). Analysis of samples treated for 20 to 28 min did not show significant variations respect to the initial content. A significant reduction was observed in the samples treated for 32 min where a reduction of lycopene nearly 19% was observed respect to control samples. These results are in agreement with Luterotti et al. (2014) who reported a reduction of 20% after 20 min of treatment.

As previously reported, the lycopene content was influenced by the time-temperature conditions. From the first and the second Bigelow laws, the decimal reduction times (D) of lycopene at 98 and 94 °C and the decimal reduction temperature (z) were calculated. D_{98} and D_{94} were respectively 93 and 144 min, while z value was about 22 °C. These parameters allowed to calculate the decimal reduction time at 100 °C (D_{100}) which was found to be 75 min. Microbiological analysis confirmed the sample stability since no microbial growth was detected.

3. Conclusions

Lycopene is the main responsible for the characteristic red colour of tomatoes. With increase in treatment time of pasteurization for the preparation of concentrated tomato paste, colour differences resulted noticeable after 16 min. The reduction of colour parameters confirmed that the excessive heat treatment can reduce the red colour of concentrated paste. In this study, the D value of lycopene was calculated. D value is the time required at a given temperature to reduce 90% of the molecule. Obtained results suggested that lycopene is a very stable molecule, since treatment carried out at 100 °C with a duration of 75 min can cause its diminution of 90% in concentrated tomato paste.

Disclosure statement

No potential conflict of interest was reported by the authors.

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