

Research Article

Kinetics of the Degradation of Carotenoid Antioxidants in Tomato Paste

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Abstract: Tomatoes show potential of lowering the risk of prostate cancer and cardiovascular diseases owing to its carotenoid and other antioxidants. In this study, the degradation of lycopene and beta-carotene contents in tomato paste produced from two cultivars (Roma and *Ajindi-kerewa*) was investigated. Tomato paste produced from the two tomato cultivars were subjected to various temperatures and heating times treatments. The results indicated that high temperature (120°C) and long time (90 min) treatments influence lycopene and beta-carotene degradation in the two cultivars during processing to a great extent. The extent of lycopene degradation was however slightly higher in Roma cultivar (7.3-3.5 mg/100 g) compared to *Ajindi-Kerewa* cultivar (2.0-1.2 mg/100 g) within the temperature and time frames and the beta-carotene degradation in the tomato paste produced from the cultivars followed a similar trend. The degradation of lycopene and beta-carotene followed first order kinetics, with the rate constants increasing with processing temperatures. The higher activation energy in the lycopene degradation process of *Ajindi-kerewa* cultivar (8.65 kJ/mol) suggested that its lycopene is more thermally stable than that in Roma cultivar and the values may be cultivar dependent. The results showed that lycopene and beta-carotene in tomato pastes are better retained using low-temperature and short-time heat processing method.

Keywords: Beta-carotene, degradation, lycopene, preservation, processing, tomato

INTRODUCTION

Raw fruits and vegetables are typically touted as superior to their processed (canned and frozen) counterparts. However, in the case of tomatoes, processing add value by increasing the absorption of lycopene (the characteristic deep-red color of ripe tomato fruits and tomato-based foods) which serves as a measure of total quality (Gärtner *et al.*, 1997). Tomatoes and tomato-based foods are the major sources of lycopene and are considered to be important contributors of carotenoids to the human diet (Porrini *et al.*, 1998). Consumers and the food industries have shown more interest in lycopene due to increased awareness on the health benefits of lycopene (Burton-Freeman and Reimers, 2011). Around 85% of the ingested lycopene comes from tomatoes and tomato products, while watermelon, papaya and pink grapefruit contribute a few percentage (Grunwald *et al.*, 2002).

Lycopene as a natural antioxidant may provide protection against a broad range of epithelial cancers. Lycopene has been associated with the prevention of prostate, head and neck cancers and might be strongly

protective against neurodegenerative diseases (Rao and Balanchandran, 2002; Freedman *et al.*, 2008; Zhang *et al.*, 2009). Regular tomato consumption has been reported to be associated with decrease in the incidence of chronic degenerative diseases such as certain types of cancer and cardiovascular diseases (Giovannucci, 1999). These beneficial effects of tomato consumption are generally attributed to carotenoids, which have the potential to reduce the risk of certain types of cancer, arteriosclerosis and cataract formation (as reviewed by Frusciante *et al.* (2007). Processing such as cooking or chopping is believed to enhance bioavailability of lycopene by breaking down sturdy cell walls, thus making carotenoids more accessible (Shi *et al.*, 2003). Processing also help to convert some of the trans-isomers of lycopene to cis-isomers. Cis-isomers are more bioavailable than the trans-isomers which is primarily found in raw ripened tomatoes (Burton-Freeman and Reimers, 2011). The uptake of lycopene was reported to be greater from heat processed tomato than from unprocessed tomato juice (Gärtner *et al.*, 1997). For instance, ingestion of tomato juice cooked in an oil medium resulted in a two-to threefold increase in

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lycopene serum concentrations a day after ingestion, but an equivalent consumption of unprocessed tomato juice caused no rise in plasma concentration (Stahl and Sies, 1992).

Preservation by heat treatment is one of the oldest and most effective means of preventing foods from spoilage. Once dehydrated and appropriately packaged, many foods can be stored successfully for long time without refrigeration (Durance and Wang, 2002). Thermal processing is the most common method of preserving tomatoes, hence, researchers have concentrated on the development of the best thermal drying method for tomatoes (Xanthopoulos *et al.*, 2012; Yousif *et al.*, 2013; Yasaman *et al.*, 2014; Nazmi and Esref, 2015). Heat and light induces lycopene oxidation and isomerization of the all-trans form to the cis-form. The level of cis-isomers increases as treatment time increases but only for a short period during the beginning of the heat treatment (Shi *et al.*, 2003).

Nigeria ranked 16th on the global tomato production scale, however, the marketing of tomatoes in the country is affected by numerous problems such as the perishability of the product, transportation inconveniences, storage and labour cost, as well as loss of tomato quality (e.g., colour, size, shape and flavour). Studies have recommended that farmers engaged in tomato production be adequately trained on post-harvest crop handling techniques (Adepoju, 2014) so as to reduce tomato wastage. On the other hand, consumer's way of curbing wastage and extending the shelf-life of tomatoes involves the conversion of ripe tomato fruit to paste. This is usually done by subjecting tomatoes to uncontrolled heat processing method. This uncontrolled heat processing method may result into lower derivation of the maximum benefits of tomatoes by the consumers. Although the lycopene and beta-carotene contents in several cultivars of Nigerian tomatoes have been previously studied (Abdul-Hammed *et al.*, 2009, 2012, 2013, 2014), data on the degradation of these carotenoids in Nigerian diets are lacking. The aim of this study is to determine the effect of temperature and time on the degradation kinetics of lycopene and beta-carotene content in tomato paste produced from Roma and *Ajindi-Kerewa* tomato cultivars.

MATERIALS AND METHODS

Sample preparation: Mature, ripe and fresh tomato fruits (Roma and *Ajindi-Kerewa cultivars*) commonly available in the South Western Nigeria, were purchased from Wazobia Market in Ogbomoso, Oyo State, Nigeria. The tomatoes were independently and randomly selected, picked and packed into opaque polythene bags to prevent light irradiation and then taken to Food Science and Engineering laboratory at Ladoko Akintola University of Technology, Ogbomoso, Nigeria, where they were rinsed with some doubly distilled water and left to drain for some minutes.

Production of tomato paste: Tomato paste was produced according to the method described by Sharma and Le Maguer (1996) (with some modifications). Tomato fruits were sorted manually. Damaged and defected tomato fruits were discarded. Firm, ripe and fleshy tomatoes were selected and washed in portable water to remove extraneous materials, including pesticide residue. Whole tomatoes (i.e., skin + flesh + seeds) from the two tomato cultivars were chopped into pieces with a knife and ground using a blender (Kenwood multi-pro compact FPP230; speed 2, 5 mins) to produce tomato pulp. The tomato pulp was passed through 0.51 mm screen to produce smooth tomato pulp. The smooth tomato pulp (10 g) from each of the tomato cultivar was weighed into a beaker and heated at varying temperatures (60-120°C) in a boiling water bath (Grant Scientific Ltd., Cambridge, UK) under atmospheric pressure for 10-90 min.

Extraction and quantification of lycopene and β-carotene: Lycopene and beta-carotene contents of the heated tomato paste samples were extracted with hexane, methanol and acetone (2:1:1) containing 2.5% Butylated Hydroxytoluene (BHT) (Perkins-Veazie *et al.*, 2001). The extract was treated with distilled water, methanol and 20% KOH/methanol (1:1:1) to saponify any triglyceride present and further with distilled water, before being re-dissolved in hexane. The absorbance of the hexane extracts were measured at 450 and 502 nm using Genesys 10S V1.200 spectrophotometer (Buck Scientific, USA) and the lycopene and beta-carotene concentrations were determined using previously reported protocol (Abdul-Hammed *et al.*, 2013).

Kinetic analysis: The data obtained from the degradation of lycopene and beta-carotene content in the tomato paste was subjected to first order kinetic analysis (Nguyen and Schwartz, 1998). Using first orders kinetic Eq. (1):

$$\ln(C_0 - C_t) = C_0 - kt \quad (1)$$

where,

k = First order rate constant

t = Heating time

C₀ = Initial concentration of lycopene and beta-carotene

C_t = Their concentrations after heating for time (t)

A plot of ln(C₀-C_t) against time (t) gives the slope-k while the intercept is given as lnC₀. The half-life (t_{1/2}) (which is the time required for the lycopene and beta-carotene concentrations in tomatoes to degrade down to 50% of their initial concentrations) was calculated by the Eq. (2):

$$t_{1/2} = \frac{0.693}{k} \quad (2)$$

Arrhenius plot was then employed using the equation below:

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T}\right) \quad (3)$$

where,

- k = Rate constant
- A = Pre-exponential factor
- E_a = Activation energy
- R = Gas constant
- T = Heating temperature

Plotting the graph of Ink against 1/T gives the slope of the graph as $-\frac{E_a}{T}$ and the intercept lnA. The activation energy, E_a, of the reaction is given as E_a = - Slope x 8.314. The lower the activation energy of reaction, the faster the rate of the degradation of beta-carotene in these tomato cultivars compared to others.

RESULTS AND DISCUSSION

Lycopene degradation pattern of Roma and Ajindi-kerewa tomato cultivars: Generally, the lycopene

content, of Roma and Ajindi-kerewa tomato cultivars decreased with increasing heat treatment and processing time (Table 1), the trend is presented in Fig. 1. The lycopene content of heat treated Roma tomato decreased from 7.9 to 4.6 mg/100g when heated from 10 to 90 min at 60°C while the final concentration reduced further to 3.5mg/100g when heated for 90 min at 120°C. The result obtained shows that subjecting Roma tomato to 60°C for 90 min resulted in 42% decrease in lycopene content, while subjecting it to 120°C for 90 min resulted in 56% decrease in its lycopene (Table 1 and Fig. 1). Similar trend was observed in the lycopene content of Ajindi-kerewa tomato (Table 1 and Fig. 1). There was a 27% decrease in the lycopene content of Ajindi-kerewa tomato paste heated for 90 min at 60°C while a 52% decrease in lycopene was observed when the tomato was heated for 90 min at 120°C (Table 1 and Fig.1). The reduction in the lycopene content of the heat processed tomato paste could be as a result of degradation of lycopene at high temperature long time heat processing method. This observation was in line with previous studies (Clinton, 1998; Nguyen *et al.*, 2001) which reported low levels of lycopene isomers in thermally processed tomato products. Kadam *et al.* (2012) also reported that a

Table 1: Lycopene degradation (mg/100 g) in Roma and Ajindi-kerewa tomato cultivars

Tomato cultivar	Heating time	Heating temperature (°C)			
		60	80	100	120
Roma	10	7.903	7.719	7.562	7.296
	20	7.310	6.464	6.240	5.983
	40	5.609	5.444	5.071	4.846
	60	4.901	4.738	4.435	4.385
	90	4.590	3.710	3.604	3.533
Ajindi-kerewa	10	2.488	2.396	2.168	2.024
	20	2.354	2.122	2.063	1.885
	40	2.197	1.882	1.832	1.798
	60	1.930	1.637	1.492	1.389
	90	1.808	1.513	1.396	1.192

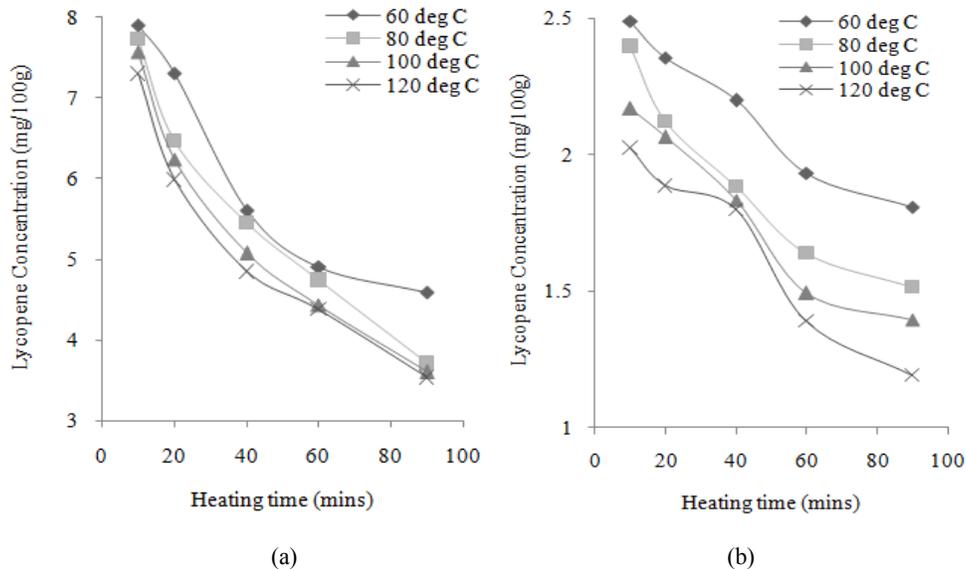


Fig. 1: Lycopene degradation in Roma; (a): And Ajindi-kerewa; (b): Tomato cultivars

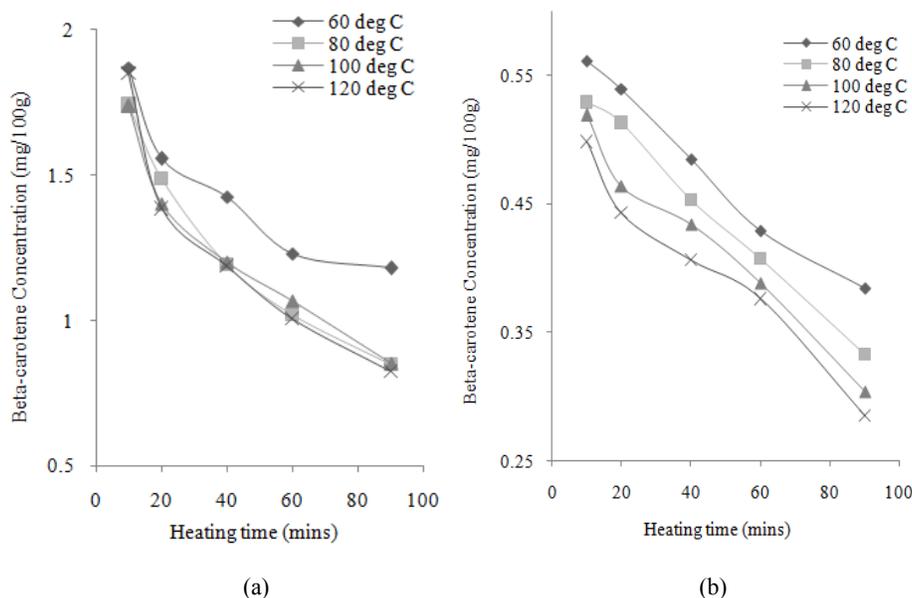


Fig. 2: Beta-carotene degradation in Roma; (a): And *Ajindi-kerewa*; (b): Tomato cultivars

Table 2: Beta-carotene degradation (mg/100 g) in Roma and *Ajindi-kerewa*

Tomato cultivar	Heating time	Heating temperature (°C)			
		60	80	100	120
Roma	10	1.870	1.743	1.737	1.851
	20	1.556	1.488	1.401	1.384
	40	1.425	1.192	1.200	1.188
	60	1.230	1.021	1.066	1.006
	90	1.180	0.847	0.852	0.824
<i>Ajindi-kerewa</i>	10	0.561	0.529	0.519	0.498
	20	0.539	0.513	0.464	0.443
	40	0.485	0.453	0.434	0.406
	60	0.429	0.407	0.388	0.376
	90	0.384	0.333	0.304	0.285

decrease in the lycopene content of dried tomato powder was due to the heat labile nature of lycopene. In another study, Baysal *et al.* (2000) reported that drying under different processing conditions may cause degradation of lycopene at different levels. Similarly, Zanoni *et al.* (1999) reported that drying tomato halves at 80°C caused no significant loss in lycopene, whereas a significant loss occur at 110°C. Bošković (1979) and Cano *et al.* (1996) also observed that processing and extended storage of dehydrated tomato products resulted in a loss of all-trans lycopene content by up to 20%. However, in contrast to what was observed in this study, Nguyen and Schwartz (1998) reported that processing does not have a significant effect on the stability of lycopene.

Beta-carotene degradation pattern in Roma and *Ajindi-kerewa* tomato cultivars: Beta-carotene content of heat processed Roma tomato paste ranged from 0.82-1.87 mg/100 g (Table 2, Fig. 2 shows the trend). Heating Roma tomato at 60°C for 90 mins resulted in 37% reduction in its beta-carotene content (from 1.87

mg/100 g to 1.18 mg/100 g). However, 58% reduction in beta-carotene was observed when the tomato was heated at 120°C for 90 mins. A similar trend was observed in *Ajindi-kerewa* tomato paste. A 33% reduction in its beta-carotene content was observed at 60°C, while heating the tomato at 120°C for 90 mins resulted in 50% reduction in its beta-carotene content. The reduction in the beta-carotene content of heat treated tomato paste produced from the two tomato cultivars could be due to thermal degradation of the carotenoid at high temperature. In contrast, Khachik *et al.* (1992) observed that common heat treatments during food preparation, such as microwaving, steaming, boiling and stewing, did not significantly change the distribution of carotenoids in tomatoes and green vegetables. In another study, Nguyen *et al.* (2001), reported that during typical cooking of tomatoes, factors such as genotypic differences in overall carotenoid composition, the presence of oil and physical changes to tomato tissue did not influence the thermal isomerization of all-trans lycopene, all-trans δ -carotene, all-trans γ -carotene, or pro-lycopene.

Degradation kinetics of lycopene and beta-carotene in roma and *Ajindi-kerewa* tomato cultivars: The kinetics of the degradation of lycopene (Fig. 3) followed a first order kinetics as monitored from the plot of the natural logarithm of lycopene concentration changes with time for each temperature. Good linear correlation coefficients ranging from 0.8738 to 0.9703 for Roma and 0.9476 to 0.9713 for *Ajindi-kerewa* tomatoes. First order kinetics was also reported in the previous studies using other tomato cultivars (Sharma and Le Maguer, 1996; Colle *et al.*, 2010; Demiray *et al.*, 2013). The rate constants for lycopene degradation at the temperature range (60-120°C) were

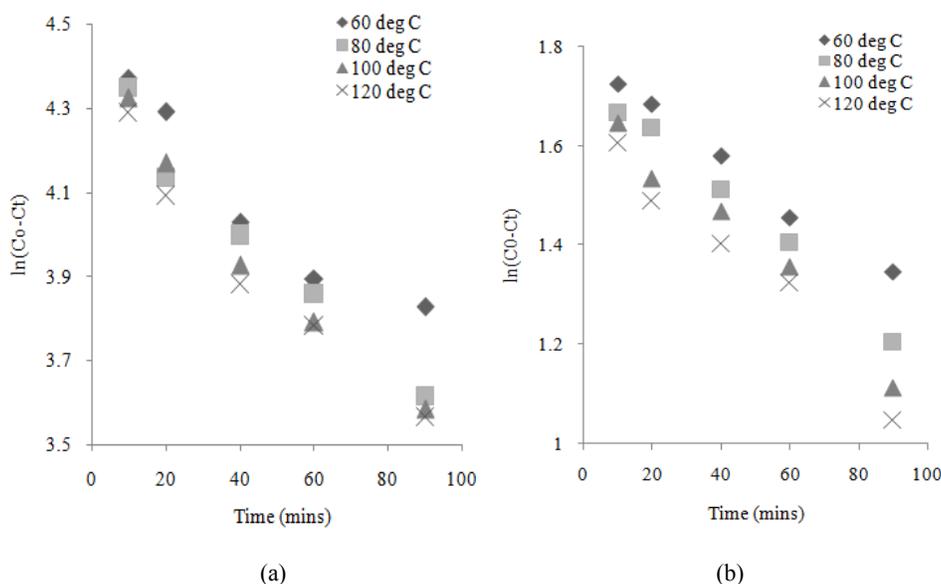


Fig. 3: First order kinetic plots for the lycopene degradation in Roma; (a): And *Ajindi-kerewa*; (b): Tomato cultivars

Table 3: Kinetic parameters for lycopene and beta-carotene degradation in tomatoes during home processing

Tomato Cultivar	Carotenoid	Temperature (°C)	K (h ⁻¹)	R ²	t _{1/2} (h)	A (h ⁻¹)	Ea (kJ/mol)
<i>Ajindi-Kerewa</i>	Lycopene	60	0.246	0.9713	2.82	5.916	8.65
		80	0.342	0.9476	2.03		
		100	0.36	0.9524	1.93		
		120	0.408	0.9595	1.70		
	β-carotene	60	0.294	0.9713	2.36	1.734	4.81
		80	0.354	0.9476	1.96		
		100	0.378	0.9524	1.83		
		120	0.384	0.9595	1.81		
Roma	Lycopene	60	0.426	0.9713	1.63	2.352	4.63
		80	0.51	0.9476	1.36		
		100	0.54	0.9524	1.28		
		120	0.552	0.9595	1.26		
	β-carotene	60	0.444	0.9713	1.56	1.992	4.14
		80	0.492	0.9476	1.41		
		100	0.528	0.9524	1.31		
		120	0.558	0.9595	1.24		

presented in Table 3. The rate constants ranged from 0.246 to 0.408 h⁻¹ and 0.426 to 0.552 h⁻¹ in *Ajindi-kerewa* and Roma tomatoes respectively. The time required for lycopene in the processed tomatoes to degrade to half its initial concentration (half-life) was highest at 60°C in both cultivars (Table 3).

Similarly, the degradation of beta-carotene also followed a first order kinetics (Fig. 4) with high precisions (R² = 0.8766 to 0.9948). The observed rate constants for beta-carotene degradation ranged from 0.294 to 0.384 h⁻¹ in *Ajindi-kerewa* cultivar with higher values (0.444 to 0.558 h⁻¹) reported in Roma cultivar. The half-lives for beta-carotene degradation seem to be lower than that obtained for lycopene degradation in both cultivars.

Arrhenius plot (Fig. 5) confirms the temperature dependence of the reaction rate constants. The activation energies of lycopene degradation obtained from the plot are 8.65 and 4.63 kJ/mol for *Ajindi-kerewa* and Roma tomato cultivars, respectively.

However, these activation energies which is a measure of the minimum energy required to accomplish this degradation is much lower than the values reported (46.96 kJ/mol) for *Rio Grande* tomatoes (Demiray *et al.*, 2013). These differences may be attributed to the processing methods and may also be cultivar dependent. The domestic or local processing of these tomatoes tends to degrade lycopene in tomatoes to a much larger extent compared to modern methods. While the activation energies of lycopene degradation in *Ajindi-kerewa* tomatoes doubled that in Roma, those of beta-carotene degradation are almost the same in the two cultivars. The higher activation energy (52 kJ/mol) reported for the isomerization of all-E-lycopene to Z-lycopene in Heinz 9997 tomatoes (Colle *et al.*, 2010) compared to that (4 kJ/mol) in thermally processed tomato puree (Shi and Maguer, 2003). This was attributed to the presence of olive oil in the former, in which the lycopene crystals can easily dissolve (Colle *et al.*, 2010).

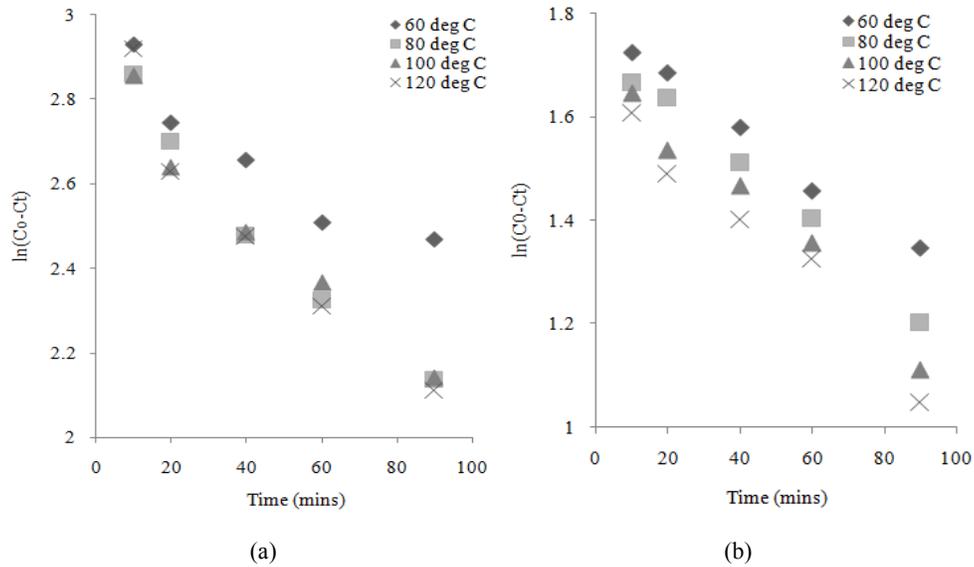


Fig. 4: First order kinetic plots for the beta-carotene degradation in Roma; (a): And *Ajindi-kerewa*; (b): Tomato cultivar

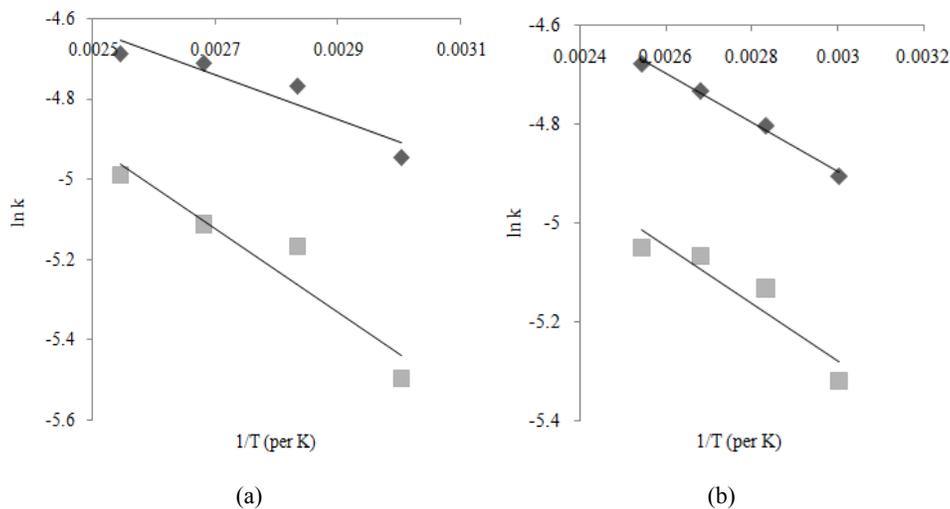


Fig. 5: Arrhenius plots for lycopene; (a): And beta-carotene; (b): Degradation in Roma (●) and *Ajindi-kerewa* (○) Tomato cultivars

CONCLUSION

In Nigeria, tomato pastes are produced domestically in order to extend the shelf life of tomato and prevent wastage. Although the process of cooking releases lycopene from the matrix into the lipid phase of meal, thus making tomato paste and tomato puree to be more bioavailable sources of lycopene than raw tomatoes, degradation of these carotenoids during processing is undesirable. This study reported that the degradation of both lycopene and beta-carotene in *Ajindi-kerewa* and Roma tomato cultivars follow first order kinetics. The low activation energies (4.14 to 8.65 kJ/mol) of the process are indication of the great extent to which the carotenoids were degraded during domestic processing. Therefore, to provide a tomato based diet that will be rich in carotenoids (lycopene and

beta-carotene) for the table, tomato paste should be subjected to low temperature short time processing method.

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