REVIEW ARTICLE
J. Food Sci. Technol. Nepal, Vol. 11 (1 - 13), 2019
ISSN: 1816-0727

Application of Thermal Kinetic Models in Liquid Foods and Beverages with Reference to Ascorbic Acid, Anthocyanin and Furan – a Review

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Food processors aim to preserve as much as desirable quality attributes without compromising food safety. Thermal processing is the cheapest and most common method of food preservation across the world due to its outstanding record of assuring safety. The major challenge associated with the conventional heating method is to protect adequately desirable quality attributes like color, flavor, texture, nutrients and bioactive compounds to address the demands of modern health conscious consumers. One approach is to use kinetic models and adopt the principle of optimization. Reaction kinetic models can be used in process design to estimate quantitative impact on food components including microorganisms in foods. There are various types of linear and nonlinear kinetic models proposed by food engineers. However, the selection of appropriate process variables (time, temperature), knowledge on the product factors (e.g. pH, °Brix) and understanding their interactions with the model parameters (rate constant, activation energy) is important for accurately estimating the impact of the process. The purpose of this review is to summarize the principles and functions of thermal processing followed by the application of reaction kinetic models to estimate the impact of thermal process on the food components, namely microbial population, ascorbic acid, anthocyanin and furan in liquid foods and beverages. In addition, it illustrates how the model parameters can be used to optimize the process through time-temperature tolerance (TTT) curve. Furthermore, it explains the significance of high temperature short time process for selected food components.

Keywords: heat, kinetics, ascorbic acid, anthocyanin, furan, TTT curve

Introduction

Nowadays, consumers demand for foods, which can meet their nutrition and personal health goals besides ensuring food safety (Sloan, 2020). To address these needs, food processors should aim to maximize the desirable quality attributes in foods through process optimization (Heldman, 2013).

This requires broad knowledge on the impact of process variables on food components including microorganisms that pose significant threat to food safety. In recent years, some non-thermal techniques like high-pressure treatment, ultraviolet radiation and pulsed electric field have emerged, but thermal processing is still the cheapest and most common method of food preservation across the world due to its proven record of accomplishment in food preservation (Heldman et al., 2018).

Pasteurization, derived from the name of a French scientist Louis Pasteur, is a mild thermal treatment process (generally below 100 °C) that is usually applied to liquid foods in order to increase their shelf life during storage. Pasteurized foods are not sterile but their shelf lives are further extended by other preservation techniques such as refrigeration, fermentation or maintaining anaerobic conditions during storage. In the strict sense, pasteurization is designed to target only the vegetative pathogens and spoilage enzymes or microorganisms but not bacterial spores (Singh & Heldman, 2001). Likewise, the magnitude of the thermal intensity (time-temperature combination) during pasteurization also depends on the pH of the product and its subsequent storage conditions. If the pH of the food is low (pH below 4.6), a lower thermal process is required to achieve the equivalent amount of lethality in comparison to food with a higher pH (> 4.6). Besides, pasteurization of acid products allows a longer shelf life even at room temperature. On the other hand, commercialization sterilization (12D process, e.g. T = 121 °C for 2.4 min; using $D_{121\,°C}$ = 0.2 min) is needed to destroy the spores of *Clostridium botulinum* in foods with pH > 4.6 to ensure safety (Silva & Gibbs, 2004; Singh & Heldman, 2001).

In addition to assuring the microbiological safety, food processors should also provide the quality assurance to win consumers' confidence. Unfortunately, the intense heat during processing might result in a nutritional loss as well as changes in sensory properties and acceptability i.e. most food components including microbial populations may be altered by heat. It is worth mentioning that the thermal impact on any foods depends on the magnitude of the process (temperature, treatment time) and sensitivity of food components that could be unique to food commodities (Martínez-Monteagudo & Balasubramaniam, 2016; Heldman, 2013).

In this perspective, the main goal of the food processor during thermal processing is to maximize the retention of

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desirable quality attributes without compromising the food safety. Therefore, two basic things are considered during thermal process design; (a) quantitatively estimate the reduction of the most heat resistant pathogens or spoilage microorganisms (b) quantitatively estimate the retention of the most heat sensitive quality attributes (color, flavor, and nutrients) during processing (Heldman, 2013; Heldman & Hartel, 1997).

Reaction kinetic models are often used in food process design to quantitatively describe and estimate the physical, chemical and microbiological changes in foods. These models are applied to find a solution set of process conditions (time-temperature combination) to maximize quality attributes and minimize the targeted species (vegetative microbial cells, spores) in food components. Conversely, based on the prior knowledge of food properties and processing conditions, empirical or semi-empirical kinetic models can be used to predict the quantitative changes in foods (Villota & Hawkes, 2018; Heldman, 2013; Boekel, 2008; Heldman & Hartel, 1997).

This review provides some background on reaction kinetic models and their application in food processing. Model parameters will be analyzed to interpret the impact of thermal treatment in liquid foods and beverages, specifically in terms of ascorbic acid, anthocyanin and furan formation. In addition, it illustrates how the kinetic model parameters can be used to optimize the process by using time-temperature tolerance (TTT) curve. It also explains the significance of high temperature short time (HTST) process for selected food components.

Basic on kinetic models and estimation of model parameters

Model development starts with expressing the rate process in terms of the mathematical equation (Villota & Hawkes, 2018). So, chemical reactions in liquid foods can be simply expressed in two steps form as follows in Equation (1):

$$A + B \underset{kr}{\overset{kd}{\rightleftarrows}} [AB] \overset{kf}{\rightarrow} P \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Here, A and B are reactants and these species should encounter the solvents hurdle to form the reaction intermediate [AB] and then collide each other to form the product (P). In most of the cases, the rate of the reaction can be expressed in form of general rate law equation (Jordan, 2012) as in Equation (2):

$$r_A = -\frac{d[A]}{dt} = k_T\,[A]^n\,[B]^m \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where, r_A is the rate of reaction, [A] and [B] are the reactants concentration, t is the process time, k_T is the rate constant at given temperature (T in ^oC or K) and n and m are the order of a reaction (can be integer or non-integer value) for reactants A and B, respectively. Reaction rate signifies how fast the concentration of the species (reactants, products) changes with time. The reactions are generally terminated by immediate reduction in driving force of the reactions (reduction of temperature) (Villota & Hawkes, 2018) or by the chemical quenchers (ascorbic acid, β-carotene) (Li, Yang & Bai, 2018) depending on the types of reactions involved. The rate of a chemical reaction is influenced by the catalyst as well as on initial concentration of reactants and products. Other process variables and product factors such as temperature, pressure, light intensity, oxygen concentration, viscosity, ionic strength and conductivity also influence the reaction rates in food systems (Villota & Hawkes, 2018). Further information on methods of monitoring changes in food properties is available in the literature (Villota & Hawkes, 2018).

The rate law equation in Equation (2) can be transformed into linear form through logarithmic transformation such as,

$$\ln(r_A) = \ln(k_T) + n\ln(A) + m\ln(B) \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Equation (3) is a multiple linear regression having intercept $\ln(k_T)$ with two independent variables in logarithmic form, $\ln(A)$ and $\ln(B)$, can be comparable to the standard form,

$$y = b_o + b_1 x_1 + b_2 x_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Hence, the terms b_o, b_1 and b_2 can be calculated by the method of least squares. Although, $n = b_1$ and $m = b_2$ can be accurately estimated to obtain the total order of reaction, many food engineers do not suggest to use $b_o = \ln(k_T)$ to obtain k_T with this method because of increase in error (Villota & Hawkes, 2018). Therefore, it is better to confirm the reaction order first and then deal with specific equation to estimate the rate constant (k_T).

For a single reactant *A*, the integrated form of equation (2) under irreversible isothermal conditions can thus be written for a elementary reaction as:

$$[A]_t = [A]_o - k_T t \quad (zero\ order) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$[A]_t = [A]_o \exp(-k_T t) \quad (first\ order) \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

$$\frac{1}{[A]_t} = \frac{1}{[A]_o} + k_T t \quad (second\ order) \ldots\ldots\ldots\ldots\ldots (7)$$

Here, $[A]_t$ is the reactant concentration at time t, $[A]_o$ is the estimated initial concentration of a reactant at t = 0 treatment time. It is important to note that above-mentioned elementary reactions are not applicable for non-elementary reactions like consecutive and competitive reactions. Illustrations of such non-elementary reactions and their mathematical derivations are found in the literature (Villota & Hawkes, 2018).

Rate constant and impact estimation

In a strict sense, the rate constant (k_T) is not a constant quantity because it is affected by a change in temperature. Therefore, k_T is denoted by subscript T, the process temperature (^oC or K) (Singh & Heldman, 2001) .For zero order reaction, the rate constant is numerically equal to the rate of reaction and is independent of the concentration of

a reactant (eg. when the reactant concentration is very large) given as,

$$k_T = r_A \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Time for 50 % retention of a reactant (eg. nutrient) , $T_{1/2}$, in zero order reaction is given as,

$$T_{1/2} = \frac{[A]_0}{(2\,k_T)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

For first order reaction, the rate constant depends on rate as well as concentration of a reactant given as,

$$k_T = r_A / [A] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Time for 50 % retention of a reactant (eg. nutrient) , $T_{1/2}$, in first order reaction is given as,

$$T_{1/2} = \frac{0.693}{k_T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

For second order reaction, the rate constant depends on the square of the initial concentration of a reactant given as,

$$k_T = \frac{r_A}{[A]^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

Time for 50 % retention of a reactant (eg. nutrient) , $T_{1/2}$, for second order reaction is given as,

$$T_{1/2} = 1/([A]_0\ k_T) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

Log linear model

Impact of heat on microbial population can be quantitatively measured by using a modified version of first order kinetics, known as log linear model (Bigelow, 1921). In this model, the natural logarithm (ln) is replaced by a logarithm with base 10, (log) and first order rate constant(k_T) is replaced with $1/D_T$. The log linear model is then expressed as,

$$\log N_t = \log N_0 - \left(\frac{t}{D_T}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

where, N_t is the microbial population remaining after treatment time (t) from initial population N_0 and $D_T = 2.303/k_T$ is known as the decimal reduction time. In other words, D_T is defined as time required for 90 % reduction (or one log cycle reduction) in microbial population at constant process temperature. Hence, the lethality associated with a thermal process is based on holding period only, without taking into consideration of heating and cooling period (Heldman, 2013; Singh and Heldman, 2001).

The pasteurization time for milk, for instance is based on D_{63} = 2.5 minutes, with total time of 12 D_{63} = 30 minutes. This process reduces target pathogen (if present) by 99.9999999999 % . Therefore, even if the initial load of target pathogen is very high (10^7 per mL), the remaining population after pasteurization (12 D process) will be very small (10^{-5} per mL) and hence it ensures that the probability of survival of the pathogen is negligible (Heldman 2013; Singh & Heldman, 2001). As mentioned in the earlier section, this criterion of 12 D process is used by food industry for low acid foods for commercial sterilization. For fruit juice, a minimum of 5 D (99.999%) pathogen (e.g *Salmonella* for citrus juice, *E. coli* O157:H7 for apple juice) reduction rule is required for pasteurization (Committee on the Review of the Use of Scientific Criteria and Performance Standards for Safe Food, National Research Council, 2003).

Evaluating temperature sensitivity from activation energy

The temperature sensitivity of rate constant (k_T) can be described by Arrhenius model (Singh & Heldman, 2001):

$$k_T = A_o \exp\left(-\frac{E_a}{RT}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15)$$

where A_o represent Arrhenius constant (frequency factor), E_a is the activation energy, R is the universal gas constant (8.3144 J/(mol K)) and T is the temperature (K).

Equation (12) could also be reparametrized as;

$$k_T = k_{ref\,T} \exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

where, k_T is the reaction rate constant at process temperature (T) and $k_{ref\,T}$ is the reaction rate constant at a reference temperature, T_{ref} (373 K).

Evaluating temperature sensitivity from thermal resistance constant

Similar to the activation energy, the influence of temperature on D_T can be evaluated from the thermal resistance constant(z) also known as thermal intensity coefficient as suggested by Singh & Heldman, (2001) given by,

$$z = (T_{ref} - T) / (\log D_T - \log D_{ref}) \quad \ldots\ldots\ldots\ldots\ldots\ldots (17)$$

where, D_{ref} is the decimal reduction time at reference temperature (T_{ref}). Hence, z is defined as an increase in temperature (Δ T) that cause 90 % reduction (or one log cycle reduction) in D_T value.

Equation (14) and Equation (15) can be combined to form the relationship between z and E_a as,

$$z = (2.303\ R\ T.\ T_{ref}) / E_a \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (18)$$

where, R is the universal gas constant (8.3144 J/(mol K) and T and T_{ref} are absolute temperatures.

The kinetic parameters (D_T and z) describing thermal inactivation of microbial cells and spores are presented in Table 1. Besides chemical and microbiological changes, kinetic models can also be applied to understand physical changes such as textural alterations in starchy foods (Villota & Hawkes, 2018) and aggregative properties in protein foods (Dhakal, Giusti & Balasubramaniam, 2016).

Table 1
Microbial/spores thermal inactivation kinetic parameters for various liquid foods.

Product (pH / °Brix)	Microorganisms /spores	D_T-value (min)	Z value °C	Temperature range °C	Reference
Dextrose tryptone broth (pH 5)	*Clostridium butyricum* strain 5520 spores	$D_{78\ °C}$ 1.4	4.75	73.8 -79.4	Morton et al., (1990)
Strawberry pulp (pH 3/ °Brix 15)	*Byssochlamys nivea* (ascospores)	$D_{90\ °C}$ 6.3	6.4	80 - 93	Silva & Gibbs, (2004)
Vegetable products	*Cl. botulinu*m 62A	$D_{110\ °C}$ 0.61 - 2.48	11.6		ICMSF, (1996)
White grape juice	*E. coli* O157:H7	$D_{60\ °C}$ 2.41- 2.7	9.2 - 9.9		Enache et al., (2006)
White grape juice	*Salmonella*	$D_{60\ °C}$ 0.87	8.8		ICMSF, (1996)

It should be pointed out that there are also others variants of kinetic models applicable in the food system, namely the n^{th} order kinetics, first order fractional conversion, biphasic first order, Weibullian kinetics and log logistic model as suggested by various researchers (Peleg et al., 2018; Daryaei and Balasubramaniam, 2013; Verbeyst et al.,2013; Rajan et al., 2006).

It should also be noted that the model parameters that is obtained by curve fitting would not provide much information on reaction mechanisms. In addition, the order of reaction obtained from such fitted model represents the overall order of reaction that is not applicable for the elementary reaction step. Therefore, these kinetic model parameters are only useful to quantitatively predict the reactants or products at specific processing conditions (Van Boekel, 2008). The success of a kinetic model (parametric model) depends upon the accuracy of its estimated parameters (with physical meaning), for reliable and realistic food process design. Adequacy of the models can be checked by several graphical (e.g.: plotting residuals and prediction interval) and numerical methods (e.g.: root mean squared error, coefficient of determination) (Vilas et al, 2016; Nunes et al., 2015).

Thermal impact on ascorbic acid in liquid foods

Ascorbic acid is a vitamin C as well as a natural antioxidant that fights cell damage (Grosso et al., 2013; Riccioni et al., 2012; Traber et al., 2011). Ascorbic acid present in freshly prepared juices are thermodynamically unstable and ascorbic acid content in it decreases due to aerobic and anaerobic degradation resulting in the formation of biologically inactive products (2, 3-diketogulonic acid, furoic acid, oxalic acid, threonic acid, and furfural) (Ebrahimi & Dabbagh, 2019). Likewise, the degradation of ascorbic acid also results in browning and deterioration of organoleptic quality attributes (Bharate & Bharate, 2014).

Some thermal degradation kinetic parameters for ascorbic acid in fruit and vegetable products are summarized in Table 2. The majority of ascorbic acid in fruit and vegetable products follow first order thermal degradation kinetics. Some researchers have also reported biphasic type of degradation behavior during processing (Al Fata et al., 2016; Verbeyst et al., 2013; Blasco et al., 2004). In this type of reactions, the fast aerobic degradation in the first phase is followed by a rather slower anaerobic degradation in second phase. The reaction kinetics model in each of these phases can also be different (Al Fata et al., 2016). Occasionally, a first order fractional conversion model has been proposed for ascorbic acid degradation (Verbeyst et al., 2013).This special type of first order degradation model takes into account of tailing effects during ascorbic acid degradation during prolonged process condition. Indeed, this type of model contains an additional parameter, known as asymptotic point to indicate some stable fraction of ascorbic acid retained in juice (Verbeyst et al., 2013). The physical significance of such asymptotic point will only be meaningful if the kinetic data could capture information close to this point (Tiwari et al., 2009; Vikram et al., 2005).

Food matrix plays an important role in ascorbic acid degradation. Consequently, the kinetic parameters, rate constant and activation energy are influenced by the type of food matrix. It has been reported that ascorbic acid is sensitive to thermal treatment in asparagus (Zheng et al., (2011) but is fairly preserved in canned sweet peas (Lathrop and Leung, 1980). The rate constant, $k_{70\ °C,}$ has been found to vary by a factor of ~ 25 between citrus fruits and a tropical forest tree-fruit nectar. It ranges from 0.00042 min^{-1} in ditax nectar (Diop Ndiaye et al., 2011) to 0.011 min^{-1} in citrus fruits (Dhuique-Mayer et al., 2007). Likewise, the thermal processing of fruit juices show the rate constant for ascorbic acid degradation increases by 1.15 to 2 times with each 10 °C rise in process temperature (Dhakal et al., 2018; Vieira et al., 2016; Dhuique-Mayer et al.,2007; Nisha, Singhal & Pandit, 2004).

Difference in total soluble solids has been reported to alter the thermal sensitivity in ascorbic acid. According to Saguy et al., (1978) ascorbic acid retention in grapefruit juice is reduced by ¼ of its value with increase in °Brix from 11.2 to 62.5 % at 96 °C. Likewise, vacuum drying retains more ascorbic acid in the mandarin slices than with oven drying, indicating the faster degradation of ascorbic acid in presence of oxygen (Akdaş and Başlar, 2015).

Another parameter, activation energy (E_a) is also used to compare the thermal sensitivity of the rate of degradation. E_a varies from 17 kJ mol^{-1} to 58 kJ mol^{-1} for ascorbic acid degradation in fruit juice (Dhakal et al., 2018; Vieira et al., 2015; Hiwilepo-van Hal et al., 2012; Dhuique-Mayer et al., 2007).

Table 2
First order thermal degradation kinetic parameters for ascorbic acid in fruit and vegetable products.

Product (pH)	k_T per min	E_a kJ mol^{-1}	$T_{1/2}$ (min)	T range (°C)	Reference
Asparagus bud (Blanching)	$k_{100\ °C}$ 0.304	101.4	2.28	60 - 100	Zheng et al., (2011)
Cashew apple (4.9)	$k_{140\ °C}$ 0.038	94	18.24	100 - 180	Lima et al., (2010)
Cupuaçu nectar (3.2)	$k_{80\ °C}$ 0.032	74	21.65	60 - 99	Vieira et al., (2000)
Ditax nectar (4.06)	$k_{70\ °C}$ 0.00042	46.4	1650	60 - 95	Diop Ndiaye et al., (2011)
Grapefruit juice;11.2 ° Brix	$k_{96\ °C}$ 0.00264	20.8	262	61 - 96	Saguy et al., (1978)
Grapefruit juice;62.5 ° Brix	$k_{96\ °C}$ 0.01068	47.3	69	68 - 96	Saguy et al., (1978)
Mandarin slices (oven drying)	$k_{75\ °C}$ 0.00122	42.34	569.6	55 - 75	Akdaş and Başlar, (2015)
Mandarin slices (vacuum drying)	$k_{75\ °C}$ 0.000869	51.63	797.6	55 - 75	Akdaş and Başlar, (2015)
Oranges and clementine (3.6)	$k_{70\ °C}$ 0.011	35.9	63	50 - 100	Dhuique-Mayer et al., (2007)
Orange juice	$k_{90\ °C}$ 0.178	40	3.89	50 - 90	Vikram et al., (2005)
Orange juice (filtered)	$k_{120\ °C}$ 0.0076	117.6	91.2	120 - 150	Van den Broeck et al., (1998)
Pineapple (3.4)	$k_{85\ °C}$ 0.005	22	138	75 - 95	Dhakal et al., (2018)
Raspberry paste	$k_{100\ °C}$ 0.0019	73	364.7	80 - 140	Verbeyst et al., (2013)
Strawberry paste (4)	$k_{80\ °C}$ 0.01515	21.36	45.74	60 - 97	Castro et al., (2004)
Sweet peas (canned)	$k_{121.1\ °C}$ 0.0025	164.4	277	110 - 132	Lathrop and Leung, (1980)
Tomato pulp (4.5)	$k_{120\ °C}$ 0.0049	114.95	141.4	120 - 150	Van den Broeck et al., (1998)
Watermelon (4.4)	$k_{70\ °C}$ 0.013	76.8	53.3	70 - 90	Tola and Ramaswamy, (2015)

E_a is also affected by processing conditions and sugar concentrations in citrus foods. For instance, E_a increases in absence of oxygen during vacuum drying of mandarin slices (Akdaş and Başlar, (2015) and can double its value when soluble solids increases from 11.2 to 62.5 % in grapefruit juice (Saguy et al., 1978). Therefore, it is worth to mention that E_a alone can't be used to predict the impact on ascorbic acid but it measures the sensitivity of the rate constant. Smaller value of E_a indicates that the rate of degradation is highly resistant to change in temperature and vice versa. It should be emphasized that E_a also depends upon the processing domain (Table 2). This information has been evident in orange juice where E_a at 120 to 150 °C is about three times higher (Van den Broeck et al., 1998) than at the lower (50 to 90 °C) processing conditions (Vikram et al., 2005).

Optimizing ascorbic acid using time temperature tolerance (TTT) curve

Time temperature tolerance curve (TTT) is a time-temperature plot that shows the same level of inactivation or retention of food components at different combinations of time-temperatures. Kinetic model parameters are used to plot the TTT curve (Claeys et al., 2004). This TTT curve is plotted to illustrate how ascorbic acid retention can be maximized in strawberry paste in concurrent with inactivation of spoilage microorganisms at the desired level. To explain, the spores of *Byssochlamys nivea* have been selected to draw TTT curve. These spores are the most heat resistant mold spores capable of deteriorating strawberry paste, a high acid fruit product (Silva et al., 2004). The pasteurization is designed to achieve 5 logarithmic reduction (5D process) to spores of *Byssochlamys nivea*. A 5 D process can be achieved at various time -temperature treatment conditions by using established kinetic parameters (Silva & Gibbs, 2004; Table 1).This data is then used to plot a TTT curve for *Byssochlamys nivea* spores inactivation at 5D reduction level (Figure 1). Similarly, two TTT curves are plotted for ascorbic acid retention levels in strawberry paste (Figure 1). To elucidate, the first TTT curve shows 79 % ascorbic retention level in a time- temperature axes. Likewise, the second TTT curve shows 46 % ascorbic acid retention level in the same axes. These curves have been plotted using the kinetic parameters available in the literature (Castro et al., 2004).

Figure 1 shows 79 % ascorbic acid TTT curve intersects with 5D *Byssochlamys nivea* spores inactivation TTT curve at the point Q (92.5 °C, 12 min). On the other side, 46 %

ascorbic acid TTT curve intersects with the 5D *B. nivea* spore TTT curve at the point P (89 ºC, 44 min). This implies that high temperature short time, HTST, (92.5 ºC for 12 min) process is better (79 % retention) than low temperature long time, LTLT, (89 ºC for 44 min) process where the ascorbic acid retention is only 46 % for same level (5D) of microbiological inactivation.

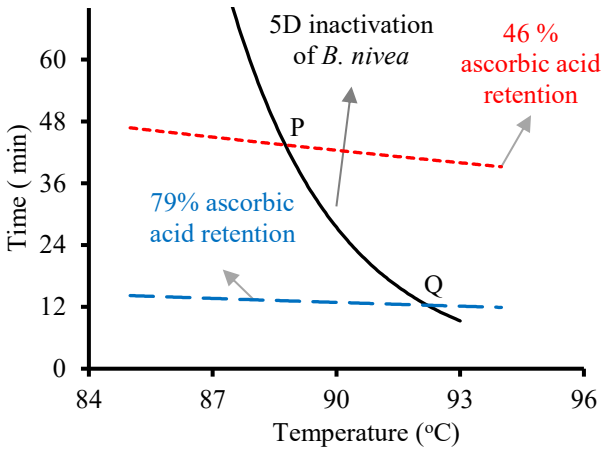

Figure 1. Time-temperature tolerance (TTT) curves for 5D inactivation of *Byssochlamys nivea* spores **(—)** and ascorbic acid retention in thermally treated strawberry pulp. Here, **(···)** represents 46% ascorbic acid, **(- - -)** represents 79 % ascorbic acid. Kinetic parameters sources: (Silva et al., 2004; Castro et al., 2004)

This phenomenon exists due to differences in temperature coefficient values between targeted microorganisms and quality attributes (Heldman, 2013). In this case, *Byssochlamys nivea* spores inactivation has high temperature coefficient (387.8 kJ/mol calculated from z = 6.4 ºC) in comparison to ascorbic acid retention (21.36 kJ/mol).These differences have helped to maximize the ascorbic acid retention using HTST process (Heldman, 2013).

Thermal impact on anthocyanin in liquid foods

Anthocyanins are generally considered phenolic compounds, and these specifically belong to subgroups of flavonoids. Anthocyanins are water-soluble and colorful bioactive compounds having anti-oxidative properties (Yousuf et al., 2015). Various factors like temperature, pH, oxygen, light and metal ions affect anthocyanins stability (Rein, 2005).

Anthocyanins have been reported to follow first order degradation kinetics during processing (Mercali et al., 2013; Zoric et al., 2013; Hillmann et al., 2011; Liang et al., 2011; Verbeyst et al., 2011; Kechinski et al., 2010). Table 3 shows kinetic parameters for the thermal degradation of anthocyanin in various fruit and vegetable products.

Structural compositions as well as other matrix properties affect anthocyanin stability during processing. In general, the higher the number of hydroxyls, acyl groups or glycosidic linkage, the more the stable will be the anthocyanin. On the other side, the higher number of methoxyl groups decreases the stability of anthocyanins and vice versa. Some intrinsic and extrinsic factors like oxygen, ascorbic acid, high pH, sugars and light decrease the stability of anthocyanin (Rein, 2005).

These interfering factors are normally higher in foods with high solids content and thus make anthocyanin less stable during thermal treatment. Increase in degradation rate constant have been reported in juice with higher solids by various researchers (Hillmann et al., 2011; Wang and Xu, 2007; Garzon and Wrolstad, 2002). For instance, anthocyanin half –life ($T_{1/2}$) is 1.6 times higher in cherry juice (15 ºBrix) treated at 80 ºC in comparison with that having 45 ºBrix (Cemeroglu et al.,1994). In contrast, Tranchev, (1972) has reported higher $T_{1/2}$ in raspberry juice with added sugar. Tanchev and Joncheva, (1973) have reported that plum juice having pH 4.5 has lower $T_{1/2}$ than juice with pH 2.5 treated at 108 ºC. Similarly, Liu et al., (2014) compared anthocyanin in Chinese red radish extract prepared in different juices, and reported that the extract prepared in apple juice was more stable than that prepared in lemon juice (Table 3).

The measure of temperature sensitivity, E_a for anthocyanin degradation depends on the type of food matrix involved. E_a for anthocyanin degradation has been found to vary in the range of 18.3 to 89 kJ/mol for different fruit and vegetable products (Patras et al., 2010). Study shows that E_a of anthocyanin extracted from purple corncob, wild strawberry and plum puree (< 38 kJ/mol) were relatively more resistant to change in temperature than those extracted from carrots, elderberry juice and black currants (> 50 kJ/mole) (Patras et al., 2010).

As one would expect, the rate of anthocyanin degradation is the function of temperature. The modes of heat transfer (conduction and convection) or the internally generated heat have the same influence on reaction rate. The effect of heating methods on anthocyanin was studied by Mercali et al., (2013) and Sarkis et al., (2013). These researchers evaluated anthocyanin degradation by conventional and ohmic heating. Mercali et al., (2013) did not observe a significant difference in rate constant (~$k_{90\ ºC,}$, 0.0171per min) and activation energy (~ 74.8 kJ/mol) values reported by Sarkis et al., (2013) who performed thermal experiments at 90 ºC using blueberry pulp as a test matrix. However, due to electrochemical reactions, ohmic heating beyond threshold voltage could cause synergistic or additive effect on rate of anthocyanin degradation. Sarkis et al., (2013) reported that anthocyanin degradation increased from 5.7 to 14.7 % (~2.5 times) with increasing voltage from 160 V to 240 V during ohmic heating of blueberry pulp.

Optimizing anthocyanin using time temperature tolerance (TTT) curve

As discussed earlier, we have selected the *Byssochlamys nivea* spores as target microorganism for plotting TTT curve for strawberry pulp (Figure 2). The pasteurization process is also designed to achieve 5 logarithmic reduction (5D process). Using the kinetic data (Table 3), two TTT curves are plotted for various anthocyanin retention levels in strawberry pulp (Figure 2).

Table 3
First order thermal degradation kinetic parameters for anthocyanin in fruit and vegetable products.

Product (pH)	k_T per min	E_a kJ mol^{-1}	$T_{1/2}$ (min)	T range (°C)	Reference
Acerola pulp (3.3)	$k_{90\ °C}$ 0.0171	74.8	40.5	75 - 90	Mercali, et al., (2013)
Blackberry juice	$k_{70\ °C}$ 0.001178	62.76	588	24 - 70	Debicki-Pospišil, et al., (1983)
Blood orange juice (3.45)	$k_{90\ °C}$ 0.0041	55.8	169	75 - 90	Cao et al., (2011)
Blueberry juice	$k_{80\ °C}$ 0.0022	80.4	315	40 - 80	Kechinski et al., (2010)
Boysenberry juice	$k_{100\ °C}$ 0.00155	83.68	488	20 - 120	Ponting et al., (1960)
Cherry juice; 15 °Brix	$k_{80\ °C}$ 0.000566	68.5	1220	50 - 80	Cemeroglu et al., (1994)
Cherry juice; 45 °Brix	$k_{80\ °C}$ 0.000953	17.85	727	50 - 80	Cemeroglu et al., (1994)
Chinese red radish extract in apple juice	$k_{90\ °C}$ 0.000830	47.78	835	70 - 90	Liu et al., (2014)
Chinese red radish extract in lemon juice	$k_{90\ °C}$ 0.00115	32.72	603	70 - 90	Liu et al., (2014)
Concord grape pigments (3.4)	$k_{121\ °C}$ 0.01879	54.81	37	76.7 - 121	Sastry and Tischer, (1952)
Cornelian cherries (*Cornus mas* L.)	$k_{75\ °C}$ 0.001377	58.57	503	2 - 75	Moldovan and David, (2014)
Grape juice	$k_{90\ °C}$ 0.0022	72.74	315	70 - 90	Hillmann et al.,(2011)
Grape blend	$k_{100\ °C}$ 0.00259	117.1	267	20 - 120	Ponting et al., (1960)
Plum juice (2.5)	$k_{108\ °C}$ 0.02028	91.21	34	78 - 108	Tanchev and Joncheva, (1973)
Plum juice (4.5)	$k_{108\ °C}$ 0.02664	94.55	26	78 - 108	Tanchev and Joncheva, (1973)
Pomegranate juice	$k_{90\ °C}$ 0.00088	104.6	788	70 - 92	Mishkin and Saguy, (1982)
Raspberry juice (3.2)	$k_{108\ °C}$ 0.01986	92.05	35	78 - 108	Tranchev, (1972)
Raspberry juice; added sugar (3.2)	$k_{108\ °C}$ 0.0171	96.23	41	78 - 108	Tranchev, (1972)
Red cabbage (*Brassica oleracea* L.) (5.5)	$k_{90\ °C}$ 0.001667	29.29	416	50 - 90	Fernandez-Lopez et al., (2013)
Strawberry paste	$k_{110\ °C}$ 0.0285	94.4	24.3	95 - 130	Verbeyst et al., (2010)
Urmu mulberry concentrate	$k_{80\ °C}$ 0.0036	46.32	192.5	60 - 80	Kara & Erçelebi, (2013)
Wild strawberry paste	$k_{90\ °C}$ 0.0111	21.6	62.4	60 - 90	Özşen & Erge, (2013)

To simplify, the first TTT curve shows 93 % anthocyanin retention level in a time- temperature axes. Likewise, the second TTT curve shows 80 % anthocyanin retention level in the same axes. These lines are plotted using the kinetic parameters available in
the literature (Verbeyst et al., 2010).

Figure 2 shows that 93 % anthocyanin TTT curve intersects with 5D microbial spore TTT curve at the point Q (92.5 °C, 12 min) in time-temperature graph. On the other side, 80 % anthocyanin TTT curve intersects with 5D microbial spore TTT curve at point P (89 °C, 44 min) (Figure 2). This implies that HTST (92.5 °C for 12 min) process is better (93 % anthocyanin retention) than LTLT process (89 °C for 44 min) where the anthocyanin retention is only 80 % for same level (5D) of microbiological inactivation.

As stated earlier, the maximum retention of anthocyanin occurs with HTST process due to differences in temperature coefficient values for *Byssochlamys nivea* spores inactivation (E_a = 387.8 kJ/mol calculated from z = 6.4 °C) and anthocyanin retention (E_a: 74.4 kJ/mol). It is worth to mention that kinetic parameters reported by Verbeyst et al. (2010) has been estimated in the temperature range of 95 – 130 °C . Therefore, to estimate anthocyanin retention within microbial TTT curve, we have extrapolated the kinetic parameters up to 85 °C. The kinetic parameters are just the estimated data and more information should be collected on the process and product characteristics while applying the model parameters in practical conditions.

Estimating impact on furan formation

Intense use of heat during food processing not only negatively affect nutrients and organoleptic properties but also might cause pose human health hazard due to processed induced compounds such as furan.

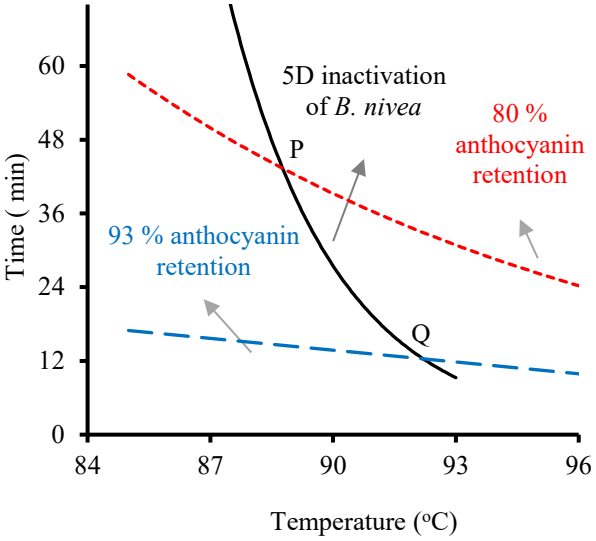

Figure 2. Time-temperature tolerance (TTT) curves for 5D inactivation of *Byssochlamys nivea* spores **(—)** and % anthocyanin retention in thermally treated strawberry pulp. Here, **(···)** represents 80 % anthocyanin and **(- - -)** represents 93 % anthocyanin. Kinetic parameters sources: (Silva et al., 2004; Verbeyst et al., 2010)

Earlier in 1995, furan, a volatile, lipophilic and heterocyclic compound, was declared as a possible human carcinogen by International Agency for Research on Cancer (IARC 1995). Later on, based on studies in experimental animals, National Toxicology Program (NTP, 2011) also recognized furan as a reasonably anticipated to be a human carcinogen.

Process-induced furans are usually the product of degradation reactions (decomposition, dehydration, dehydration and oxidation) resulting from precursors like sugars, amino acids, ascorbic acid, polyunsaturated fatty acids and carotenoids (Yaylayan, 2006). The concentration of furan in processed foods depends on several factors like the type and concentration of precursors, food characteristics, and treatment intensity. Indeed, furan has been reported in the wide range of concentrations (up to 122 µg kg^{-1}) in canned fruits and vegetable products (Dhakal et al., 2018; FDA, 2009).

Measuring the effects of process variables (temperature and time) on furan formation in foods is useful to facilitate food processors for process optimization and hence to mitigate furan formation by processing based approaches. Furan formation is reported to follow zero order kinetics in pineapple and spinach (Dhakal et al., 2017; Palmers et al., 2015). Some kinetic parameters on furan formation in fruit and vegetable juices are summarized in Table 4.

As discussed earlier, the rate constants and activation energies of furan formation are also the matrix dependent. The rate of furan formation in pineapple increases by 2.25 times for each 10 °C rise in temperature after 90 °C (Dhakal et al., 2017). According to Dhakal et al., (2017), the rate of furan formation in pineapple varies from 0.043 µg/kg/min at 90 °C to 0.5 µg/kg/min at 120 °C. Likewise, the rate constant ($k_{110\ °C}$ = 0.035 µg/kg puree /min) has been reported to double with every 7 °C rise in temperature in spinach puree following zero order kinetics (Palmers et al., 2015). Whereas in tomato pulp, the rate constant of furan formation does not change linearly with change in temperature and it follows first order kinetics (Akıllıoğlu et al., 2015). Furan formation rate constant $k_{70\ °C}$ (0.00000986 per min) increases by a factor of 1.8 from 70 to 80 °C, and then by a factor of 1.2 from 80 to 90 °C during thermal processing. So, the rate of furan formation in tomato pulp (E_a = 40.6 kJ mol^{-1}) is more resistance to change in temperature than in pineapple juice (E_a = 98 - 114 kJ/mol) and in spinach puree (E_a = 127.6 kJ/mol) (Dhakal et al., 2017; Akıllıoğlu et al., 2015; Palmers et al., 2015). In another study by Huang & Barringer, (2016), the activation energy of furan formation in soy sauce has been reported to vary between 72 – 77 kJ/mole.

Previously, Mogol and Gokmen, (2013) studied thermal kinetics of furan formation in ascorbic acid solution at a temperature range of 100 to 140 °C, slightly higher than the practical conditions. This study has helped to explain mechanistic insights of furan formation in the presence of oxidizing and reducing agents. Accordingly, the rate constant of furan formation in ascorbic acid model solution has been reported to increase by an order of three from 2.13×10^{-05} at 100 °C to 0.0422 min^{-1} at 140 °C, indicating very high temperature sensitivity (244.93 $kJmol^{-1}$). These researchers also reported that oxidation-reduction potential of the model solution could affect rate constant and temperature sensitivity by a factor of two to three depending upon the type of constituents.

Recently, Shen et al., (2017) has also evaluated the effect of antioxidants like polyphenolic compounds, butylated hydroxyl toluene on model systems (ascorbic acid, linoleic acid and linolenic acid), and has found that not all antioxidants have the potential to suppress furan formation. As reported by Dhakal et al., (2017) and Anese & Suman, (2013), formation of furan in real food system is a complex phenomenon governed by more than one factors (pH, phosphates, sugars and other constituents). Study on effect of pH has also shown mixed results during thermal treatment of model foods (Shen et al., 2015; Huang, Duan and Barringer, 2011; Fan, 2005).

Time-temperature-tolerance (TTT) for minimizing furan formation

Liu et al., (2013), have identified *Clostridium butyricum* as a gas forming anaerobic spoilage bacteria in bottle soy sauce. In absence of kinetic data in actual food matrix, we have selected kinetic data in dextrose tryptone broth (pH 5) for inactivation of *Clostridium butyricum* (Morton et al., 1990; Table 1). The pasteurization process for soy sauce is designed to achieve 5 logarithmic reduction (5D process) for inactivation of *Clostridium butyricum,* a target microorganism.

A TTT curve (Figure 3) for thermal inactivation (5D) of *Clostridium butyricum* is constructed using the kinetic data reported by Morton et al. (1990). Then, another two TTT curves has been constructed using the data (Table 4) reported by Huang and Barringer (2016). One of the

Table 4
Thermally induced furan formation kinetic parameters in fruit and vegetable products.

Product	Order of reaction	k_T	E_a kJ/mol	Temperature range (°C)	Reference
Pineapple juice	0th order	$k_{100\ °C}$ 0.089 µg kg^{-1} min^{-1}	98 -114	90 -120	Dhakal et al., (2017)
Soy sauce	0th order	$k_{80\ °C}$ 0.0042 – 0.0079 µg kg^{-1} min^{-1}	72-77	30 - 80	Huang and Barringer, (2016)
Spinach puree	0th order	$k_{117\ °C}$ 0.071 µg kg^{-1} min^{-1}	127.6	110 – 124	Palmers et al., (2015)
Tomato paste	1st order	$k_{90\ °C}$ 0.00002 min^{-1}	40.58	70 – 90	Akıllıoğlu et al., (2015)

TTT curves represents furan formation at a level of 50 µg furan /kg soy sauce and the other TTT curve represents furan formation at twice the previous one (100 µg furan /kg soysauce) as shown in Figure 3.

In the example case shown in Figure 3, thermally induced furan formation in soy sauce will be minimized with HTST process (Point Q). Since, furan formation results from degradation of food components, a lesser amount of furan formation has been possible due to lower degradation of quality attributes at the point Q. This is attributed due to high temperature sensitivity on the rate of inactivation of *Clostridium butyricum* (E_a = 492.8 kJ/mol calculated from z = 4.75) when compared with the rate of furan formation (77 kJ/mol). It can be estimated that while, treatment at 76.5 °C for 15 min can form 50 µg furan/kg soysauce, its concentration can reach 100 µg furan/kg soysauce if the soysauce will be processed at 74.5 °C for 45 min.

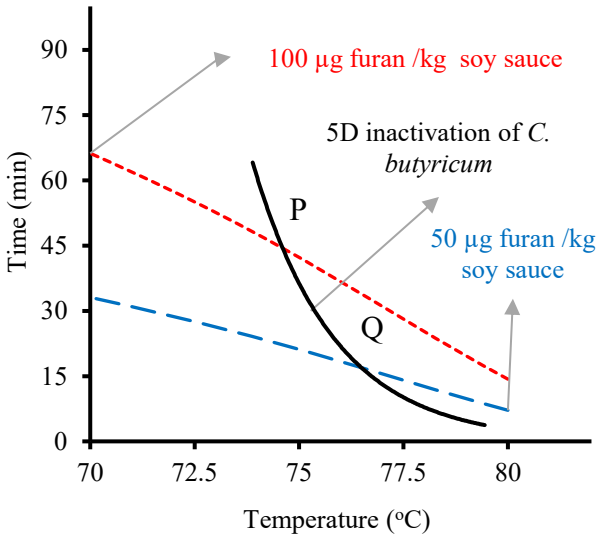

Figure 3. Time-temperature tolerance (TTT) curves for furan formation and 5 log inactivation of *Clostridium butyricum* in thermally treated soy sauce. Here, **(⋯)** represents 100 µg furan /kg soysauce and **(- - -)** represents 50 µg furan /kg soysauce. Kinetic parameters sources: (Morton et al., 1990; Huang and Barringer, 2016)

Concluding remarks

Thermal pasteurization and commercial sterilization have an outstanding record of assuring microbiological safety. Despite being the cheapest method, the major challenge with this traditional technology is to adequately protect volatile compounds, nutrients, flavor, and then to fulfil the demands of modern health conscious consumers. Process optimization is a technique to maximize quality attributes without violating the required safety. Kinetic model parameters (reaction order, rate constant, and temperature coefficient) would help to estimate the quantitative impact of the process on food components, including microorganisms of public health significance. These model parameters are useful to draw a time-temperature tolerance (TTT) curve for quality components (ascorbic acid, anthocyanin, and furan) and targeted species (microorganisms), and hence find out the best treatment conditions from the available time-temperature combinations. It is to be noted that, in most of the cases the activation energy of microbial inactivation is higher than the quality attributes in the time-temperature domain commonly selected by food processors. This natural advantage can be exploited by the food processor to retain maximum quality attributes in foods.

Acknowledgement

Santosh Dhakal PhD, the Executive Editor of the Journal of Food Science and Technology, Nepal was not involved in making any decision of this review paper.

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