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Kinetics of the thermal degradation of lycopene in tomatoes

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ABSTRACT

This research studied the kinetics of the thermal degradation of lycopene in tomatoes using elevated temperature testing. Understanding the nature and the extent of sensitive nutrient degradation in tomatoes will assist in reducing postharvest nutrient losses during storage and processing. Ripe tomatoes were sorted, washed, and blinded. Juice was obtained by filtering the blinded pulp through a muslin cloth. The samples were heated using a water bath at 70, 80, 90, and 100 °C for 20, 40, 60, and 80 minutes. The determination of lycopene was done using spectrophotometric methods at 503 nm, in hexane: ethanol: acetone (2:1:1 v/v/v) lycopene extract. The concentrations of lycopene were determined immediately after processing. The data was found to fit into first order equations. Degradation constants (k), D-value, and half-life for the thermal degradation of lycopene were determined at each processing temperature. Models were also developed for each of the chosen temperatures, which can be used to predict the degradation pattern of lycopene at other processing conditions. Z-value, Q_{10}, and activation energy for the degradation of lycopene were also determined. Analyses showed a considerable decrease in lycopene concentration and decimal reduction time (D-value), and a significant increase in the thermal degradation rate (*k*) during heating from 70 to 100 °C. The finding shows that the degradation of lycopene in tomatoes followed the first order kinetics and it shows that the lycopene content decreased at 80 to 100 °C.

Introduction

Tomatoes and its products are rich sources of carotenoids, such as lycopene, β-carotene, and lutein (Laura et al., 2013). Lycopene ($C_{40}H_{56}$) is a carotenoid with a molecular weight of 536.85 g/mol and it occurs in food predominantly in the *trans* form (EFSA, 2008). Lycopene is a lipid soluble carotenoid that is mainly synthesised by plants and microorganisms (Anese et al., 2013). Lycopene is an antioxidant which is responsible for the colour of ripe tomatoes, and can easily suffer losses when subjected to higher temperatures (Manzo et al., 2018). The potential of tomatoes for reducing chronic diseases, including cancer and cardiovascular related diseases, was reported in many epidemiological studies (Hackett et al., 2004; Ishida et al., 2007; Ademoyegun et al., 2009; Anese et al., 2013; Srivastava, 2017). Lycopene was reported to prevent many ailments such atherosclerosis, coronary artery disease, prostate cancer, and breast cancer. It prevents the oxidation of low-density lipoprotein and helps to reduce the cholesterol level in the blood. Moreover, lycopene may lower the risk of molecular degenerative disease, lipid oxidation, serum, and cancer of the lungs, skin, and bladder (Rao and Agarwal, 1999). Health benefits and colouring potentials of lycopene make it important to food manufacturers (Davis et al., 2003).

Tomato is botanically a fruit and it is considered a vegetable for culinary purposes, which has caused some confusion. Tomato may be consumed as raw or as an ingredient in several dishes, sauces, salads, and drinks. Tomatoes are rich in carbohydrates, minerals, and important antioxidants, and they are considered

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the most important source of lycopene in many human diets (Rao et al., 1998). As an antioxidant, lycopene has a singlet oxygen quenching capacity twice than that of β-carotene and 10 times than that of α-tocopherol (Weisburger et al., 2002).

Chemical kinetics helps food scientists in understanding the mechanisms and the extent of chemical reactions in foods during storage and processing. It also helps to predict what will happen to quality parameters under a range of storage and processing conditions (Martinus and Boekel, 2008).

Reduction in quality is encountered during fruit and vegetable processing, micronutrients such as vitamins and lycopene suffer more during transformation and storage, and this is of important concern to food producers (Pénicaud et al., 2010). Nutrient retention during processing is a prerequisite to the production of a better-quality end product. The stability of nutrients during processing depends on the nature of the commodity and the severity of the processing. Information in kinetics studies assists in quality retention through process optimisation (Tola and Ramaswamy, 2015).

Thermal degradation of lycopene obeys first order kinetics and its reaction rate constant depends on the processing conditions (Galicia et al., 2008). The temperature effect and the kinetic study of lycopene during degradation shows that all-trans-lycopene is partially modified to a cis-trans isomer and it is an end reaction product (Kanasawud and Crouzet, 1990).

Materials and methods

Tomatoes

Nigerian grown *UC 82B* variety of tomato was used in this research. Fresh matured tomatoes were collected from a local farm in Wudil town Kano State, Nigeria. The collected samples were sorted according to similarity in colour, size, ripening level, and absence of surface defects (Adak et al., 2017). The sorted tomatoes were washed using distilled water and pulped using an electric blender (Master Chef, MC-J2101). Juice was obtained by passing the pulp through a muslin cloth.

Chemicals

Acetone was purchased from Moller Chemie, Germany. Hexane and ethanol were purchased from Merck, Germany.

Thermal treatments

The juice (30 ml) was transferred into a test tube and heated at 70, 80, 90, and 100 °C for 20, 40, 60, 80, and 100 minutes in a thermostatic water bath (Techmel USA, TT420). The non-heated sample was used as control. Analyses were carried out immediately to avoid further degradation of the lycopene by environmental factors.

Spectrometry and lycopene assay

Lycopene in the tomato samples was extracted using a mixture of hexane: ethanol: acetone in the ratio 2:1:1 (v/v/v) (Sharma and Maguer, 2006). Two grams of thoroughly homogenised sample was mixed with 25 ml of hexane: ethanol: acetone, the mixture was vortexed for 30 minutes, 10 ml of distilled water was then added and vortexed for another 2 minutes. The solution was then allowed to stand for 10 minutes to allow the separation into distinct phases and the disappearance of air bubbles.

Spectrophotometry

Spectrometric analysis was done using an UV/Vis spectrophotometer (Jenway Germany, 752). The absorbance was measured at 503 nm using hexane as blank. (Fish et al., 2002). The lycopene concentration was calculated according to the following equation.

$$\text{Lycopene} = A_{503} \times 171.7/W \qquad (1)$$

where: W = weight of sample; A = absorbance

Determination of Kinetics Parameters

Degradation constant (k)

The degradation of lycopene was reported to obey the first order reaction model (eqn 2) (Petros et al, 1997; Devinder et al., 2006). The rate constants at different temperatures were calculated by plotting the logarithm of the ratio C/C_o against time ***t***. The slop of the plot equalled to the rate constant *k*.

$$ln\frac{C}{C_o} = -kt \qquad (2)$$

where: C_o is the initial lycopene concentration at time equal to zero, and C is the concentration at time t

Half-Life

Half-life is the time required for the initial concentration to reduce by 50%. Half-life of the lycopene was determined using equation 3 below

$$t_{1/2} = -\frac{\ln(0.5)}{k} \qquad (3)$$

D-Value

The Decimal Reduction Time (D-value) indicates the heating time results in the 90% destruction of a quality parameter as compared to the initial concentration (at *t*=0) at constant temperature. D-value was determined using equation 4.

$$D = \frac{2.303}{k} \quad (4)$$

Thermal sensitivity (z-value)

The Z-value represents the temperature level increase required to decrease the *D* value by a factor of 10. The slope of log D against temperature represents the z-value.

Q_{10} Value

The Q_{10} value of a reaction is often used for reporting the temperature dependence of biological reactions. It is defined as the number of times a reaction rate changes with a 10 °C change in temperature. The Q_{10} value was calculated using equation 5.

$$Q_{10} = \left(\frac{k_2}{k_1}\right)^{\frac{10}{T2-T1}} \quad (5)$$

Activation Energy

Activation energy represents the sensitivity of the reaction rate to changes in temperature. Activation energy was determined using the Arrhenius law (equation 6) by plotting lnk against 1/T.

$$\ln(k) = \ln(A) - \frac{E_a}{R}\frac{1}{T} \quad (6)$$

where: R = 8.31 J·mol^{-1}·K^{-1}, the parameter A is the frequency factor which is taken as independent of temperature and the Ea is the Arrhenius activation energy.

Results and discussion

The lycopene content and degradation during heat treatment is shown in Table 1. The lycopene from a fresh tomato was found to be 10.99 mg/100 g, which was recorded to be lower than the value reported by Liana et al. (2009) in a fresh tomato and paste, which were respectively 12.34 mg/100 g and 15.83 mg/100 g. The higher content may be due to geographical or environmental factors such as soil nutrient composition, post planting operation adopted, etc. During thermal processing, the lycopene content shows a decrease from 0 to 80 min in all the processing temperatures. The reduction in lycopene concentration during thermal treatment was reported by Luterotti et al. (2014) in commercial double concentrated tomato puree, a contrary opinion was reported by Dewanto et al. (2002) in the lycopene extracted from fresh cooked tomato slurry. There was less heat sensitivity of lycopene evaluated at 70 °C, while the processing at 80, 90, and 100 °C caused high degradation. Szalóki-Dorkó et al. (2015) also observed the greatest thermal degradation of anthocyanin at 90 °C in sour cherries.

Table 1. Lycopene in tomatoes during heat treatment

Time (Mins)	Lycopene (mg/100g) Processing Temperature (°C)			
	70	**80**	**90**	**100**
0	10.99±0.03	10.99±0.02	10.99±0.01	10.99±0.00
20	10.82±0.01	10.65±0.00	10.47±0.02	10.39±0.01
40	10.73±0.01	10.39±0.01	10.04±0.00	9.87±0.00
60	10.39±0.02	10.04±0.01	9.62±0.02	9.36±0.02
80	10.13±0.01	9.79±0.00	9.36±0.01	9.01±0.01

Note: Values are Mean±SD of triplicate measurements

The first-order reaction kinetics of lycopene in tomatoes treated at temperatures from 70 to 100 °C is illustrated in Fig. 1. High correlations (R^2 = 0.9554 to 0.9981) were obtained in linear regressions (Table 2). Fig. 2 is a plot of Temperature against Log D for the thermal degradation of lycopene. Plot of ln k vs. 1/T for lycopene degradation during heating is presented in Fig. 3. The reaction rate constants at different temperatures were different and they ranged from 0.001 m-^{1} at 70 °C to 0.0025 m-^{1} at 100 °C (Table 2). Thermal treatment and mechanical processing disrupt food matrices and increase the bioavailability of carotenoids through formation of *cis*-isomers (Urbonavičienė et al., 2015). Temperatures between 75 – 100 °C enhanced lycopene isomerisation during storage (Hackett et al., 2004). Laura et al. (2013) reported partial degradation and isomerisation of lycopene in tomatoes exposed to higher temperatures, and they also opined that the thermal denaturation of protein and breaking down of crystal aggregates enhance lycopene extractability, because lycopene was reported to be more stable when bound to proteins inside a vegetable matrix. The degradation of lycopene during the lyophilisation process and lower extractability of lycopene in freeze-dried tomatoes were reported by Georgé et al. (2011).

The destruction rate of lycopene is faster during thermal processing than during other methods like high pressure processing (Tola and Ramaswamy, 2015). A moderate heat treatment has no negative effects on the

bioavailability of carotenoids (Marx et al., 2003). Antioxidants such α-tocopherol and BHT and the addition of turmeric and lime mixture during blanching minimises lycopene oxidation during the thermal treatment (Hackett et al., 2004; Dutta et al., 2013). Low-temperature processing and storage, and the use of an oxygen-resistant packaging system minimises lycopene degradation during processing and storage (Li et al., 2018).

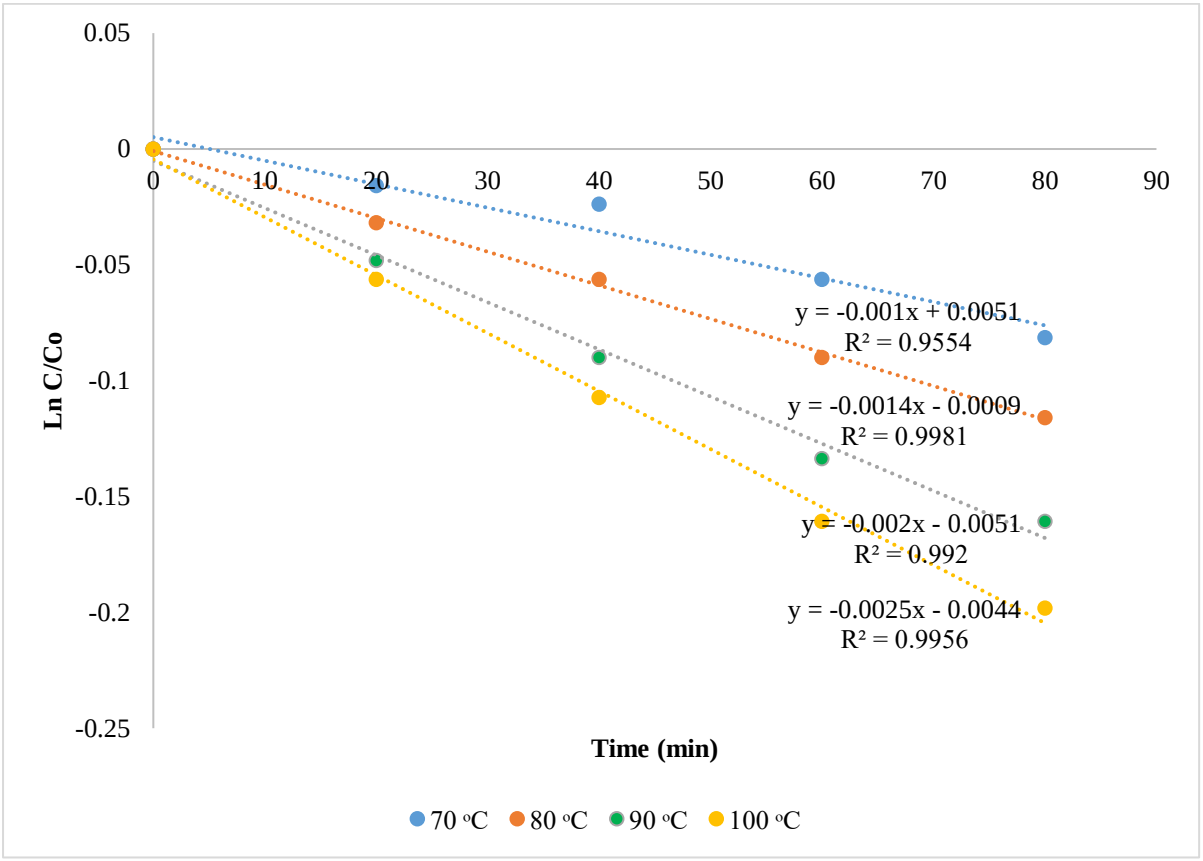

Fig. 1. First order plot for lycopene degradation at 70, 80, 90, and 100 °C

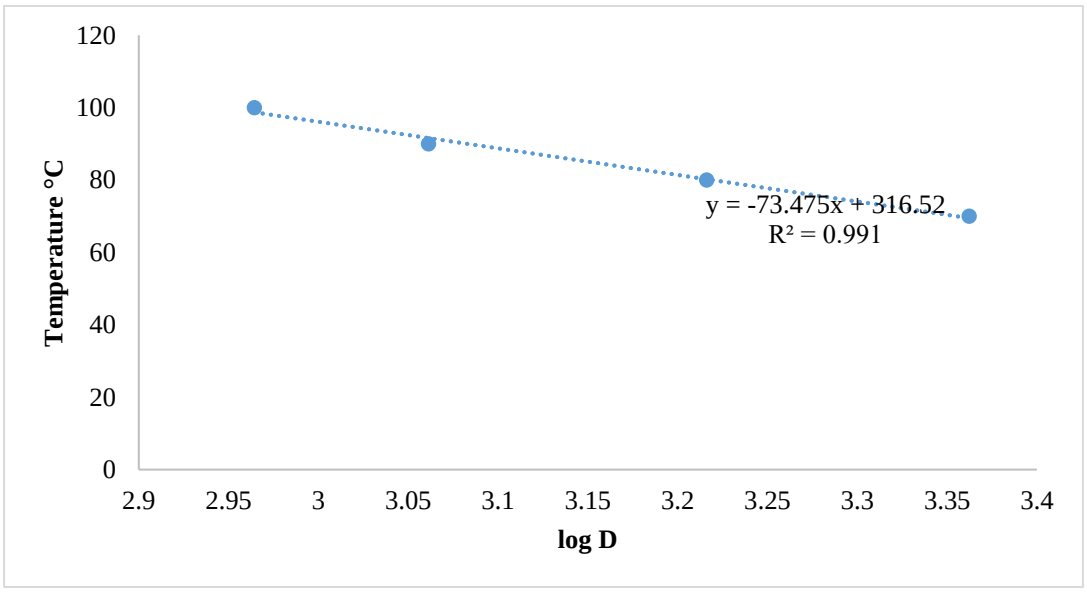

Fig. 2. Plot of temperature against log D for the thermal degradation of lycopene

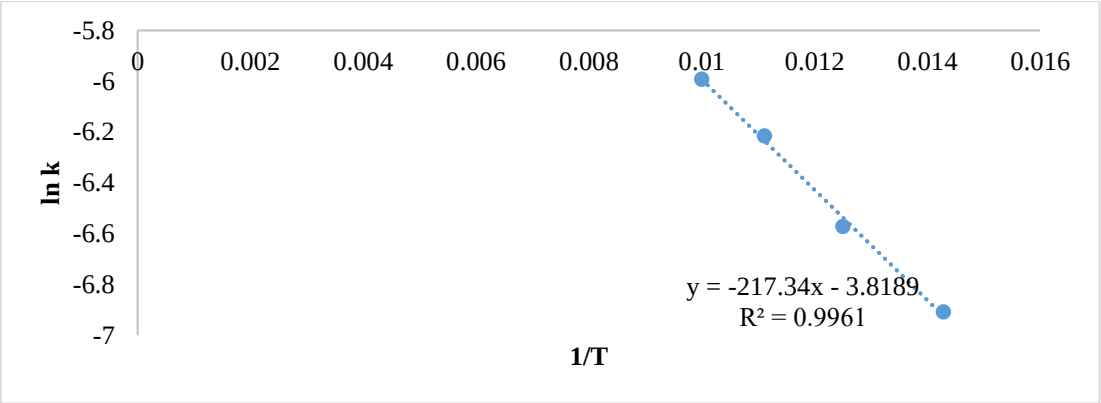

Fig. 3. Plot of ln k vs. 1/T for lycopene degradation during heating

Table 2. Rate constant, D-value, half-life, and the proposed model for the thermal degradation of lycopene in tomatoes

Temperature (°C)	Rate Constant (*k*) (m^{-1})	D-Value (min)	Half-Life (min)	Proposed Model	R^2
70	0.001	2303	693	y = -0.0010x + 0.0051	0.9554
80	0.0014	1645	495	y = -0.0014x - 0.0009	0.9981
90	0.002	1152	347	y = -0.0020x - 0.0052	0.992
100	0.0025	921	277	y = -0.0025x - 0.0044	0.9956

Table 3. Z-value, Q_{10}, and activation energy for the thermal degradation of lycopene in tomatoes

z-value (°C)	Q_{10}	Activation energy (kJ/mol)
73.48	1.40	1.8

Conclusion

Models for the prediction of the degradation trend of lycopene during thermal processing were successfully developed. The finding shows that the degradation of lycopene in tomatoes followed the first order kinetics. Further, it showed that at the temperatures (70 to 100 °C) used in this study, there was a significant increase in the thermal degradation rate (k). The lycopene content showed a significant decrease during the treatment at 80 to 100 °C compared to 70 °C, which led to the conclusion that the heat stability of lycopene in tomatoes depended on the temperature. The present finding will serve as a basis for the selection of the best temperature suitable for processing, in order to preserve the lycopene content in tomato products. A lower temperature is recommended for thermal processing of tomatoes to achieve better quality.

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