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### Carotene Degradation and Isomerization during Thermal Processing: A Review on the Kinetic Aspects

Ines J. P. Colle<sup>a</sup>, Lien Lemmens<sup>a</sup>, Griet Knockaert<sup>a</sup>, Ann Van Loey<sup>a</sup> & Marc Hendrickx<sup>a</sup>

<sup>a</sup> Laboratory of Food Technology and Leuven Food Science and Nutrition Research Centre (LFoRCe), Department of Microbial and Molecular Systems (M<sup>2</sup>S) KU Leuven, Kasteelpark Arenberg 22, Box 2457, B-3001 Leuven, Belgium

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Carotene degradation and isomerization during thermal processing: a review on the kinetic aspects

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Ines J. P. Colle, Lien Lemmens, Griet Knockaert, Ann Van Loey, Marc Hendrickx

Laboratory of Food Technology and Leuven Food Science and Nutrition Research Centre (LFoRCe). Department of Microbial and Molecular Systems (M<sup>2</sup>S). KU Leuven.

Kasteelpark Arenberg 22, Box 2457, B-3001 Leuven, Belgium

Corresponding author

Prof. Dr. Ir. Marc Hendrickx, Kasteelpark Arenberg 22, Box 2457, B-3001 Leuven, Belgium

Tel.: +32 16 32 15 85; Fax: +32 16 32 19 60

Email: [Marc.Hendrickx@biw.kuleuven.be](mailto:Marc.Hendrickx@biw.kuleuven.be)

## Abstract

Kinetic models are important tools for process design and optimization to balance desired and undesired reactions taking place in complex food systems during food processing and preservation. This review covers the state of the art on kinetic models available to describe heat-induced conversion of carotenoids, in particular of lycopene and  $\beta$ -carotene. Firstly, relevant properties of these carotenoids are discussed. Secondly, some general aspects of kinetic

modeling are introduced including both empirical single-response modeling and mechanism-based multi-response modeling. The merits of multi-response modeling to simultaneously describe carotene degradation and isomerization are demonstrated. The future challenge in this research field lies in the extension of the current multi-response models to better approach the real reaction pathway and in the integration of kinetic models with mass transfer models in case of reaction in multi-phase food systems.

## Keywords

Kinetics, single-response modeling, multi-response modeling, lycopene,  $\beta$ -carotene

## 1 Introduction

Carotenoids are fat soluble phytochemicals which are largely responsible for the red, orange and yellow color of fruits and vegetables. Recent interest in these compounds arises from their purported health benefits. Some carotenoids possess important provitamin A activity. Moreover, over the past decade, the effect of non-provitamin A carotenoid intake has been studied with respect to a wide range of diseases (various cancers, cardiovascular diseases, eye related diseases). Although several studies (Giovannucci, 1999; Krinsky & Johnson, 2005) suggest an inverse correlation between carotenoid consumption and the risk of chronic diseases, all the cause and effect relations are still not well established (Kavanaugh et al., 2007; Agostoni et al., 2011; Key, 2011). Nevertheless, increasing awareness of potential health benefits of certain carotenoids has triggered the food industry to create functional food products with carotenoid containing ingredients. At the same time, carotenoid containing fruit and vegetable derived

ingredients can act as natural colorants. The same carotenoid properties that may lead to their functional properties, create challenges with regard to carotenoid stability during processing. Therefore process optimization is of major importance. In this perspective qualitative mechanistic insight and quantitative kinetic models describing carotenoid changes as a function of process parameters are valuable tools. This review will specifically focus on the carotenoids lycopene and  $\beta$ -carotene and their conversions during thermal food processing. Lycopene is responsible for the red to pink colors observed in fruits and vegetables including tomatoes, pink grapefruit, guava and watermelon (Matulka et al., 2004; USDA, 2010) while  $\beta$ -carotene is encountered in carrot, spinach, sweet potatoes, apricot, orange, etc. (Maiani et al., 2009).

## 2 Chemical and biological properties of lycopene and $\beta$ -carotene

Although all carotenoids differ in structure, they can be considered as variations on a single structural theme. The carbon skeleton of carotenoids consists of a symmetrical  $C_{40}$  tetraterpenoid hydrocarbon backbone which corresponds to the structure of lycopene (Figure 1). This molecule can be further modified by cyclization. In this way  $\beta$ -carotene, which contains a  $\beta$ -ionone ring at each end of its hydrocarbon chain (Figure 2), is formed. The two  $\beta$ -ionone rings of  $\beta$ -carotene render its valuable provitamin A activity. Other possible modifications of the general carotenoid backbone occur by changes in hydrogenation level, double bond migration, methyl migration, chain shortening or extension, and introduction of oxygen containing functional groups. Carotenoids are divided into two classes: (i) the carotenes, which are strictly hydrocarbons and to which lycopene and  $\beta$ -carotene belong and (ii) the xanthophylls, which contain one or more oxygen functions.

The tetraterpenoid structure of lycopene and  $\beta$ -carotene implies a long system of conjugated double bonds and creates an electron rich environment which makes these carotenoids efficient antioxidants (Edge et al., 1997; El-Agamey et al., 2004) but which makes them at the same time highly reactive (Britton, 1995a). Carotenoids are expected to undergo two types of changes: degradation and isomerization. Oxidation is by far the major cause of carotenoid degradation (Bonnie & Choo, 1999). Carotenoid oxidation is an irreversible reaction which is believed to be mainly a free radical process (Boon et al., 2010) and which gives rise to degradation products such as epoxides, apocarotenones, and apocarotenals (Pénicaud et al., 2011b; Rodriguez & Rodriguez-Amaya, 2009). Subsequent fragmentation yields a series of low-molecular compounds including acetone, methylheptenone, laevulinic aldehyde, and probably glyoxal (Cole & Kapur, 1957a; Cole & Kapur, 1957b) for lycopene oxidation and 5,6-epoxy- $\beta$ -ionone, ionene,  $\beta$ -cyclocitral,  $\beta$ -ionone, dihydroactinidiolide and 4-oxo- $\beta$ -ionone for  $\beta$ -carotene oxidation (Sommerburg et al., 2003). Oxidation depends on the availability of oxygen and is stimulated by heat, light, metals, and co-oxidation with lipid hydroperoxides (Shi & Le Maguer, 2000; Rodriguez-Amaya, 2001). Moreover the action of enzymes can directly or indirectly affect carotenoid degradation. Of the more than 200 putative carotenoid cleavage oxygenase enzymes to be found in sequence databases, 26 have been characterized and tested for *in vitro* cleavage activity (Kloer & Schulz, 2006). For example, enzymatic activity directly capable of converting  $\beta$ -carotene to  $\beta$ -ionone has been found and partially characterized in quince fruit (Fleischmann et al., 2002), in star fruit (Fleischmann et al., 2003) and in nectarine (Baldermann et al., 2005). Besides direct cleavage action, a number of enzymes are known to indirectly mediate carotenoid

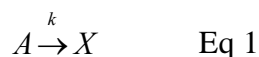
degradation. Fatty acid hydroperoxides produced by lipoxygenase, for example, have been shown to affect carotenoid cleavage (Yeum et al., 1995).

In principle, each double bond in the polyene chain of carotenoids can exist in two isomeric configurations: *Entgegen* (*E*) or *Zusammen* (*Z*). However some of these stereoisomers are sterically hindered and therefore only a few are encountered in nature. For lycopene all-*E*-, 5-*Z*-, 9-*Z*-, 13-*Z*-, and 15-*Z*-lycopene have been identified in various foods (Schierle et al., 1997). For  $\beta$ -carotene, the major isomers found after thermal processing are all-*E*-, 9-*Z*-, 13-*Z*- and 15-*Z*-  $\beta$ -carotene (Chen et al., 1994; Rodriguez-Amaya & Kimura, 2004; Henry et al., 1998). Isomerization of carotenoids may proceed via a triplet excited state (Fujii et al., 2002; Guo et al., 2008) or may be mediated by cation radical or dication formation (Gao et al., 1996). *Z*-isomers have the same molecular weight as their all-*E* counterpart but have slightly different spectral characteristics. The main difference is the appearance of a *Z*-peak in the near-ultraviolet region. The intensity of the *Z*-peak increases as the *Z*-double bond is nearer to the centre of the molecule. In addition, *E* to *Z* isomerization causes a decrease in the degree of spectral fine structure, a small hypsochromic shift (2 to 6 nm for mono-*Z*-carotenoids), and a hypochromic effect (Zechmeister, 1962; Britton, 1995b). Furthermore, isomerization influences the potential health benefits of lycopene and  $\beta$ -carotene. On the one hand, isomerization of all-*E*-lycopene to *Z*-lycopene can be of interest because of increasing antioxidant activity (Böhm et al., 2002). Moreover, *Z*-lycopene has shown improved solubilization in micelles (Failla et al., 2008) and could consequently be better absorbed by the human body (Unlu et al., 2007; Porrini et al., 1998; Stahl & Sies, 1992). On the other hand, it was demonstrated that the *Z*-isomers of  $\beta$ -carotene have similar or lower antioxidant properties than all-*E*-  $\beta$ -carotene (Böhm et al., 2002) and

generate about two-fold less vitamin A activity (Schieber & Carle, 2005). Results regarding the preferential absorption of *Z*-carotene or all-*E*-carotene are rather controversial. Micellarization of *Z*-carotene isomers was shown greater than that of all-*E*-carotene (O'Sullivan et al., 2010; Levin & Mokady, 1995) but absorption of all-*E*-carotene was favored over *Z*-carotene (Gaziano et al., 1995; During et al., 2002).

### 3 General aspects of kinetic modeling

In general, kinetic models describe the rate of a reaction in such a way that a reaction can be predicted and controlled. Suppose the degradation of a single compound (A) to unidentified degradation products (X):



In most cases, the disappearance of A (single-response) is expressed by the so-called general rate law:

$$-\frac{d[A]}{dt} = k[A]^n \quad \text{Eq 2}$$

with  $A$  the compound under consideration at treatment time  $t$ ,  $k$  the reaction rate constant and  $n$  the order of the reaction. In the food science literature, changes are usually modeled by means of zero to second order reactions (Van Boekel, 2008). When  $k$  can be assumed constant in time, the differential equation (**Error! Reference source not found.**) can be integrated with respect to time resulting in:

$$[A] = [A]_0 - kt \quad \text{Eq 3}$$

for a zero order reaction, in:

$$[A] = [A]_0 \exp(-kt) \quad \text{Eq 4}$$

for a first order reaction, and in:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \quad \text{Eq 5}$$

for a second order reaction.

Knowledge on how the kinetics of reactions in foods are affected by temperature changes is essential since many foods are heat treated for various reasons. The temperature dependency of a reaction renders useful information to design and determine time and temperature conditions during processes such as pasteurization and sterilization. In many cases the temperature dependency of the rate constant can be quantified by the activation energy ( $E_a$ ) according to the Arrhenius law (Arrhenius, 1889):

$$k = k_{ref} \exp \left[ \frac{E_a}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad \text{Eq 6}$$

where  $R$  represents the universal gas constant (8.314 J/mol K),  $T$  the temperature concerned and  $k_{ref}$  the reaction rate constant at a reference temperature ( $T_{ref}$ ). Two different approaches can be followed to estimate the kinetic parameters (Van Boekel, 2008; De Vleeschouwer et al., 2009; Van Loey et al., 2003). Following a two-step procedure, rate constants are firstly estimated by linear or non-linear regression and secondly the activation energy is determined from linear regression of  $\ln k$  compared with  $1/T$ . The drawback of this two-step approach is the accuracy of the parameter estimates since the errors of the first regression are not taken into account during



the second regression. An alternative approach is the one-step procedure in which only one non-linear regression is performed by substituting the rate constant (**Error! Reference source not found.**) in the appropriate rate equation (e.g. first order reaction (**Error! Reference source not found.**)). The one-step regression procedure yields unbiased and precise estimates of parameters. Another advantage of the one-step approach is that it can also be used when heating was performed under non-isothermal conditions. In such case, the integrated effect of temperature on the reaction rate has to be taken into account (De Vleeschouwer et al., 2009) and **Error! Reference source not found.** becomes:

$$-\frac{d[A]}{dt} = k_{ref} \exp \left[ \frac{E_a}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T(t)} \right) \right] [A]^n \quad \text{Eq 7}$$

in which  $T(t)$  describes the time dependency of the process temperature. In both approaches kinetic parameters are estimated by fitting the model to the experimental data. The most commonly used fitting criterion is least-squares fitting which searches for parameters that minimize the sum of squares of residuals (Van Boekel, 1996). This fitting criterion is only appropriate when several assumptions, including normally distributed experimental errors, are fulfilled (Johnson, 1992; Van Boekel, 1996).

Reactions in foods often do not occur isolated but rather within a complex reaction network, in which several reactants, intermediates and end-products take part. Measuring multiple responses of a reaction system at the same time and using all the available information when modeling experimental data, is much more powerful than solely considering a single response (Van

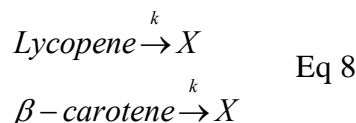
Boekel, 1999; Quintas et al., 2007). The multi-response approach requires the proposition of a reaction pathway. This pathway is translated into a mathematical model by setting up differential equations. For multi-response modeling, the fit criterion depends on the experimental error structure of the data (Van Boekel, 1996). Only when the variance-covariance matrix is known and under the strict conditions that all variances are equal and that covariances within a run are zero, least-squares fitting can be applied. In most cases, this information is not available or the requirements are not fulfilled. Instead of minimization of the sum of squares, the minimization of the dispersion matrix is described as the best fit criterion. The dispersion matrix does not only contain the sum of squares for each response but also the cross products of the responses (Van Boekel, 2009; Box & Draper, 1965). Some advantages of multi-response over single-response modeling are: (i) kinetic models can be tested much more rigorously because all the information contained in the data is linked and used, (ii) better results in terms of precision of parameters, (iii) useful to gain insight into the actual reaction network (De Vleeschouwer et al., 2009; Van Boekel, 1996).

## **4 Modeling the kinetics of carotene conversions**

### **4.1 Carotene degradation during thermal processing**

Although lycopene and  $\beta$ -carotene degrade in various oxidized and cleavage molecules (Pénicaud et al., 2011b; Rodriguez & Rodriguez-Amaya, 2009), the majority of the kinetic models used to describe  $\beta$ -carotene and lycopene degradation are single-response kinetic models. For  $\beta$ -carotene degradation, Pénicaud et al. (2011b) have reviewed the degradation mechanism and argued that the proposed reaction schemes, which still are simplifications of the reality, are

already highly complex hampering the evaluation of kinetic constants by the necessity of detection and quantification of appearing and disappearing intermediary products whose lifetimes can be very short. Currently, no kinetic studies could be found which included modeling the formation of degradation products. However some degradation products may play an important role. Certain carotene scission products (e.g. norisoprenoids) are important aroma compounds (Winterhalter & Rouseff, 2001), while others (e.g. acetone) may be detrimental for human health. Table 1 and Table 2 give an overview of the kinetic data currently available describing respectively lycopene and  $\beta$ -carotene degradation. This overview is restricted to kinetics in (i) model systems and (ii) either tomato based systems in case of lycopene or carrot based systems in case of  $\beta$ -carotene. In addition, only studies examining degradation during thermal processing are considered. Temperatures included vary from 50-60 °C for blanching purposes to 90 °C for pasteurization up to 100-120 °C for sterilization. Even temperatures up to 180 °C have been scrutinized for deep-fat frying applications. Research regarding storage conditions (< 50 °C) are not included here. All studies reported, modeled the overall decay of the total (= sum of *Z*- and *E*-isomers) carotenoid content or the decay of a certain isomer (e.g. all-*E*) (Error! Reference source not found.).



Most studies used a first order reaction (Error! Reference source not found.) with respect to the concentration of lycopene or  $\beta$ -carotene. Nevertheless, some authors found a fractional

conversion model (**Error! Reference source not found.**) more suitable to describe the experimental data.

$$-\frac{d[A]}{dt} = k[A - A_{final}] \quad \text{Eq 9}$$

This model only differs from a first order reaction model in the fact that a non-zero equilibrium value ( $A_{final}$ ) is reached after long treatment time. In all cases the Arrhenius equation was applied to determine the temperature dependency of the rate constants. However, only few authors (Achir et al., 2010; Colle et al., 2010b; Colle et al., 2013; Knockaert et al., 2012) recently estimated  $k$ - and  $E_a$ -values using the more favorable one-step regression approach. Unfortunately, some studies did not supply the uncertainty in parameter estimates which makes the information less useful for interpretation (Van Boekel, 2008). Both for lycopene and  $\beta$ -carotene degradation, quite different rate constants and activation energies were found. Differences might be ascribed to several factors. Firstly, activation energies obtained in different temperature ranges (e.g. 75-95 °C versus 120-180 °C) may be hard to compare. Secondly, different heating methods (e.g. water/oil as heating medium versus air as heating medium) result in varying heat transfer efficiencies. Although rarely encountered, taking into account the temperature history of each sample during modeling is of indispensable value. Lastly, it must be acknowledged that food systems are very complex and that many interactions may occur. In many cases, model parameters will be apparent and in fact embed all kinds of confounding factors. Indeed carotene reactions are very dependent on the presence of co-substrates (Rodriguez-Amaya, 2001). As long as this is realized, there is no real problem. However there could be a serious problem when making illegitimate extrapolations (Van Boekel, 2008). Colle et

al. (2013), Qiu et al. (2012) and Achir et al. (2010) have shown that the lipid type in which the carotene is dissolved determines the kinetic parameters of lycopene and  $\beta$ -carotene degradation during processing. This observation was attributed to the compositions of the lipid present. Lipids differ by their fatty acid composition and their peroxide and vitamin E content. It is well known that fatty acids can be oxidized thereby producing radicals. Furthermore, the oxidative stability of fatty acids depends on their degree of saturation (Goulson & Warthesen, 1999). The highly unsaturated chain of lycopene and  $\beta$ -carotene can be attacked by radicals produced during fatty acid oxidation leading to the production of peroxy radicals which may further participate in cleavage reactions of both unsaturated lipids and carotenes. Next to the lipid composition of the reaction system, the availability of oxygen is a major factor influencing the rate of carotene degradation. Oxygen free conditions significantly retarded lycopene degradation in an oil/water emulsion compared to in oxygen saturated conditions (Ax et al., 2003). Also in gac oil, the degradation rate of lycopene and  $\beta$ -carotene was lower when the oil was treated with butylated hydroxytoluene or with a stream of nitrogen compared to the control oil (Nhung et al., 2010). Unfortunately, few data are available concerning the quantified impact of the amount of oxygen available on carotene degradation rates. Several authors worked on  $\beta$ -carotene autoxidation models in organic solvents (Takahashi et al., 2003) or in oils (Shibasaki-Kitakawa et al., 2004) based on a multistep free-radical chain reaction mechanism under various conditions of initial dissolved oxygen and antioxidant content. However, constructed models were based on experimental content of antioxidants or oxidation products instead of on oxygen levels. Therefore, the effect of oxygen which is obtained from these models can be disputed. Technical

limitations are still the bottleneck to collect data on oxygen available for reactions in fruit- and vegetable-based systems (Pénicaud et al., 2011a).

At first sight, Table 1 and Table 2 show that the activation energy for lycopene degradation is slightly lower than the activation energy for  $\beta$ -carotene degradation. However, to correctly compare kinetics of lycopene and  $\beta$ -carotene one needs kinetic data in the same reaction system using similar processing conditions. Moreover to correctly compare correlated parameters, joint confidence regions (JCR $\phi$ ) need to be constructed according to the following equation (Draper & Smith, 1981):

$$SSQ_{error} = SSQ_{error}(\theta) \left\{ 1 + \frac{p}{m-p} F(p, m-p, 1-\phi) \right\} \text{ Eq 10}$$

where  $SSQ_{error}(\theta)$  represents the error sum of squares associated with the least square estimate  $\theta$ ,  $p$  the number of simultaneously estimated parameters,  $m$  the number of observations and  $F$  the upper  $1-\phi$  quantile for an F-distribution with  $p$  and  $m-p$  degrees of freedom. In the scientific literature, JCR $\phi$  have rarely been encountered because it involves grid search methods which in the past required a large amount of computer time. In Figure 3, the kinetic parameters for total lycopene degradation in an olive oil/tomato emulsion (Colle et al., 2010b) are compared to the kinetic parameters for total  $\beta$ -carotene degradation in an olive oil/carrot emulsion (Knockaert et al., 2012). Both sets of kinetic parameters were obtained by one-step regression using a fractional conversion model and the Arrhenius equation. Furthermore, both studies applied similar heat treatments and took into account the dynamic heating conditions by including the temperature history of each sample. The JCR $\phi$  do not overlay which indicates that the correlated estimated parameters are significantly different from one another. This difference can be

attributed to the carotenoid type studied (lycopene versus  $\beta$ -carotene). However, it can not be excluded that the difference arises from the difference in carotenoid source and the structural organization of the carotenes in the different matrices (tomato versus carrot).

## 4.2 Carotene isomerization during thermal processing

Kinetic parameters for carotene isomerization reactions either in model systems or in real food systems are scarce. In a few recent studies (Lemmens et al., 2010; Colle et al., 2010b; Knockaert et al., 2012) thermally induced lycopene and  $\beta$ -carotene isomerization was modeled independently from degradation. Hereto, for each treatment condition the contribution of each isomer to the total content was calculated as follows:

$$Y(\%) = \frac{[A]_{isomer,t}}{[A]_{total,t}} 100 \quad \text{Eq 11}$$

with  $[A]_{isomer,t}$  the concentration of a certain isomer at treatment time  $t$  and  $[A]_{total,t}$  the total concentration of all isomers at treatment time  $t$ . The time course of each isomer contribution can be studied as such using single-response modeling. In addition, interconversions between different isomers can be assessed which demands a reaction pathway represented by a reaction scheme and multi-response modeling. Recently, interconversions of lycopene isomers during thermal processing have been described using a multi-response mechanistic model in different reaction systems including olive oil (temperature range 70-130 °C), fish oil (temperature range 50-130 °C) and an olive oil/tomato emulsion (temperature range 80-140 °C) (Colle et al., 2013). The proposed reaction scheme (Figure 4A) allowed conversion of all-*E*-lycopene to 9-*Z*-lycopene, 13-*Z*-lycopene and to a group of unidentified *Z*-lycopene isomers (= x-*Z*-lycopene). In

addition, back-isomerization from *Z*-lycopene to all-*E*-lycopene was included. However, direct conversions between *Z*-isomers were not allowed to reduce the complexity of the model. The corresponding differential equations were set up:

$$\frac{d[\text{all-E-lycopene}]}{dt} = -(k_{F1} + k_{F2} + k_{F3})[\text{all-E-lycopene}] + k_{E1}[\text{x-Z-lycopene}] + k_{E2}[\text{9-Z-lycopene}] + k_{E3}[\text{13-Z-lycopene}] \quad \text{Eq 12}$$

$$\frac{d[\text{x-Z-lycopene}]}{dt} = k_{F1}[\text{all-E-lycopene}] - k_{E1}[\text{x-Z-lycopene}] \quad \text{Eq 13}$$

$$\frac{d[\text{9-Z-lycopene}]}{dt} = k_{F2}[\text{all-E-lycopene}] - k_{E2}[\text{9-Z-lycopene}] \quad \text{Eq 14}$$

$$\frac{d[\text{13-Z-lycopene}]}{dt} = k_{F3}[\text{all-E-lycopene}] - k_{E3}[\text{13-Z-lycopene}] \quad \text{Eq 15}$$

The different reaction rate constants and activation energies were obtained by substituting the Arrhenius equation into the individual differential equations and taking into account the temperature history of each sample. Kinetic parameters are summarized in Table 3. The rate constants of *Z*-isomer formation were generally lower than the rate constants of back-isomerization suggesting that after a certain treatment time the *Z*-contributions will attain a maximum. The kinetic parameters estimated for the model describing the isomerization in olive oil were similar to those in fish oil indicating limited effect of lipid type present. The rate constants of *Z*-isomer formation as well as of back-isomerization were significantly lower in the olive oil/tomato emulsion than in the enriched olive oil while the activation energies were of the same magnitude. Since lycopene isomerization hardly occurs in plain tomato pulp (Colle et al.,



2010a) isomerization in the olive oil/tomato emulsion should have occurred primarily in the oil phase. Smaller rate constants for lycopene isomerization in the olive oil/tomato emulsion than in the olive oil are consequently comprehensible since the rate constants were expressed with regard to the system as a whole. It is important to realize that the model parameters, in particular the rate constants, are apparent.

Similar to lycopene isomerization, the reaction medium might also affect the  $\beta$ -carotene isomerization kinetics as can be concluded from the data of Lemmens et al. (2010) and Knockaert et al. (2012). These authors modeled the thermally induced isomerization of all-*E*- $\beta$ -carotene and the formation of some *Z*- $\beta$ -carotene isomers in plain carrot puree (temperature range 80-150 °C), in olive oil (temperature range 85-130 °C) and in an olive oil/carrot emulsion (temperature range 85-130 °C) using a fractional conversion model and the Arrhenius equation. The apparent rate constants and activation energies were considerably lower in the absence of lipids. In addition, the reaction rate constants were slightly higher in the oil phase compared to the oil/carrot emulsion, whereas the activation energy values were similar. Although the data were suitable for multi-response analysis, only single-response modeling was performed. Therefore, the data of these studies were reanalyzed using a multi-response approach. A reaction pathway similar to the isomerization scheme of lycopene is proposed (Figure 4B). This reaction scheme consist of three reversible concurrent reactions from all-*E*- $\beta$ -carotene to its major *Z*-isomers 9-*Z*-, 13-*Z*- and 15-*Z*- $\beta$ -carotene. The *Z*- $\beta$ -carotene isomers can only be converted into each other after they change to all-*E*- $\beta$ -carotene as was also proposed by Pesek et al. (1990) and Chen et al. (1994). An overview of the sets of kinetic parameters is shown in Table 4. In all three reaction media, the rate constants of *Z*-isomer formation were lower than the rate constants of

back-isomerization as was also found for lycopene isomerization. This implies that after a certain treatment time a maximal *Z*-isomer contribution will be reached. Furthermore, for 13-*Z*-carotene, for example, it was observed that the initial period of increase shortened as treatment temperature increased (Figure 5). The rate constants of *Z*-isomer formation as well as of back-isomerization were not consistently lower in carrot puree than in the olive oil/carrot emulsion or in the enriched olive oil which is in contrast to the conclusion drawn from the kinetic parameters obtained by single-response modeling. Kinetic parameters are inextricably linked to the model they belong to and cannot be compared as such. Because the multi-response model takes into account the four responses of the reaction system at the same time this model is believed to be more accurate.

### 4.3 Simultaneous carotene conversions during thermal processing

Approaching the degradation and isomerization reactions simultaneously is very interesting from a mechanistic point of view. As already indicated above, such approach requires the proposition of a reaction scheme and multi-response modeling.

Shi et al. (2003) proposed a reaction pathway to explain lycopene conversions during thermal treatment of tomato pulp (0-6 h at 90-150 °C). Their reaction pathway included not only reversible isomerization and irreversible degradation of all-*E*-lycopene but also degradation of *Z*-lycopene (Figure 4C). The rate constants and corresponding activation energies are tabulated in Table 5. The low value for  $k_2$  showed that the back-isomerization from *Z*-isomers to all-*E*-isomers was slow. From the remaining rate constants, it was concluded that the main pathway was the degradation of all-*E*-lycopene directly into oxidized by-products ( $k_4 > k_1$ ). A simplified pathway with two parallel irreversible and reversible reactions (Figure 4D) was suggested to

explain the thermal degradation of carotenoids (mainly  $\beta$ -cryptoxanthin and  $\beta$ -carotene) in cashew apple juice (Zepka et al., 2009). The rate constant of degradation ( $k_3$ ) was an order of magnitude larger than the rate constants of isomerization ( $k_1$  and  $k_2$ ) indicating that degradation was favored above isomerization. Since the conversions were only studied at two different temperatures (60 and 90 °C), the estimation of activation energies for each individual reaction is rather unreliable. Achir et al. (2011) proposed two reaction schemes to describe thermally induced (0-120 min at 120-180 °C)  $\beta$ -carotene conversions in palm olein and copra fat. They concluded that the most appropriate reaction scheme included backward and forward changes in configurations and the same degradation rate for all isomers (Figure 4E). The temperature dependency differed markedly for isomerization and for degradation. For the latter reactions, the rate constants followed the Arrhenius law. In the case of isomerization rate constants, the Arrhenius equation was not suitable.

Multi-response modeling clearly helps in choosing the most probable reaction scheme and more work should be done to extend the current multi-response models to better approach reality.

## 5 Conclusions

The complexity of simultaneous degradation and isomerization reactions of carotenes during thermal processing is not to be underestimated. Different approaches to quantitatively describe carotene conversions have been followed. However, most research focused on the degradation reaction and used single-response models based on total lycopene or  $\beta$ -carotene input data only. The single-response models represent a straightforward and useful pragmatic approach in modeling changes occurring during processing. Nevertheless, the obtained kinetic parameters

must be handled with precaution since they are empirically calculated and apparent. Consequently, kinetic parameters are only useful for process design purposes for the corresponding application due to the inherent reaction environment. The single-response kinetic models give no insight into the reaction pathway and therefore no transposition for other products or processes can be made. Recently, the isomerization reactions as such and the simultaneous isomerization and degradation of lycopene and  $\beta$ -carotene have been assessed using multi-response modeling. Multi-response modeling is a very promising tool in modeling multiple reaction systems such as carotene conversions. It forces the modeler to build reaction schemes behind the model which helps to understand the reaction pathway involved. More work in this context should be encouraged to obtain more complete models which are in closer agreement with reality. This will require input of additional responses of different intermediates and end-products and therefore an increased analytical effort. In addition, carotene conversions could be studied in different reaction media with increasing complexity from single phase, over multiple phase systems up to highly complex multiple ingredient containing food products (e.g. sauces). In these complex multiple phase systems, it would be of great interest to couple the kinetic models to mass transfer models. These integrated models should take into account the kinetics in different phases rather than expressing the concentration based on the food system as a whole.

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**Table 1: Available kinetics of lycopene degradation in model systems and in tomato based systems.**

Processing	System	Kinetic model	Reaction	k (min <sup>-1</sup> )(T <sub>ref</sub> )	E <sub>a</sub> (kJ/mol)	Reference
0-24 h at 75 °C- 95 °C	lycopene in safflower oil	first order kinetic model Arrhenius equation 2-step regression	disappearance of total lycopene	0.0086 ± 0.0001 (95 °C)	83 ± 10	Henry et al. (1998)
0-100 h at 50-150 °C	lycopene in hexane, dried	first order kinetic model Arrhenius equation 2-step regression	disappearance of total lycopene	0.0124 (100 °C)	61	Lee & Chen (2002)
0-30 h at 5-90 °C	lycopene in oil/water emulsion	first order kinetic model Arrhenius equation 2-step regression	disappearance of total lycopene oxygen saturated oxygen free	0.00228 (90 °C) 0.00078 (90 °C)	18 23	Ax et al. (2003)
0-10 h at 50-100 °C	lycopene in tomato pomace	fractional conversion model Arrhenius equation 2-step regression	disappearance of total lycopene	0.00104 ± 0.00012 (100 °C)	18	Kaur et al. (2006)
21-576 h at 50-100 °C	lycopene in oleoresin from tomato paste	first order kinetic model Arrhenius equation 2-step regression	disappearance of total lycopene	0.0001 ± 0.0063 (75 °C)	58.8	Narula et al.(2009)

0-60 min at 100-140 °C	lycopene in olive oil/tomat o emulsion	fractional conversion model Arrhenius equation 1-step regression	disappearanc e of total lycopene	$0.1527 \pm 0.0248$ (110 °C)	$28 \pm 9$	Colle et al. (2010b)
0-120 min at 70-130 °C	lycopene in olive oil	fractional conversion model Arrhenius equation 1-step regression	disappearanc e of total lycopene	$0.0964 \pm 0.0179$ (110 °C)	$25 \pm 7$	Colle et al. (2013)
0-120 min at 50-130 °C	lycopene in fish oil	fractional conversion model Arrhenius equation 1-step regression	disappearanc e of total lycopene	$0.1755 \pm 0.0281$ (110 °C)	$26 \pm 7$	Colle et al. (2013)

**Table 2: Available kinetics of  $\beta$ -carotene degradation in model systems and in carrot based systems.**

Processing	System	Kinetic model	Reaction	$k$ ( $\text{min}^{-1}$ )( $T_{\text{ref}}$ )	$E_a$ ( $\text{kJ/mol}$ )	Reference
5-30 min at 50-150 °C	- carotene crystals	first order kinetic model Arrhenius equation 2-step regression	disappearance of total - carotene	0.018 (125 °C)	39	Chen & Huang (1998)
0-24 h at 75 °C- 95 °C	all- <i>E</i> - carotene in safflower oil	first order kinetic model Arrhenius equation 2-step regression	disappearance of all- <i>E</i> - carotene	$0.0020 \pm 0.0001$ (85°C)	109	Henry et al. (1998)
0-24 h at 75 °C- 95 °C	9- <i>Z</i> - carotene in safflower oil	first order kinetic model Arrhenius equation 2-step regression	disappearance of 9- <i>Z</i> - carotene	$0.0018 \pm 0.0000$ (85 °C)	105	Henry et al. (1998)
0-120 min at 120-180 °C	- carotene in palm olein	first order kinetic model Arrhenius equation 1-step regression	disappearance of total - carotene	0.0108 (120 °C)	$48 \pm 6$	Achir et al. (2010)
0-120 min at 120-180 °C	- carotene in Vegetaline	first order kinetic model Arrhenius equation 1-step regression	disappearance of total - carotene	0.0012 (120 °C)	$154 \pm 21$	Achir et al. (2010)

0-744 h at 60-120 °C	- carotene in olive oil	first order kinetic model Arrhenius equation 2-step regression	disappearance of total carotene	$0.0005 \pm 0.0000$ (120 °C)	60	based on data of Aparicio-Ruiz et al. (2011)
0-120 min at 85-130 °C	- carotene in olive oil/carrot emulsion	fractional conversion model Arrhenius equation 1-step regression	disappearance of total carotene	$0.10 \pm 0.01$ (110 °C)	$45 \pm 9$	Knockaert et al. (2012)
0-45 h at 140-180 °C	all- <i>E</i> - carotene in soybean oil	first order kinetic model Arrhenius equation 2-step regression	disappearance of total carotene	$0.0073 \pm 0.0003$ (140 °C)	59.0	Qiu et al. (2012)
0-45 h at 140-180 °C	all- <i>E</i> - carotene in peanut oil	first order kinetic model Arrhenius equation 2-step regression	disappearance of total carotene	$0.0076 \pm 0.0002$ (140 °C)	94.6	Qiu et al. (2012)
0-45 h at 140-180 °C	all- <i>E</i> - carotene in glyceryl caprylate -caprate	first order kinetic model Arrhenius equation 2-step regression	disappearance of total carotene	$0.0147 \pm 0.0004$ (140 °C)	97.4	Qiu et al. (2012)

**Table 3: Available multi-response kinetics of lycopene isomerization in model systems and in tomato based systems.**

Processing	System	Kinetic model	Reaction	$k$ ( $\text{min}^{-1}$ )( $T_{\text{ref}}$ )	$E_a$ ( $\text{kJ/mol}$ )	Reference
0-60 min at 80-140 °C	lycopene in olive oil/tomato emulsion	multi-response model with first order differential equations of the proposed reaction scheme Arrhenius equation 1-step regression	all- <i>E</i> to x- <i>Z</i>	$0.0073 \pm 0.0030$ (100 °C)	$85 \pm 19$	Colle et al. (2013)
			all- <i>E</i> to 9- <i>Z</i>	$0.0019 \pm 0.0003$ (100 °C)	$143 \pm 8$	
			all- <i>E</i> to 13- <i>Z</i>	$0.0019 \pm 0.0003$ (100 °C)	$114 \pm 25$	
			x- <i>Z</i> to all- <i>E</i>	$0.0482 \pm 0.0122$ (100 °C)	$57 \pm 22$	
			9- <i>Z</i> to all- <i>E</i>	$0.0349 \pm 0.0166$ (100 °C)	$125 \pm 10$	
			13- <i>Z</i> to all- <i>E</i>	$0.0073 \pm 0.0017$ (100 °C)	$92 \pm 25$	
				$0.3761 \pm 0.1025$ (100 °C)		
0-120 min at 70-130 °C	lycopene in olive oil	multi-response model with first order differential equations of the proposed reaction scheme Arrhenius equation 1-step regression	all- <i>E</i> to x- <i>Z</i>	$0.0165 \pm 0.0041$ (100 °C)	$60 \pm 10$	Colle et al. (2013)
			all- <i>E</i> to 9- <i>Z</i>	$0.0049 \pm 0.0004$ (100 °C)	$127 \pm 5$	
			all- <i>E</i> to 13- <i>Z</i>	$0.0049 \pm 0.0004$ (100 °C)	$101 \pm 17$	
			x- <i>Z</i> to all- <i>E</i>	$0.1435 \pm 0.0541$ (100 °C)	$43 \pm 13$	
			9- <i>Z</i> to all- <i>E</i>	$0.0379 \pm 0.0101$ (100 °C)	$105 \pm 8$	
			13- <i>Z</i> to all- <i>E</i>	$0.0150 \pm 0.0026$ (100 °C)	$100 \pm 18$	
				$0.8111 \pm 0.3109$ (100 °C)		

0-120 min at 50-130 °C	lycopene in fish oil	multi-response model with first order differential equations of the proposed reaction scheme Arrhenius equation 1-step regression	all- <i>E</i> to x- <i>Z</i>	$0.0151 \pm 0.0041$	$66 \pm 11$	Colle et al. (2013)
			all- <i>E</i> to 9- <i>Z</i>	(100 °C)	$117 \pm 7$	
			all- <i>E</i> to 13- <i>Z</i>	$0.0050 \pm 0.0007$	$129 \pm 8$	
			x- <i>Z</i> to all- <i>E</i>	(100 °C)	$43 \pm 13$	
			9- <i>Z</i> to all- <i>E</i>	$0.4396 \pm 0.1054$	$91 \pm 13$	
			13- <i>Z</i> to all- <i>E</i>	(100 °C)	$120 \pm 9$	
				$0.0303 \pm 0.0090$		
				(100 °C)		
				$0.0170 \pm 0.0046$		
				(100 °C)		
				$1.2610 \pm 0.3074$		
				(100 °C)		

**Table 4: Available multi-response kinetics of  $\beta$ -carotene isomerization in model systems and in carrot based systems.**

Processing	System	Kinetic model	Reaction	$k$ ( $\text{min}^{-1}$ )( $T_{\text{ref}}$ )	$E_a$ (kJ/mol)	Reference
0-60 min at 80-150 °C	- carotene in carrot puree	multi-response model with first order different equations of the proposed reaction scheme Arrhenius equation 1-step regression	all- <i>E</i> to 9- <i>Z</i> all- <i>E</i> to 13- <i>Z</i> all- <i>E</i> to 15- <i>Z</i> 9- <i>Z</i> to all- <i>E</i> 13- <i>Z</i> to all- <i>E</i> 15- <i>Z</i> to all- <i>E</i>	$0.0031 \pm 0.0017$ (100 °C) $0.0175 \pm 0.0093$ (100 °C) $0.0239 \pm 0.0126$ (100 °C) $0.0107 \pm 0.0092$ (100 °C) $0.3253 \pm 0.1634$ (100 °C) $0.1519 \pm 0.0841$ (100 °C)	$54 \pm 14$ $60 \pm 6$ $91 \pm 30$ $33 \pm 21$ $34 \pm 4$ $74 \pm 31$	based on data of Lemmens et al. (2010)

0-120 min	-	multi-response model with	all- <i>E</i> to 9- <i>Z</i>	$0.0010 \pm 0.0003$	$89 \pm 8$	based on data of
at 85-130 °C	carotene	first order different equations	all- <i>E</i> to 13- <i>Z</i>	(100 °C)	$129 \pm$	Knockaert et al.
	in olive	of the proposed reaction	all- <i>E</i> to 15- <i>Z</i>	$0.0265 \pm 0.0020$	8	(2012)
	oil	scheme	9- <i>Z</i> to all- <i>E</i>	(100 °C)	$131 \pm$	
		Arrhenius equation	13- <i>Z</i> to all- <i>E</i>	$0.0112 \pm 0.0021$	22	
		1-step regression	15- <i>Z</i> to all- <i>E</i>	(100 °C)	$22 \pm 6$	
				$0.0173 \pm 0.0062$	$124 \pm$	
				(100 °C)	8	
				$0.1489 \pm 0.0130$	$106 \pm$	
				(100 °C)	23	
				$0.1777 \pm 0.0379$		
				(100 °C)		



0-120 min	-	multi-response model with	all- <i>E</i> to 9- <i>Z</i>	$0.0007 \pm 0.0002$	$87 \pm$	based on data of
at 85-130 °C	carotene	first order different equations	all- <i>E</i> to 13- <i>Z</i>	(100 °C)	14	Knockaert et al.
	in olive	of the proposed reaction	all- <i>E</i> to 15- <i>Z</i>	$0.0337 \pm 0.0048$	$120 \pm$	(2012)
	oil/carrot	scheme	9- <i>Z</i> to all- <i>E</i>	(100 °C)	15	
	emulsion	Arrhenius equation	13- <i>Z</i> to all- <i>E</i>	$0.0092 \pm 0.0019$	$76 \pm$	
		1-step regression	15- <i>Z</i> to all- <i>E</i>	(100 °C)	17	
				$0.0012 \pm$	$47 \pm$	
				$0.0036^*$ (100	45	
				°C)	$108 \pm$	
				$0.1357 \pm 0.0229$	16	
				(100 °C)	$59 \pm$	
				$0.0691 \pm 0.0167$	19	
				(100 °C)		

\* estimated after fixing the other parameters

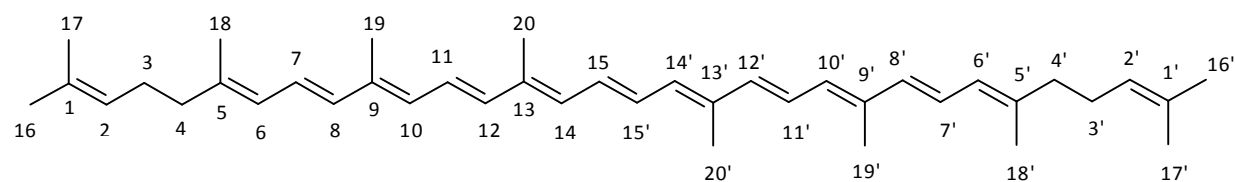
**Table 5: Available kinetics of simultaneous degradation and isomerization of lycopene in tomato based systems and  $\beta$ -carotene in model systems.**

Processing	System	Kinetic model	Reaction	$k$ ( $\text{min}^{-1}$ )( $T_{\text{ref}}$ )	$E_a$ (kJ/mol)	Reference
0-6 h at 90-150 °C	lycopene	multi-response model with	All-E to	0.0114 (110 °C)	6	Shi et al. (2003)
	in	first order differential	OCP	0.0026 (110 °C)	3	
	tomato	equations of the proposed	Z to OCP	0.0043 (110 °C)	4	
	pulp	reaction scheme	All- <i>E</i> to <i>Z</i>	0.0000 (110 °C)	/	
		Arrhenius equation	<i>Z</i> to all- <i>E</i>			
		2-step regression				

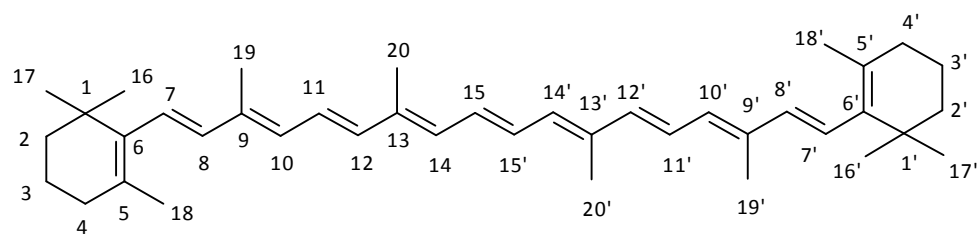
0-120 min	-	multi-response model with	all-E, 9-Z,	0.011 ± 0.001	51	Achir et al. (2011)
at 120-180	carotene	first order different equations	13-Z to OCP	(120 °C)		
°C	in palm	of the proposed reaction	all-E to 9-Z		k	
	olein	scheme	all-E to 13-Z	0.021 ± 0.002	values	
		Arrhenius equation	9-Z to all-E	(120 °C)	did not	
		2-step regression	13-Z to all-E	0.063 ± 0.010	follow	
				(120 °C)	Arrhen	
				0.077 ± 0.012	ius law	
				(120 °C)		
				0.185 ± 0.002		
				(120 °C)		

0-120 min	-	multi-response model with	all-E, 9-Z,	0.000 ± 0.000	171	Achir et al. (2011)
at 120-180	carotene	first order different equations	13-Z to OCP	(120 °C)		
°C	in copra	of the proposed reaction	all-E to 9-Z		k	
	fat	scheme	all-E to 13-Z	0.042 ± 0.002	values	
		Arrhenius equation	9-Z to all-E	(120 °C)	did not	
		2-step regression	13-Z to all-E	0.141 ± 0.015	follow	
				(120 °C)	Arrhen	
				0.128 ± 0.008	ius law	
				(120 °C)		
				0.269 ± 0.032		
				(120 °C)		

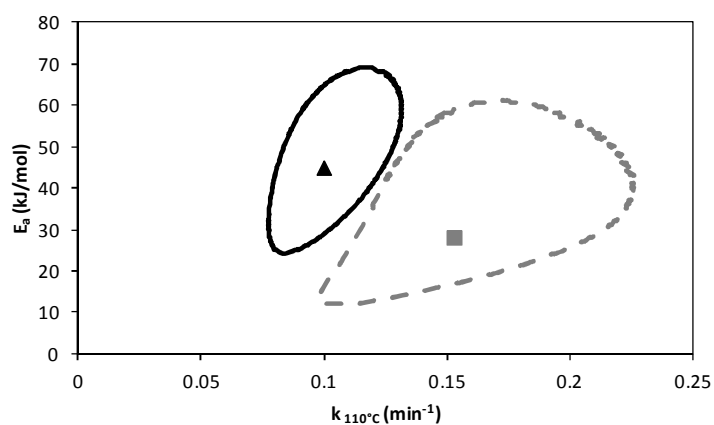
OCP = oxidation and cleavage products



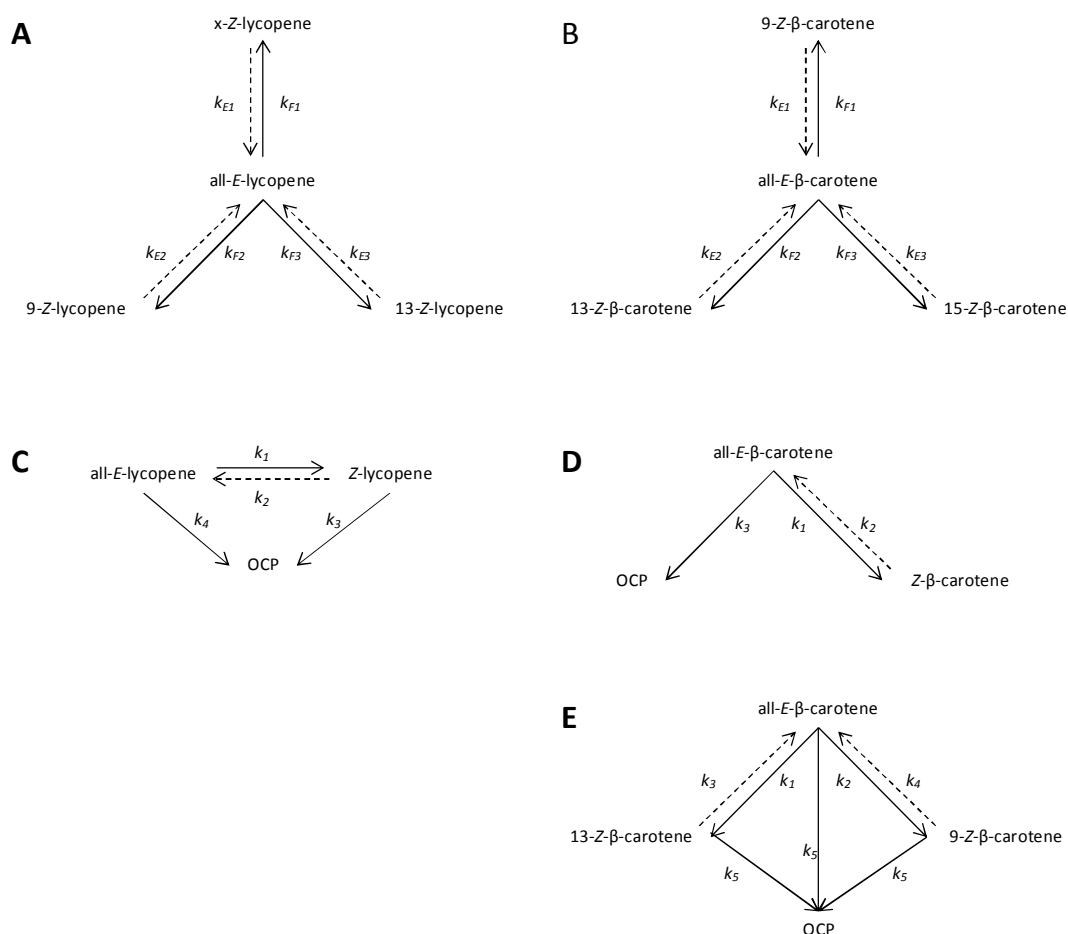
**Figure 1: Chemical structure of all-*E*-lycopene.**



**Figure 2: Chemical structure of all-*E*-β-carotene.**

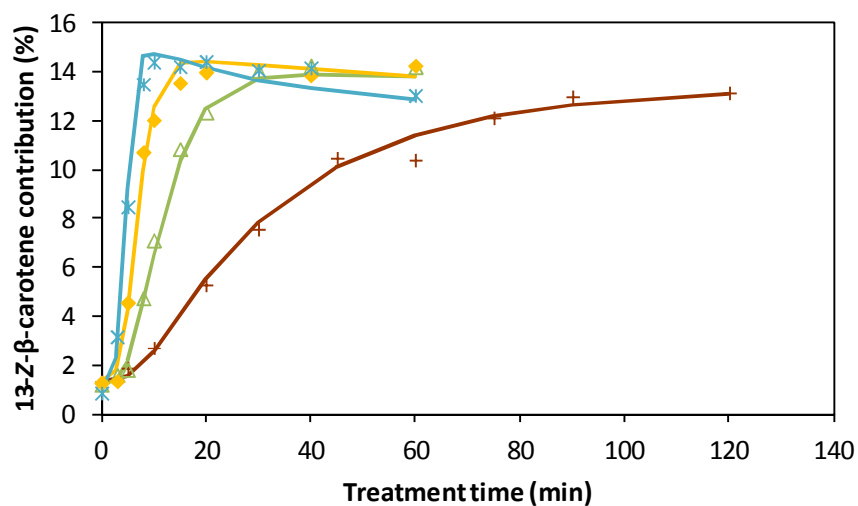


**Figure 3: Joint confidence regions (90%) for total  $\beta$ -carotene degradation kinetics in olive oil/carrot emulsion (▲) and for total lycopene degradation kinetics in olive oil/tomato emulsion (■). The symbols represent the least-squares estimates; the lines represent the JCR's.**



**Figure 4: Reaction schemes to model carotene conversions proposed by Colle et al. (2013) (A), Chen et al. (1994) (B), Shi et al. (2003) (C), Zepka et al. (2009) (D) and Achir et al. (2011) (E). OCP = oxidation and cleavage products.**





**Figure 5:** Time course of 13-Z-β-carotene contribution in olive oil heated at 85 °C (+), 100 °C (Δ), 115 °C (◆), and 130 °C (\*). The solid lines represent the fit of the Figure B model, while experimental data are represented by single data points.