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Study on the Generalization of the Equivalent Point Method for Thermal Evaluation

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Abstract

The existence of the equivalent point for a thermal processing system was demonstrated using arbitrarily chosen ideal direct heating curves, i.e. isothermal heating curves at 120 °C for 10 min and at 135 °C for 10 sec. Under these conditions, G-values and F-values were calculated at various values of Ea- and z-values by applying the Arrhenius and the Bigelow models respectively. The equivalent time and equivalent temperature were determined by both line intersection and linear regression methods. The equivalent points estimated by both the line intersection and the linear regression methods were consistent and their values were the same as the heating time and temperature of the ideal direct heating curves.

Key words: equivalent point method, thermal evaluation, Arrhenius model, Bigelow model

Introduction

With the advent of aseptic processing in food industry, it is necessary to develop new thermal evaluation methods for better prediction of quality changes or microbial destruction during thermal processing. It is because most of aseptic processes use much higher temperature and shorter time than the conventional canning processes. Aseptic processing is a continuous operation in nature. Usually, two types of time-temperature relationships are observed for continuous-flow thermal processing depending on the mode of heating methods as shown in Fig. 1[1,2]. In a direct heating system, the temperature of the product is raised rapidly to the holding temperature by the steam injection or the steam infusion method. After holding at that temperature for a predetermined period, it cools rapidly by the flash cooling method. Therefore, the thermal lags between the product and the heating medium is almost negligible[1]. The direct heating curve shown in Fig. 1 has never been observed in the practical situation, but this curve can be assumed for an ideal direct heating system. Cleland and Robertson[3] named this ideal process as a 'square' process in which the product temperature inside a container is raised uniformly and instantaneously to the process temperature at time zero, and cooled uniformly and instantaneously at the end of the heating period. In this case, the thermal effect on physical, chemical, and biological changes of the products can be easily analyzed algebraically. On the other hand, an indirect heating system shows significant thermal lags during heating and cooling periods (Fig. 1). This type of heating pattern is also observed in a batch heating method. The heating and the cooling processes also have a great influence on changes of the thermal evaluation index materials such as nutrient loss, color change, or destruction of microorganisms. Because the thermal evaluation for holding period is as simple as for the ideal direct heating system, most effort for thermal evaluation has been focused on analyzing the thermal effect during heating and cooling periods. For these purposes several thermal evaluation methods for continuous-flow system have been developed[2,4-8]. As pointed out by Rhim[9], most of such thermal evaluation methods can be interpreted as a converting process from an indirect heating curve into a corresponding ideal direct heating curve which has the same thermal effect for a certain thermal evaluation index material. One of the most interesting thermal evaluation method is the equivalent point method[2,8]. The equivalent point method (EPM) of thermal evaluation is a technique that defines the thermal treatment with unique one time and one temperature, independent of kinetic parameters associated with temperature dependence (z, Q_{10}, or Ea). The EPM was originally developed to compare the continuous thermal process of direct and indirect heating systems[2]. Using thermal reduction

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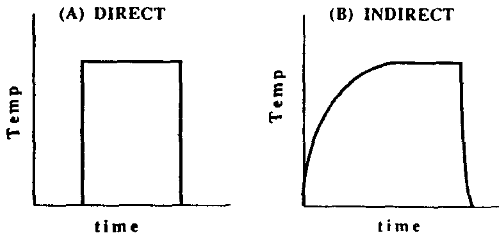

Fig. 1. Representative time-temperature relationships for an idealized direct heating and an indirect heating curves

relationships (G values), Swartzel developed a method for evaluating the cumulative thermal effect for heating, holding, and cooling parts of an indirect thermal processing for one food constituent, i.e., for one activation energy (Ea) by applying an Arrhenius relationship and the resulting total G values (G_{total}) for the indirect heating system can be equated with the G values of the corresponding direct heating system. In this way, any indirect heating curve can be converted into a direct heating curve with the same thermal effect for any constituent.

Swartzel[7] also demonstrated that this procedure can be used for the basis of defining the thermal treatment in the non-isothermal tubular flow reactor for reaction kinetic data generation.

The main advantage of this method is to make it possible to evaluate any type of thermal process by setting a unique pair of parameters to each thermal treatment. These parameters are the equivalent time (t_E) and equivalent temperature (T_E). Only data on thermal history and initial and final concentration of targeted materials are needed in this new thermal evaluation method.

Although Swartzel demonstrated two examples of the equivalent point using hypothetical data[7] and literature data[8], the uniqueness of the equivalent point is still unclear.

The objectives of this work were to demonstrate the generalized use of the equivalent point by applying kinetic data computed based on isothermal heating curves and to extend the concept of the equivalent point to the other thermal evaluation model, i.e. the Bigelow model[10].

It will be appropriate to show some theoretical backgrounds underlied in the method.

Arrhenius model

For a first order elementary irreversible decomposition reaction, the rate of decomposition of the substance can be expressed as:

$$-\frac{dC}{dt}=kC \tag{1}$$

Integration of eq. (1) after separating variables yields:

$$\ln\left(\frac{C_0}{C}\right)=\int_0^t k\ dt \tag{2}$$

The temperature dependence of the reaction rate constant, k, is usually expressed using Arrhenius equation.

$$k=k_0\ \exp(-E_a/RT) \tag{3}$$

In the case of non-isothermal heating as observed in heating and cooling period of an indirect continuous flow heating system or a conventional batch system, the change of temperature can be expressed as a function of time. Under this condition, eqns (2) and (3) can be combined as:

$$\ln\left(\frac{C_0}{C}\right)=k_0\int_0^t \exp(-E_a/RT(t))\ dt \tag{4}$$

This equation may be integrated either graphically or numerically. In the isothermal heating case, as shown in the ideal direct heating or the holding period of indirect heating system, eqn (4) becomes

$$\ln\left(\frac{C_0}{C}\right)=k_0\ \exp(-E_a/RT)\ t \tag{5}$$

Swartzel[2] introduced the thermal reduction relationships (G values) by dividing each side of eqns (4) and (5) by the Arrhenius frequency factor, k_0.

For heating or cooling

$$G_{heating}\text{or } G_{cooling}=\ln\left(\frac{C_0}{C}\right)/k_0=\int_0^t \exp(-E_a/RT(t))\ dt \tag{6}$$

For holding

$$G_{holding}=\{\exp(-E_a/RT)\}\ t \tag{7}$$

The G values of each section of the indirect system can be evaluated using above equations and summed up to obtain the cumulative thermal effect of whole thermal process. Consequently, the total G values for the indirect heating system can be expressed as:

$$G_{total}=G_{heating}+G_{holding}+G_{cooling} \quad (8)$$

To establish the same degree of thermal effect on the same constituent (or same Ea-value) with the ideal direct heating system would require that

$$(G_{total})_{Indirect}=(G)_{Direct} \quad (9)$$

Recognizing that G-values for the direct heating system can be expressed with the same form as eqn (7). So the total G-value of the indirect heating system can be expressed as follows;

$$(G_{total})_{Indirect}=(G)_{Direct}=\{\exp(-E_a/RT)\}\ t \quad (10)$$

Taking logarithms of eqn (10) yields:

$$\ln(G)=\ln(t)-\frac{E_a}{RT} \quad (11)$$

where subscript was removed for convenience. Infinite time-temperature conditions would satisfy the equation. By plotting ln(t) vs. 1/T, a straight line results. By repeating the process for the same thermal curve for different constituents or Ea values, new straight line emerge in the same plot. Swartzel[2] calimed that uniquely these lines tend to intersect at one defined point. Swartzel[8] defined this point as the equivalent time and temperature point (t_E and T_E). Swarzel and Jones[7] also showed that the concept of the obtaining the equivalent point can be universally applied with other reaction ordrs.

As noted by Rhim[9], the main idea of EPM is to convert a non-isothermal heating curve into the corresponding isothermal heating curve which has the same thermal effect on the selected constituent (or Ea-value). Figure 2 shows schematic representation of the procedure to determine the equivalent time and temperature point from an indirect heating curve.

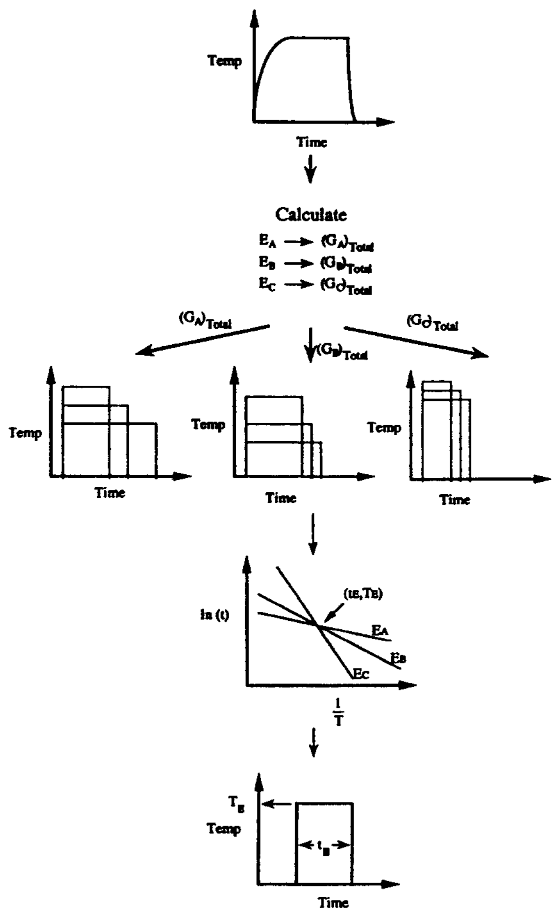

Fig. 2. Schematic representation of determining the equivalent time and temperature point for a defined thermal process

Bigelow model

Conventionally, the Bigelow model has been widely used in canning industry instead of the Arrhenius model for evaluation of thermal processing. The Bigelow model represents a series of equivalent processes at different temperatures and is represented by the equation:

$$F=t\ 10^{(T-121.1)/z} \quad (12)$$

Originally, this model was developed by using destruction of microorganisms as an index of thermal evaluation. Because the thermal destruction of microorganisms is known to follow first order kinetics[10-12], the same approach as used in the Arrhenius model can be applied to compare each heating method. If the process is not at a constant temperature as observed in the heating and cooling periods of indirect heating system, the total thermal effect on the defined microorganism (or z-value) should be integrated through the whole process and expressed as an equivalent heating time at 121.1 °C. For the heating and cooling period, the equivalent heating time can be expressed as:

$$F=\int_0^t 10^{\{T(t)-121.1\}/z}\ dt \quad (13)$$

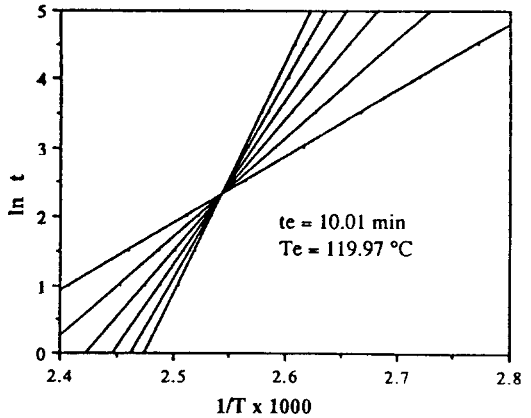

Fig. 3. Time-temperature relationships for different Ea-values for a defined heating curve plotted by the line intersection method using the Arrhenius model

For the holding period, eqn (11) can be used without modification. Consequently, the total equivalent heating time is represented as:

$$F_{total} = F_{heating} + F_{holding} + F_{cooling} \quad (14)$$

Then, infinite number of time and temperature conditions producing the same effect can be calculated by eqn (12) using F_{total}-value. Logarithmic transformation of eqn (12) yields:

$$\log(F) = \log(t) + \frac{T - 121.1}{z} \quad (15)$$

By plotting log(t) vs. T, a straight line will be obtained. Repeating this procedure with different microorganisms (or z-values), different straight lines will be obtained in the same plot and each line will meet at one definite point. This intersection point also represents the equivalent time and temperature point.

Methods

Arrhenius model

To illustrate the EPM with the Arrhenius model, an arbitrarily selected ideal direct heating curve was assumed, i.e. a constant temperature at 120°C for 10 min. Under this condition, G-values were calculated using eqn (10) by plugging a series of Ea-values from 80 to 280 kJ/mol by increment of 40 kJ/mol. In this way, same number of G-values were determined from corresponding Ea-values. Applying each set of Ea- and G-values in eqn (11), several sets of time-temperature data were obtained. Then, ln(t) was plotted against 1/T. This procedure was repeated with other set of Ea- and G-values. From the intersection point, the equivalent time and temperature were determined. This procedure of determining the equivalent point was originally suggested by Swartzel[2] and later, it was named as line intersection method. Another approach, which is called linear regression method, was also tried to determine the equivalent time and temperature. To test linear regression method under the assumed time-temperature condition, ln(G) was plotted against Ea-values using eqn (11) which resulted in a straight line. Then t_E was determined from the intercept of the resulting straight line and T_E was calculated from the slope of the line.

Bigelow model

Another ideal direct heating curve was assumed to demonstrate the equivalent time and temperature point with the Bigelow model. A different time-temperature condition (135°C for 10 sec) was chosen to show that the proposed method works in the same way at different conditions. First, z-values were selected arbitrarily from 6 to 16°C by increment of 2°C. Then, F-values were calculated using eqn (12) under the assumed time-temperature condition. By plugging each set of F- and z-values into eqn (15), several sets of time-temperature data were generated. The line intersection method was tested by plotting log(t) vs. T. In the same way as the Arrhenius model, the equivalent time and temperature point was determined from the intersection point of each line. Linear regression method was also tested with the Bigelow model by plotting log(F) vs. 1/z according to eqn (15) and the equivalent time and temperature were determined from the intercept and the slope of the resulting straight line.

Results and Discussion

Arrhenius model

The results of line intersection method tested with an ideal direct heating curve (120°C for 10 min) are shown in Fig. 3. In this Figure, each line represents each Ea- or G-values, i.e. every point on a line indicates the same degree of thermal effect for the selected constituent. As noted by Swartzel[2], all the equivalent thermal effect lines intersect

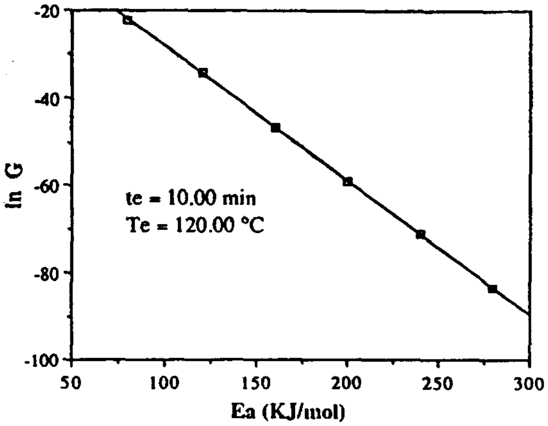

Fig. 4. Thermal reduction relationship for different Ea-values for a defined heating curve plotted by the linear regression method using the Arrhenius model

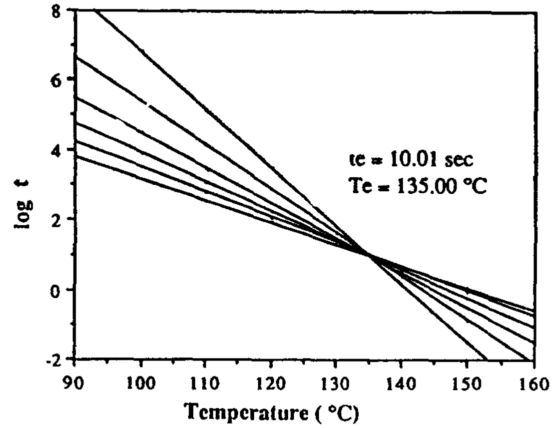

Fig. 5. Time-temperature relationships for different z-values for a defined heating curve plotted by the line intersection method using the Bigelow model

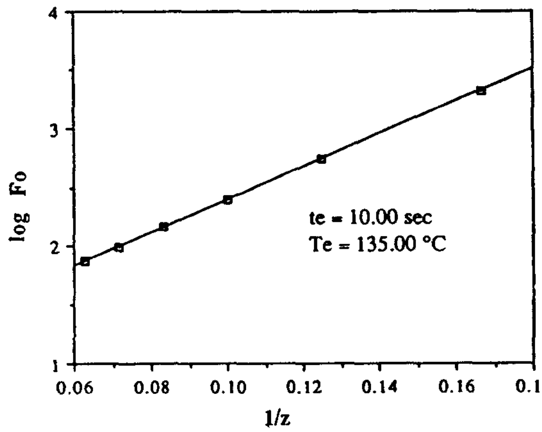

Fig. 6. Thermal lethality relationship for different z-values for a defined heating curve plotted by the linear regression method using the Bigelow model

at one definite point. From this intersection point, the equivalent time of 10.01 min and the equivalent temperature of 119.97 °C were determined. These values are in good agreement with the initially assumed values. This fact indicates that the time and temperature of the ideal direct heating curve are in themselves the equivalent time and temperature of the thermal process.

The linear regression method was also tested by plotting ln(G) vs. Ea as shown in Fig. 4. As expected from eqn (11), this yields a straight line. From the intercept of the line, t_E of 10.00 min, and from the slope, T_E of 120.00 °C were determined. Again, they are exactly coincided with the assumed time and temperature values of the ideal indirect heating curve.

Bigelow model

The results of the line intersection method with the Bigelow model for an ideal direct heating curve (135 °C for 10 sec) are shown in Fig. 5. These lines represents a series of equivalent process at different temperature. All equivalent process lines also meet at one point. From this intersection point, the equivalent time and the equivalent temperature were determined. They were 10.01 sec and 135.00 °C, respectively. The linear regression method with the Bigelow model yielded a straight line (Fig. 6). From the intercept, t_E of 10.00 sec, and from the slope, T_E of 135.00 °C were determined. In both the line intersection and the linear regression methods, the equivalent time and the equivalent temperature determined were consistent with the initially assumed time and temperature of the ideal direct heating curve.

Though several cases of the line intersection phenomena in a certain thermal process were observed by chances in the literature[13-15], nobody payed attention to this phenomenon until Swartzel[2] developed a procedure to compare a non-isothermal heating curve to the corresponding ideal direct heating curves with selected kinetic parameters (Ea or z). In this paper, hypothetical direct heating curves were assumed to demonstrate the existence of the equivalent time and temperature point for a thermal process. For the ideal direct heating curves, definite equivalent points were observed and the time and temperature of the ideal direct heating curve themselves proved to be the equivalent time and temperature of the process. In addition, the linear regression method was shown to be a more accurate and more convenient way to find the equivalent point compared with the line intersection method. As shown in both illustrations, the equivalent time and temperature point really exists. This fact implies that any thermal process can be uniquely defined by a pair of parameters i.e., the equivalent time (t_E) and the equivalent temperature (T_E) It should be emphasized that, in practice, the calculation of any thermal evaluation is more complicated than the examples shown in this paper in which constant heating curves have been used for clarity and simplicity. The temperature of the material to be heated varies with time in a way that may be difficult to describe analytically. In such case, the accumulated thermal effect should be calculated through the entire heating process by a numerical integration technique.

Nomenclature

Symbol	Quantity Represented	Units
C	Concentration of constituent at any time	mole/l
C_o	Initial concentration of constituent	mole/l
E_a	Activation energy	J/mole
F	Lethality of a process defined by equivalent at some. temperature for a specified z-value	s or min
G	Thermal reduction relationship	
k	Reaction rate constant	
k_o	Frequency factor	
Q_{10}	Reaction rate constant	Dimensionless
R	Universal gas constant (8.314)	J/mol °K
t	Processing time	s or min
t_E	Equivalent time	s or min
T	Processing temperature	°C or °K
T_E	Equivalent temperature	°C
z	Temperature interval for a 10-fold change in Decimal Reduction Time	°C

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Equivalent Point Method의 일반적 이용을 위한 연구

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일정한 열처리 공정에 대해 Equivalent point가 존재함을 이상적인 두가지의 직접가열곡선 즉, 120℃에서 10분간, 135℃에서 10초간의 등온가열 곡선을 이용하여 예시하였다. 이러한 조건하에서 Arrhe nius model을 적용한 경우 임의의 Ea-값을 사용하여 G-값을 결정하고 Bigelow model을 적용한 경우, 임의의 z-값을 사용하여 F-값을 결정하였다. 이들 값을 사용하여 Equivalent time과 Equivalent Temperature를 두가지 방법 즉, 직교좌표법과 회기분석법에 의해 결정하였다. 이들 두 방법에 의해 결정된 Equivalent Point는 서로 일치하였으며 각각의 값은 초기에 가정했던 직접가열곡선의 가열시간 및 온도와 일치하였다.