International Food Research Journal 25(5): 1912-1919 (October 2018)
Journal homepage: *http://www.ifrj.upm.edu.my*

# Thermal degradation kinetics of total carotenoids and antioxidant activity in banana-pumpkin puree using Arrhenius, Eyring-Polanyi and Ball models

[1*]Jirasatid, S., [2]Chaikham, P. and [3]Nopharatana, M.

[1]*Department of Food Science, Faculty of Science, Burapha University, Chonburi 20131, Thailand*
[2]*Division of Food Science and Technology, Faculty of Science and Technology, Phranakhon Si Ayutthaya Rajabhat University, Phranakhon Si Ayutthaya 13000, Thailand*
[3]*Department of Food Engineering, Faculty of Engineering, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand*

**Article history**

*Received: 5 June 2017*
*Received in revised form: 12 October 2017*
*Accepted: 13 October 2017*

**Keywords**

*Banana-pumpkin puree*
*Thermal treatment*
*Degradation kinetics*
*Total carotenoids*
*Antioxidant activity*

**Abstract**

The effect of thermal treatment (60, 70, 80 and 90°C) on degradation kinetics of total carotenoids and antioxidant activity (DPPH assay) in banana-pumpkin puree was investigated using Arrhenius, Eyring-Polanyi and Ball models. The heating temperatures had a significant effect on total carotenoids loss, but little effect on loss of DPPH inhibition in banana-pumpkin puree. 37% of total carotenoids content was remained after heat at 90°C for 60 mins, while the remaining of DPPH inhibition was 96% at this heating condition. Degradation kinetics was best described by first-order kinetics reactions for the reduction of total carotenoid and antioxidant activity. Temperature dependence of rate constants followed the Arrhenius, Eyring-Polanyi and Ball models. According to Arrhenius model, activation energies were 35.36 and 27.83kJ/mol, respectively for degradation of total carotenoids and DPPH inhibition in banana-pumpkin puree during heating at 60-90°C. Arrhenius, Eyring-Polanyi and Ball models predicted accurately the total carotenoids content and DPPH inhibition during isothermal heating.



## Introduction

Banana (*Musa* spp.) and pumpkin (*Cucurbita* spp.) are cultivated in tropical and subtropical regions including Thailand and consumed as various products throughout the world. Banana may be processed as puree, banana powder, chip, vinegar and wine, and pumpkin can be processed to as puree, syrup and chip (Tsen and King, 2002; Gliemmo *et al*., 2009). Commonly, fruit-vegetable purees are used as an ingredient of food products including beverages, jams and jellies. Purees are ideal foods for infants, senile and dysphagia adults. Additionally, purees/pastes are market favorites in fast food industries.

Banana and pumpkin are rich in nutrients and phytochemical compounds especially carotenoids (Englberger *et al*., 2003; Gliemmo *et al*., 2009), which contribute to color synthesis in fruits and vegetables with color ranging from yellow to red (Gliemmo *et al.,* 2009). Carotenoids are pro-vitamin A, which has antioxidant, anticarcinogenic and antimutagenic activities. Many studies indicated that carotenoids intake reduce the risk of certain types of cancer, cardiovascular diseases, cataracts and macular degeneration. Carotenoids also play a significant function in disease prevention (Provesi *et al.,* 2011; Demiray *et al.,* 2013).

Carotenoids can be degraded into another form by oxidation and isomerization during processing and storage, resulting in discoloration, reduction in nutrition and changes in biochemical properties (Provesi *et al.*, 2011). Many factors affect oxidation of carotenoids including temperature, light, oxygen, pro-oxidant metals, and co-oxidation with unsaturated lipids. *Trans-cis* isomerization reactions are normally induced by heat, acids and light (Bonnie and Choo, 1999; Gliemmo *et al*., 2009).

Food processing often involves heating that inhibits or kills microorganisms extending shelf life. It has also significant influence on nutrients and functional health properties. Thermal degradation of carotenoids and antioxidative properties of food products have been reported. Provesi *et al*. (2011) found the predominant carotenoids viz. violaxanthin, lutein, ζ-carotene, α-carotene and all-*trans*-β-carotene in pumpkin purees apparently decreased after thermal treatments at 100 and 121°C for 20 mins concurrently with an increase of *cis*-β-carotene. Benlloch-Tinoco *et al.* (2015) also reported a decline of the major carotenoids such as lutein, neolutein A and B, β-carotene, neoxanthin and violaxanthin in kiwifruit puree following heating at 97°C for 30s, as compared to fresh puree. Moreover, the thermal degradation of antioxidant activity has been reported

*Corresponding author.
Email: *sani@buu.ac.th*

in red flesh and peel plum puree (Garcia-Parra *et al*., 2014), strawberry puree (Cheng *et al*., 2014) and plum extracts (Turturica *et al*., 2016).

Temperature is important in the process of a safe food product and maximum retention of nutrients and bioactive constituents. Kinetic models such as Arrhenius, Eyring-Polanyi and Ball are important in prediction remaining of nutrients and/or bioactive compounds in foods during thermal processing (Cisse *et al*., 2009; Remini *et al*., 2015; Nambi *et al*., 2016). Arrhenius model is an empirical collision model for chemical reaction. It has proven to be very good model in chemical kinetics. Eyring-Polanyi model is based on transition state theory. This equation explains the effect of temperature on the reaction rate constant to change in enthalpy and entropy terms. Ball model is used frequently in food processing, especially in bacteriology to investigate microorganism inactivation (Cisse *et al.*, 2009; Van Boekel, 2009). However, these kinetic models have not been applied for evaluating loss of total carotenoids and antioxidant activity in banana-pumpkin puree. The objective of this study was to monitor the effect of temperature and create kinetic models to quantify thermal degradation of total carotenoids and antioxidant activity (DPPH assay) in the production of banana-pumpkin puree. This study also reported the equations, namely, Arrhenius, Eyring-Polanyi and Ball for estimating appropriate heat condition with respect to the total carotenoids and DPPH radical scavenging activity for developing a banana-pumpkin puree production.

## Materials and Methods

*Preparation of banana-pumpkin puree*

Ripe bananas (*Musa sapientum* L.) and ripe pumpkins (*Cucurbita moschata* Duchesne ex. Poiret) were purchased from a local market in Chonburi, Thailand. Banana was washed in a 20 ppm chlorine solution, peeled, cut into pieces with 2 cm thickness and blanched in boiling water for 7 mins (Tsen and King, 2002). Pumpkin fruit was washed in a 50ppm chlorine solution, peeled, cut into pieces 2x3 cm and steamed at 100°C for 12 mins (Gliemmo *et al*., 2009). After heating, the blanched banana and steamed pumpkin were cooled quickly by immersion in chilled water, and then placed on absorbent paper to purge excess water.

Banana-pumpkin puree was prepared by mixing of blanched banana and steamed pumpkin in the ratio of 1:1, and homogenized using a blender (Philips, China). The pH value of puree was adjusted to 4.2 with 0.05% of ascorbic acid (Gliemmo *et al*., 2009) and analyzed for total soluble solid content (TSS) or °Brix value, pH, water activity ($a_w$) and moisture content.

*Thermal treatment*

Loss of total carotenoids and antioxidant activity due to thermal processing was studied by isothermal heating at temperatures of 60, 70, 80 and 90°C for a residence time of 0 to 60 mins. A 20ml of puree was added into a glass tube and covered with a plastic screw cap. Subsequently, the samples were heated at different temperatures by placing them in a thermostatic water bath (Model 11DT-1, Heto, Denmark). The thermocouples were immersed in sample tubes to monitor temperature during heating. Once temperatures reached those required tubes were removed and rapidly cooled in an ice water bath to stop reactions. Samples were stored at -18°C for further analysis. The experiment was performed in the two replications.

*Physicochemical properties determination*

Samples were analyzed for moisture content, aw, pH according to AOAC (1995). Total soluble solid content (°Brix) was measured with a handheld refractometer at 25°C (Master, Atago, Japan).

*Total carotenoids content determination*

Total carotenoids in all samples were determined by the spectrophotometric method described by Carvalho *et al.* (2012). A 15g of puree were well mixed with 25ml acetone, transferred into a sintered funnel, coupled to a 250 ml Buchner flask and vacuum-filtered through a 5 μm membrane until a colorless sample was obtained. The extract was poured into a separatory funnel (500 ml) containing 40ml petroleum ether. Distilled water was added slowly to remove acetone and prevent the formation of an emulsion. The watery phase was then discarded and the extract poured into a volumetric flask (100ml) containing 15 g of anhydrous sodium sulfate and volume made up with petroleum ether. Extract absorbance was measured at 450 nm (Genesys 20, Thermo Scientific, USA). Total carotenoids (mg/g wet basis) were expressed as:

$$\text{Total carotenoids (mg/g)} = \frac{A \times V(ml) \times 10^4}{A_{1\,cm}^{1\%} \times P\,(g) \times 1000}$$

where A is absorbance, V is total extract volume, P is sample weight and $A_{1\,cm}^{1\%}$ is 2592 (β-carotene extinction coefficient in petroleum ether).

*Antioxidant activity determination*

In polar compounds extraction, twenty grams of

puree and 80 ml of chilled 80% of acetone (4°C) were blended using a blender for 10 mins. The mixture was vacuum-filtered through a Whatman filter paper No. 1 (Liaotrakoon *et al*., 2013).

2,2-Diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity in the puree extract was assessed following a colorimetric procedure (Karagozler *et al*., 2008). A 1 ml of 0.1 mM DPPH in ethanol solution was well mixed with 3 ml of the puree extract with different concentration (5-250 µg/ml), vortexed and then allowed to react in the dark room for 30 mins at room temperature. Absorbance was measured at 517 nm (Genesys 20, Thermo Scientific, USA). Absorbance of DPPH solution in the absence of sample was used as a control. % DPPH radical scavenging activity or % inhibition was expressed as:

$$\%\ \text{DPPH radical scavenging activity} = \left(\frac{A_0 - A_1}{A_0}\right) \times 100$$

where $A_0$ is the absorbance of the control and $A_1$ is the absorbance of the sample

*Degradation kinetics modeling*

Degradation rate of total carotenoids and/or antioxidant activity (% DPPH inhibition) during heating was modeled using simple kinetics equation as shown in Equation (1):

$$\frac{dC}{dt} = -kC^n \quad (1)$$

where $t$ is time (min), $k$ is reaction rate constant, $n$ is kinetics order of reaction (Horia, 2006) and $C$ is total carotenoids (mg/100g), or % DPPH radical scavenging activity.

A kinetics model was proposed and translated to mathematical model by deriving a differential equation using zero-, first- and second-order reaction kinetics. Each differential equation was simultaneously solved by numerical integration and fitted with experimental data as the $k$ value was predicted. Numerical integration and parameters estimation were determined by Euler and Runge-Kutte. Acceptance was related directly to coefficient of determination $(R^2)$. Temperature dependence on rate constant of degradation of total carotenoids or DPPH scavenging activity was then expressed by Arrhenius equation as shown in Equation (2). Activation energy $(E_a)$ was obtained from slope of ln $k$ versus $1/T$ plot by regression analysis (Horia, 2006; Karim and Adebowale, 2009; Jirasatid *et al*., 2013).

$$k = k_0 exp\left[-\frac{E_a}{RT}\right] \quad (2)$$

where $k$ is rate constant, $k_0$ is the frequency factor, $R$ is gas constant (8.314 J/mol.K), $T$ is absolute temperature (K) and $E_a$ is activation energy (J/mol).

The half-life time ($t_{1/2}$) is the time required for degradation of total carotenoids content or DPPH scavenging activity to 50% of its initial concentration. The half-life time of the first-order kinetics reaction was calculated using Equation (3):

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

The coefficient $Q_{10}$ (temperature coefficient) shows the characteristic of the effect of temperature on reaction rate, which represents degradation with a temperature increase of 10°C, as in Equation (4) (Kechinski *et al*., 2010; Ozsen and Erge, 2013):

$$Q_{10} = \left(\frac{k_2}{k_1}\right)^{\left(\frac{10}{T_2 - T_1}\right)} \quad (4)$$

where $k_2$ is the rate constant of reaction at $T_2$ temperature and $k_1$ is the rate constant of reaction at $T_1$ temperature.

Thermodynamic functions of activation such as enthalpy (ΔH), entropy (ΔS) and free enthalpy (ΔG) for degradation of total carotenoids or DPPH scavenging activity were obtained from relationship between ln $(k{\cdot}h/k_B{\cdot}T)$ and $1/T$ according to Eyring-Polanyi model, based on transition state theory as in Equations (5) and (6), respectively (Cisse *et al.,* 2009; Van Boekel, 2009; Kechinski *et al.*, 2010):

$$k = \frac{k_B}{h} T \exp\left(-\frac{\Delta G}{RT}\right) = \frac{k_B}{h} T \exp\left(-\frac{\Delta H - T \cdot \Delta S}{RT}\right) \quad (5)$$

$$\Delta G = \Delta H - T \cdot \Delta S \quad (6)$$

where $k_B$ is Boltzmann's constant ($1.381 \times 10^{-23}$ J/K), $h$ is Plank's constant ($6.626 \times 10^{-34}$ J·s), T is absolute temperature (K), $R$ is gas constant (8.314 J/mol·K), $\Delta H$ is activation enthalpy (J/mol), $\Delta S$ is activation entropy (J/mol·K) and $\Delta G$ is free activation enthalpy (J/mol).

The Ball model (Equations (7) and (8)) is used commonly in food processing for microorganisms destruction. It is applied to determine decimal reduction time ($D$ value), which is related to temperature via a Z value. Z value was obtained by the reciprocal from slope of $\log_{10} D$ versus $T$ plot by regression analysis (Cisse *et al.*, 2009; Van Boekel, 2009).

$$D = \frac{\ln 10}{k} \quad (7)$$

$$D = D_0 10^{\frac{-T}{Z}} \quad (8)$$

where $D$ is the heating time required to reduce total carotenoids or DPPH scavenging activity by 90% (min), $D_0$ is value of $D$ at $T$ = 0°C (min), T is temperature (°C) and Z (°C) is the required

temperature for one $\log_{10}$ D value reduction.

*Statistical analysis*

A completely randomized design (CRD) was developed for four levels of heating temperature. Statistical analysis was performed by analysis of variance (ANOVA). Difference in mean values was analyzed by Duncan's multiple range tests (DMRT). Significant differences of samples were determined at $p<0.05$.

## Results and Discussion

Physicochemical properties of the unheated banana-pumpkin puree showed that the initial moisture content, aw, pH and total soluble solid content were 85.6±2% (wet basis), 0.96±0.03, 4.2±0.1 and 13.6±0.2 °Brix, respectively.

*Degradation kinetics of total carotenoids*

The decrease of total carotenoids in banana-pumpkin puree corresponded with the increases of heating temperature and time. Initial total carotenoids in banana-pumpkin purees were 2.47±0.04, 2.46±0.33, 2.56±0.19 and 2.51±0.28 mg/100g and after heating for 60 mins at 60, 70, 80 and 90°C, significantly decreased to 1.73±0.35, 1.68±0.31, 1.58±0.09 and 0.93±0.07 mg/100g respectively. Total carotenoids remaining in the heated purees at 60, 70, 80 and 90°C were approximately 70, 68, 61 and 37%, respectively. This indicated that carotenoids were heat sensitive compounds, particularly at high thermal temperature (90°C). Under thermal treatment, the breakdown of carotenoids molecule occurred by isomerization and thermal oxidation. Two thermal degradation products were synthesized representing the volatile and non-volatile fraction. The volatile fraction is composed of volatile low molecular weight compounds, is vaporized, while the non-volatile fraction is the residual fraction after vaporization of the volatile fraction (Bonnie and Choo, 1999). The results in this study were in agreement with those reported in previous studies, indicating thermal treatment of several food products caused a decrease in heat susceptible nutrients such as carotenoids found in pumpkin puree (Provesi *et al*., 2011), dried tomato (Demiray *et al*., 2013) and kiwifruit puree (Benlloch-Tinoco *et al.,* 2015).

Isothermal degradation of total carotenoids closely followed first-order reaction kinetics with respect to temperature very well with high $R^2$ values ($R^2$=0.906-0.959) (Figure 1). Kinetic parameters of total carotenoids degradation during heating based on first-order kinetics are shown in Table 1. The k values of first-order reaction were within the range of 0.0050-0.0152 $min^{-1}$. The reaction rate was influenced significantly by heating temperature. When the heating temperature increased, the degradation rate of total carotenoids was also risen. The first-order kinetics model for carotenoid compounds degradation showed in this study was in agreement with earlier findings with heated citrus juice and dried tomato by Dhuique-Mayer *et al.* (2007) and Demiray *et al.* (2013), respectively.

Time required for 50% degradation of total carotenoids in banana-pumpkin puree varied from 139-45 mins in the temperature ranges applied in the present study (Table 1). The high value of 139 mins for half-life time was due to the slow rate of total carotenoids degradation at 60°C, verification

Table 1. Isothermal kinetic parameters $k$ and $t_{1/2}$ values vs temperature for degradation of total carotenoids and DPPH radical scavenging activity in banana-pumpkin puree

| Reaction | Temperature (°C) | Rate constant, $k$ ($min^{-1}$) | Correlation coefficient, $R^2$ | Half-life value, $t_{1/2}$ (min) |
|---|---|---|---|---|
| Total carotenoids | 60 | 0.0050 | 0.906 | 139 |
| | 70 | 0.0058 | 0.946 | 119 |
| | 80 | 0.0072 | 0.933 | 96 |
| | 90 | 0.0152 | 0.959 | 45 |
| DPPH radical scavenging activity | 60 | $4.57\times10^{-4}$ | 0.941 | 1516 |
| | 70 | $4.56\times10^{-4}$ | 0.908 | 1518 |
| | 80 | $7.97\times10^{-4}$ | 0.819 | 869 |
| | 90 | $9.59\times10^{-4}$ | 0.774 | 723 |

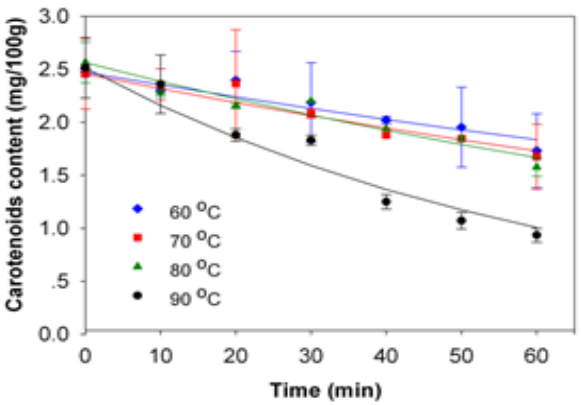


Figure 1. Fit of the first-order kinetics models to the experimental data for total carotenoids degradation in banana-pumpkin puree during heating. Simulation and experimental data are solid line and symbol.

Table 2. Isothermal kinetic parameters $Q_{10}$ values for degradation of total carotenoids and DPPH radical scavenging activity in banana-pumpkin puree

| Reaction | Temperature (°C) | $Q_{10}$ |
|---|---|---|
| Total carotenoids | 60 to 70 | 1.16 |
| | 70 to 80 | 1.24 |
| | 80 to 90 | 2.11 |
| DPPH radical | 60 to 70 | 1.00 |
| scavenging activity | 70 to 80 | 1.75 |
| | 80 to 90 | 1.20 |

the idea that lower the temperature, lower the total carotenoids degradation. The result in this study was in agreement with Demiray *et al*. (2013), who reported that the half-life time value for β-caratene degradation in dried tomato decreased when drying temperature increased from 60°C to 100°C. Half-life time was 495.6 mins at 60°C, which dropped to 108.6 mins at 100°C.

Table 2 illustrates the $Q_{10}$ values for total carotenoids degradation at temperatures used in this study. The $Q_{10}$ values for total carotenoids degradation in banana-pumpkin puree increased according to the increasing of temperature from 60-90°C. The $Q_{10}$ value was the highest in range of 80-90°C, demonstrating its importance in total carotenoid degradation in banana-pumpkin puree as compared to other temperature ranges (60 to 70°C and 70 to 80°C).

Temperature dependence of the rate constant followed the Arrhenius model. The *k* values were well fitted with Arrhenius law with high regression coefficient (Table 3). Activation energy for total carotenoids degradation at 60-90°C in banana-pumpkin puree was 35.36bkJ/mol (Table 3). Dhuique-Mayer *et al.* (2007) reported the activation energy value for degradation of β-carotene and β-crytoxanthin at 75-100°C in citrus juice approximate 110.0 and 156.0kJ/mol, respectively. This showed that the total carotenoids degradation in banana-pumpkin puree was less sensitive to change in the temperature than that of β-carotene and β-crytoxanthin degradation in citrus juice. It is possible that several interactions between the different solutes in banana-pumpkin puree system could modulate carotenoids degradation. Moreover, the degradation of carotenoids depends on environmental conditions such as dissolved oxygen content, temperature and light (Dhuique-Mayer *et al*., 2007).

Thermodynamic functions of activation for total carotenoids degradation corresponding to Erying model were calculated as 32.47 (kJ/mol), -193.47 (J/mol·K) and 99.83 (kJ/mol) for *ΔH, ΔS* and *ΔG*, respectively (Table 3).

Activation free enthalpy *(ΔG)* for total carotenoids degradation in this study was similar to that the studied by Kechinski *et al.* (2009), who reported the value of *ΔG* for anthocyanin degradation in blueberry juice of about 91.3 (kJ/mol) during heating at 40-80°C for 2 hours. The similar value of *ΔG* denoted that similar factors influence degradation rate. The *ΔG* value represents the difference between the activated state and reactants, thus it must be positive sign. In addition, the positive sign of ΔH explains an endothermic state between activated complex and reactant, which an increase in degradation was induced with increasing temperature. The high value of ΔS means high significance of this thermodynamic function. Its negative sign implies that an increase in order is necessary to form an activated complex (Al-Zubaidy and Khalil, 2007; Kechinski *et al*., 2009).

The thermal resistance approach in term of decimal reduction value (*D* value) using first-order kinetics reaction was calculated from Equation (7) (Van Boekel, 2009). *D* values were within the range of 460.5-151.5 mins for heating temperatures of 60-90°C. *D* values significantly decreased when the heating temperatures increased, indicating that at higher heating temperature, the heating time required to reduce total carotenoids by 90% was shorter. The D values were fitted well with Ball model with a high R2 value. The values of *Z* and $D_0$ were 67°C and 4.4 x$10^3$ min, respectively (Table 3).

*Degradation kinetics of antioxidant activity*

DPPH radical scavenging activity of banana-pumpkin purees were 69.1±1.5, 74.9±3.6, 74.4±3.1 and 65.9±4.1% at the beginning of heating at 60, 70, 80 and 90°C, respectively. Antioxidant activity (% DPPH inhibition) decreased slightly according to heating temperatures and times. After heating for 60 min at temperature of 60, 70, 80 and 90°C, these values were 67.4±3.3, 72.4±0.4, 71.5±3.6 and 63.1±1.2%, respectively. The remaining of antioxidant activity in banana-pumpkin puree was within the range of 96-97%. It was suggested that DPPH radical scavenging activity in banana-pumpkin puree indicated thermal stability.

The kinetics of degradation in antioxidant activity followed a first-order reaction with higher $R^2$ intervals ($R^2$=0.774-0.941) (Figure 2) as compared with zero- ($R^2$=0.768-0.940) and second-order reactions ($R^2$=0.742-0.940). Table 1 shows the kinetics data of degradation in antioxidant activity in banana-

Table 3. Kinetic parameters for thermal degradation of total carotenoids and DPPH radical scavenging activity using different models

| Reaction | Arrhenius model | | | Eyring model | | | Ball model | | |
|---|---|---|---|---|---|---|---|---|---|
| | $k_0$ ($min^{-1}$) | $E_a$ (kJ/mol) | $R^2$ | $\Delta H$ (kJ/mol) | $\Delta S$ (J/mol·K) | $R^2$ | $D_0 \times 10^3$ (min) | $Z$ (°C) | $R^2$ |
| TC | 1537.63 | 35.36 | 0.846 | 32.47 | -193.47 | 0.823 | 4.4 | 67 | 0.863 |
| DPPH RSA | 9.56 | 27.83 | 0.873 | 24.93 | -235.72 | 0.847 | 29.2 | 83 | 0.881 |

TC: total carotenoids, DPPH RSA: DPPH radical scavenging activity

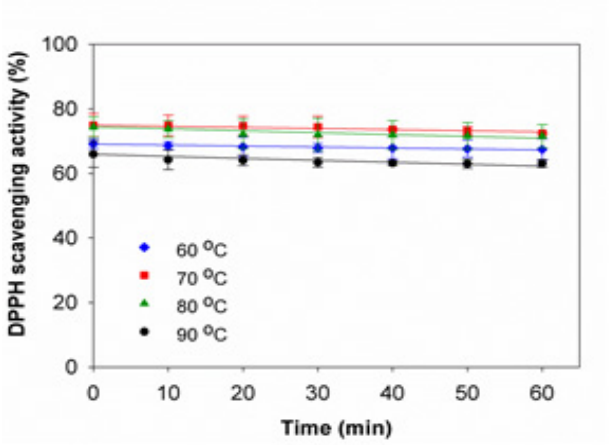


Figure 2. Fit of the first-order kinetics models to the experimental data for DPPH radical scavenging activity degradation in banana-pumpkin puree during heating. Simulation and experimental data are solid line and symbol.

pumpkin puree during heating. The k values increased from $4.57 \times 10^{-4}$ to $9.59 \times 10^{-4}$ min-1 as temperature increased from 60 to 90°C. This indicated that the rate of degradation in antioxidant activity varied with temperature. The half-life time (t1/2) of thermal degradation of DPPH radical scavenging activity in banana-pumpkin puree was 1516 mins at 60°C, but it reduced greatly to 723 mins at 90°C (Table 1). The results showed that the DPPH radical scavenging activity in banana-pumpkin puree was more stable under lower temperature treatment, indicating by lower rate constant and higher half-life value. In accord Garcia-Parra *et al.* (2014), reported that thermal degradation of antioxidant activity (DPPH assay) in plum extracts followed a first-order reaction. The degradation half-life of DPPH radical scavenging activity in plum extracts decreased from 173.28 to 33.00 mins when temperature increased from 70 to 110°C. These results indicated that the degradation of antioxidant activity in banana-pumpkin puree was less sensitive to heating temperature as compared to that for plum extracts.

The highest $Q_{10}$ value was observed within the heating temperature range of 70-80°C (Table 2), implying that the degradation kinetics in antioxidant activity was strongly affected under this temperature range. On the other hand, $Q_{10}$ was least with an increasing temperature from 60 to 70°C, indicating that the degradation kinetic of antioxidant activity was barely affected under this temperature range. The relatively low value of $Q_{10}$ suggested that the significance of molecular associations decreased the reaction rate of antioxidant activity degradation (Al-Zubaidy and Khlil, 2007).

Within the heat treatment range studied (60-90°C), the activation energy ($E_a$) for the degradation of antioxidant activity was 27.83kJ/mol (Table 3), which obtained from the slope of the Arrhenius plot with a high coefficient of determination (Table 3). The low activation energy implied that the degradation of antioxidant activity in banana-pumpkin puree was less sensitive to temperature change than that in plum extracts (under 70-110°C), with a higher activation energy of 47.22kJ/mol (Garcia-Parra *et al.,* 2014).

Over the temperature range in this study (60-90°C), the calculated values of $\Delta H$, $\Delta S$, and $\Delta G$ for degradation of DPPH inhibition in banana-pumpkin puree were 24.93 (kJ/mol), -235.72 (J/mol·K), and 107.00 (kJ/mol), respectively (Table 3). Total carotenoids degradation in banana-pumpkin puree presented higher values of $\Delta H$ and $\Delta S$ than that of degradation in DPPH inhibition (Table 3), indicating that the $k$ value from total carotenoids degradation was more influenced by temperature.

The heating time required to reduce antioxidant activity by 90% from an initial value ($D$ values) were within the range of 5,035.7 to 2,401.0 mins as the heating temperature increased from 60 to 90°C. $D$ values for degradation of antioxidant activity were higher than those of $D$ values for total carotenoid degradation. This suggested that antioxidant activity (DPPH assay) was more heat stable than that for total carotenoids in banana-pumpkin puree. The heated purees showed high potential in antioxidant activity, although total carotenoids degraded. The Ball model fitted well the temperature dependence of $D$ values

($R^2$=0.881). Z and $D_0$ were 83°C and 29.2x10$^3$ min, respectively for thermal degradation of antioxidant activity in banana-pumpkin puree from 60-90°C (Table 3).

*Validation of kinetics modeling*

To verify model predictability, the correlation coefficients for actual and predicted data were investigated. For the Arrhenius model, k values for degradation of total carotenoids or DPPH inhibition were simulated by replacing kinetics parameters such as Ea and $k_0$ to Arrhenius equation (Equation (2)). For Eyring-Polanyi model, the k values were calculated by substituting $\Delta H$ and $\Delta S$ to Eyring-Polanyi model (Equation (5)). For Ball model, the k values were obtained from replacing the $D$ values at any temperature to Equation (7) in which $D$ values was simulated by replacing the value of Z and $D_0$ to Ball equation (Equation (8)). The k values for degradation of total carotenoids or DPPH inhibition from each model were then substituted into the differential equation (Equation (1)) using first-order reaction in order to calculate the yield of total carotenoids or DPPH inhibition at any time of heating. The results showed that Arrhenius, Eyring and Ball models (Figure not shown) fitted reasonably well with the experimental data of total carotenoids content with $R^2$ within the ranges of 0.908-0.963, 0.908-0.963 and 0.908-0.964, respectively. In addition, the three models also gave similar results in predicting the experimental data of DPPH inhibition with $R^2$ within the range of 0.774-0.941, 0.774-0941 and 0.774-0.941, respectively for Arrhenius, Eyring and Ball models (Figure not shown). Therefore, the accuracy of three models was verified. The simple kinetics approach followed in this study was validated already for isothermal treatments.

## Conclusion

This study found negative correlation between carotenoids and antioxidant potential. Total carotenoids in banana-pumpkin puree were unstable during heating, particularly at high temperature (90°C), while antioxidant activity (DPPH assay) changed little during heat treatment. Higher stability of total carotenoids and DPPH inhibition in the puree was found at lower temperature and shorter heating time. Maximum residual of total carotenoids and antioxidant activity were 70 and 97%, respectively at 60°C for 60 mins. Degradation of total carotenoids and antioxidant activity in banana-pumpkin puree during heating was best explained by first-order kinetics. Rate constants for degradation of total carotenoids and antioxidant activity indicated that heat accelerated degradation. Variation in degradation rate constants according to temperature followed the Arrhenius, Eyring and Ball models very well. This information provided guidelines for determining optimum heating conditions to minimize losses in biologically active compounds and antioxidative properties in banana-pumpkin puree for industrial scale production.

## Acknowledgement

The authors wish to thank Professor Dr. Frederick W.H. Beamish (Faculty of Science, Barapha University) for English proofreading, Mrs. Rucnida Boonyong and Mrs. Soysuda Simsa (Department of Food Science, Faculty of Science, Burapha University) for the analysis of experimental data. We gratefully acknowledge the Research Grant of Burapha University through Nation Research Council of Thailand (Grant no.33/2559).

## References

Al-Zubaidy, M. M. I. and Khalil, R. A. 2007. Kinetic and prediction studies of ascorbic acid degradation in normal and concentrate local lemon juice during storage. Food Chemistry 101: 254-259.

The Association of Official Analytical Chemists. 1995. Official Method of the Association of Official Analytical Chemists. 15th ed. Virginia: The Association of Official Analytical Chemists.

Benlloch-Tinoco, M., Kaulmann, A., Corte-Real, J., Rodrigo, D., Martinez-Navarrete, N. and Bohn, T. 2015. Chlorophylls and carotenoids of kiwifruit puree are affected similarly or less by microwave than by conventional heat processing and storage. Food Chemistry 187: 254-262.

Bonnie, T. Y. P. and Choo, Y. M. 1999. Oxidation and thermal degradation of carotenoids. Journal of Oil Palm Research 2: 62-78.

Carvalho, L. M. J., Gomes, P. B., Godoy, R. L. O, Pacheco, S., Monte, P. H. F., Carvalho, J. L. V., Nutti, M. R., Neves, A. C. L., Vieira, A. C. R. A. and Ramos, S. R. R. 2012. Total carotenoid content, β-carotene and β-carotene, of landrace pumpkins (*Cucurbita moschata* Duch): A preliminary study. Food Research International 47: 337-340.

Cheng, X. F., Zhang, M. and Adhikari, B. 2014. Changes in quality attributes of strawberry purees processed by power ultrasound or thermal treatments. Food Science and Technology Research 20: 1033-1041.

Cisse, M., Vaillant, F., Acosta, O., Dhuique-Mayer, C. and Dornier, M. 2009. Thermal degradation kinetics of anthocyanins from blood orange, blackberry, and roselle using the Arrhenius, Erying, and Ball models. Journal of Agricultural and Food Chemistry 57: 6285-

6291.
Demiray, E., Tulek, Y. and Yilmaz, Y. 2013. Degradation kinetics of lycopene, β-caratene and ascorbic acid in tomatoes during hot air drying. Food Science and Technology 50: 172-176.
Dhuique-Mayer, C., Tbatou, M., Carail, M., Caris-Veyrat, C., Dornier, M. and Amitot, M. J. 2007. Thermal degradation of antioxidant micronutrients in citrus juice: kinetics and newly formed compounds. Journal of Agricultural and Food Chemistry 55: 4209-4216.
Englberger, L., Darnton-Hill, I., Fitzgerald, M. H. and Marks, G. C. 2003. Carotenoi-rich bananas: A potential food source for alleviating vitamin A deficiency. Food and Nutrition Bulletin 24: 303-318.
Garcia-Parra, J., Gonzalez-Cebrino, F., Cava, R. and Ramirez, R. 2014. Effect of a different high pressure thermal processing compared to a traditional thermal treatment on a red flesh and peel plum puree. Innovative Food Science and Emerging Technologies 26: 26-33.
Gliemmo M. F., Latorre M. E., Gerschenson, L. N. and Campos, C.A. 2009. Color stability of pumpkin (*Cucurbita moschata,* Duchesne ex Poiret) puree during storage at room temperature: Effect of pH, potassium sorbate, ascorbic acid and packaging material. Food Science and Technology 42: 196-201.
Horia M. 2006. Physical chemistry kinetics, p.11-33. New York: Taylor and Francis Group.
Jirasatid, S., Nopharatana, M., Kitsubun, P. and Tongta, A. 2013. Degradation kinetics of monacolin K in red yeast rice powder using mutiresponse modeling approach. Journal of Food Engineering 116: 436-443.
Karagozler, A. A, Erdag, B., Emek, Y. C. and Uygun D. A. 2008. Antioxidant activity and proline content of leaf extracts from Dorystoechas hastate. Food Chemistry 111: 400-407.
Karim, O. R. and Adebowale, A. A. 2009. A dynamic method for kinetic model of ascorbic acid degradation during air dehydration of pretreated pineapple slices. International Food Research Journal 16: 555-560.
Kenchinski, C. P., Guimaraes, P. V. R., Norena, C. P. Z., Tessaro, I. C. and Marczak, L. D. F. 2010. Degradation kinetics of anthocyanin in blueberry juice during thermal treatment. Journal of Food Science 75: 173-176.
Liaotrakoon, W., Clercq, N. D., Hoed, V. V., Walle, D. V., Lewille, B. and Dewettinck, K. 2013. Impact of thermal treatment on physicochemical, antioxidative and rheological properties of white-flesh and red-flesh dragon fruit (*Hylocereus* spp.) puree. Food and Bioprocess Technology 6: 416-430.
Ozsen, D. and Erge, H. S. 2013. Degradation kinetics of bioactive compounds and change in the antioxidant activity of wild strawberry *(Fragaria vesca)* pulp during heating. Food and Bioprocess Technology 6: 2261-2267.
Provesi, J. G., Dias, C. O. and Amante, E. R. 2011. Changes in carotenoids during processing and storage of pumpkin puree. Food Chemistry 128: 195–202.
Tsen, J. A. and King, V. A. E. 2002. Density of banana puree as a function of soluble solids concentration and temperature. Journal of Food Engineering 55: 305–308.
Turturica, M., Stanciuc, N., Bahrim, G. and Rapeanu, G. 2016. Effect of thermal treatment on phenolic compounds from plum *(Prunus domestica)* extracts-A kinetic study. Journal of Food Engineering 171: 200-207.
Van Boekel, M. A. J. S. 2009. Kinetic modeling of reactions in foods. Florida: Taylor and Francis group.