

Application of the Equivalent Point Method for Estimation of Kinetic Parameters

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Abstract

A method for application of the equivalent time and temperature point for estimating kinetic parameters was proposed. The feasibility of the method was demonstrated with both theoretical and empirical kinetic data. The theoretical kinetic data were obtained from the arbitrarily chosen time-temperature data for three chemical reactions whose kinetics are well established. The experimental kinetic data were obtained for the acid (0.0005 N HCl) catalyzed hydrolysis of sucrose (2%). The activation energy and the frequency factor determined by the proposed method were 104.74 ± 1.87 kJ/mol and 5.62×10^{14} hr⁻¹ respectively and the results agreed well with those obtained by a different method of kinetic parameter estimation, i.e. the linearly increasing temperature method.

Key words: equivalent point method, kinetic parameters

Introduction

Quality deterioration in the form of changes in nutritional value, color, flavor, or texture may occur during processing and storage of foods. In order to prevent these quality losses, it is essential to know how and to what extent such changes occur in specific environmental conditions. For these purposes, kinetics has been widely used in the area of processing and storage of foods. The major application of kinetics in the food industry are as follows: (1) evaluation of thermal processing or sterilization process, (2) prediction of quality changes of foods occurring in processing and storage, (3) investigation of the mechanism of the reactions, (4) new design or optimization of the thermal process, (5) shelf-life test of food products, and (6) quality control of the raw material or the finished products.

Generation of reliable kinetic parameters for thermal destruction of microorganisms or food constituents is essential to achieve these goals. The most common methods now in use for obtaining empirical informations on destruction of food components or microorganisms are batch or continuous flow methods. When capillary or thermal death time (TDT) tube containing spore suspension or food material is placed in a heating bath, the temperature within the suspension varies both with

position within the tube and with time after immersion. Consequently, the temperature inside tube does not rise immediately to the desired temperature, i.e. there is a thermal lag between the sample and the heating medium. There will also be a thermal lag during cooling of sample. Due to the thermal lags, the effective holding time will be less than the actual immersion time, the effect becoming important with increase in temperature and with reduction in immersion time. Temperature profiles of the indirect heating continuous flow system are very similar to those observed in the batch system. Generally, they consist of heating, holding, and cooling parts. Though there are differences in size and principle of operation, the problems are essentially the same with the batch method.

In the canning industry, numerous methods have been developed for evaluation of the lethality of heating and cooling period⁽¹⁻³⁾. These evaluations have been performed by calculating effective heating times for the slowest heating point in the can. This is satisfactory when minimum safe processing conditions are being determined as has been done in canning industry, but it is not suitable for the analysis of laboratory thermal destruction kinetic data or for the thermal evaluation of the continuous flow system. To obtain accurate kinetic data, it is necessary to integrate the thermal destruction effect throughout the whole volume of suspension for all temperature and all times and use the integrated effect to modify the experimental holding times by

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correcting the effect of thermal lags⁽⁴⁻⁸⁾.

Several methods were developed for this purpose and applied to obtain kinetic parameters of change of quality factors of food or destruction of microorganisms⁽⁹⁻¹³⁾. Among them, Swartzel's equivalent point method^(12,13) is very unique in that the method characterizes any kind of non-isothermal heating curve with only two parameters, the equivalent time (t_p) and the equivalent temperature (T_p), which are independent of kinetic parameters (E_a or z -values).

Later, Swartzel⁽¹⁴⁾ extended this idea for the determination of reaction kinetic parameters of constituents in fluid foods during continuous flow. He illustrated the procedure using hypothetical data of time-temperature profiles and constituent changes which were assumed to follow first order kinetics. According to this procedure, one needs to know only final concentrations and time-temperature profiles of at least two different thermal processes. The basic assumption underlied in Swartzel's method is that the flow of fluid through the reactor is orderly with no element of fluid overtaking or mixing with any other element ahead or behind, i.e. an ideal plug flow.

One difficulty encountered when using a continuous flow system for kinetic studies² is that of non-ideal fluid flow. The assumption of plug-flow in a tubular reactor can lead to serious errors in both conversion calculations and rate determinations. The effect and degree of this deviation from plug flow reactors differs considerably from system to system. Therefore, to obtain meaningful results from a continuous flow system, the residence time distribution of the system must be carefully specified⁽¹⁵⁻²⁰⁾.

Originally, Swartzel's method⁽¹²⁾ for calculation of the equivalent point is based on Deindorfer and Humphery's method⁽⁹⁾ of thermal evaluation, which is in nature an analytical solution. This kind of analytical solution is very tedious to use and not so accurate. As pointed out by Cleland and Robertson⁽²¹⁾, use of such an analytical integration is not warranted with the increasing ease of carrying out numerical integration by computer.

Even though the EPM for generating kinetic data is more convenient and much easier than the conventional kinetic method, no experimental data obtained by the EPM are available in the literature.

The main objective of this work was to demonstrate the applicability of the EPM for determination of kinetic parameters using both computer simulated data and experimentally obtained kinetic data.

The basic theoretical backgrounds underlied in the method are as follows:

For an elementary irreversible decomposition reaction, if the mechanism of the reaction is not known, the experimental data is usually fitted with an n th-order rate equation of the form

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

which on separation and integration yields

$$\frac{C_f^{1-n} - C_0^{1-n}}{n-1} = kt, \quad n \neq 1 \quad (2)$$

or

$$\ln\left(\frac{C_0}{C_f}\right) = kt, \quad n=1 \quad (3)$$

For convenience, both eqns (2) and (3) can be expressed as:

$$M = kt \quad (4)$$

where

$$M = \frac{C_f^{1-n} - C_0^{1-n}}{n-1} \quad (\text{for } n \neq 1)$$

$$\text{or } M = \ln\left(\frac{C_0}{C_f}\right) \quad (\text{for } n=1).$$

The rate constant k of the reaction is dependent on temperature, which follows the Arrhenius equation, so eqn (4) becomes

$$M = k_0 e^{-E_a/RT} t \quad (5)$$

By the way, any thermal process can be characterized with only two parameters, i.e. the equivalent time (t_p) and the equivalent temperature (T_p)^(12,22). Therefore, with a certain thermal process, eqn. (5) becomes

$$M = k_0 e^{-E_a/RT_E} t_E \quad (6)$$

In order to obtain kinetic parameters, it is necessary to determine the initial (C_0) and the final (C_f) concentrations for at least two process conditions⁽¹⁴⁾. Then, two equations will be evolved from the relationship of eqn (6)

$$M_1 = k_0 e^{-E_a/RT_{E1}} t_{E1} \quad (7)$$

$$M_t = k_0 e^{-E_a/RT_E} t_E^n \quad (8)$$

When the order of reaction (n) is known, E_a and k_0 can be determined by solving eqns (7) and (8) simultaneously. However, researchers in this area^(23,25) do not recommend to use only two data points to estimate meaningful kinetic parameters. Therefore, several sets of data determined at different thermal processes are needed to determine all the kinetic parameters (E_a , k_0 , and n) using a regression or a graphical analysis. Taking logarithms of both sides of eqn (6) yields

$$\ln(M) = \ln(k_0) - \frac{E_a}{RT_E} + \ln(t_E^n) \quad (9)$$

Then, E_a and k_0 can be determined by performing a multiple linear regression of $\ln(M)$ against $1/T_E$ and $\ln(t_E^n)$. A simple linear regression can also be used by transforming eqn (9)

$$\ln\left(\frac{M}{t_E^n}\right) = \ln(k_0) - \frac{E_a}{RT_E} \quad (10)$$

Plotting $\ln(M/t_E^n)$ vs. $1/T_E$ will result in a straight line. From the slope and the intercept of the line, E_a and k_0 can be calculated. The order of reaction, n , cannot be found explicitly from eqns (9) or (10), so a trial-and-error solution must be made. This is not too difficult, since a value for n can be selected and $\ln(M)$ or $\ln(M/T_E^n)$ be calculated based on this selected n value. The value of n which gives the best fit of experimental data is the desired value of n .

Materials and Methods

The proposed method was illustrated using two types of kinetic data i.e. computer simulated theoretical data and empirical data.

Theoretical kinetic data

To demonstrate the method using theoretical kinetic data, three sets of kinetic data were chosen from the literature (Table 1). Concentration changes at selected time and temperature conditions for each reaction shown in Table 1 were calculated using eqn (5). For this calculation, ideal direct heating temperature profiles were assumed. The heating time and temperature themselves were used as the equivalent time and temperature as indicated by Rhim⁽²²⁾.

Sucrose hydrolysis

Acid-catalyzed hydrolysis of sucrose was chosen for experimental kinetic data generation. Two percent sucrose dissolved in 0.0005 N HCl solution was used for thermal treatment. An aliquot of sucrose solution (1.5 ml) was introduced into the thermal death time (TDT) tube which was made by heat sealing one end of a Pyrex glass tube (7.0-8.0 × 120 mm), then heat sealed the other end after introducing sample solution. The TDT tubes containing the samples were immersed into an oil bath (Lauda K-2/R; Brinkmann Instrument Inc., Westbury, N.Y.) at each temperature for predetermined time. Immediately after heating, the tubes were rapidly cooled in an ice-water bath and analyzed after proper dilution with distilled water. The glucose enzyme kits (Glucose Procedure No. 510, Sigma Diagnostics, St. Louis, MO) were used to determine the glucose concentration produced from hydrolysis of sucrose. Sucrose concentration at each condition was determined by subtracting glucose concentration from the initial concentration of sucrose. Three replications were made on each test, and the average value was reported. While thermal treatment of sample at each condition, temperature profile of sample in the tube was measured using a digital

Table 1. Kinetic parameters of selected reactions

Reaction	E_a (kJ/mol)	k_0	n	Ref.
Browning of Whey Powder ($a_w = 0.44$)	123.3	$2.940 \times 10^{18} \text{ day}^{-1a}$	0	(25)
Sucrose (2%) Hydrolysis by acid (0.0005 N HCl)	99.0	$3.704 \times 10^{13} \text{ hr}^{-1}$	1	(27)
Loss of Lysine in Heated Milk	109.0	$7.020 \times 10^{13} \text{ hr}^{-1a}$	2	(28)

^a)Unit of concentration is omitted.

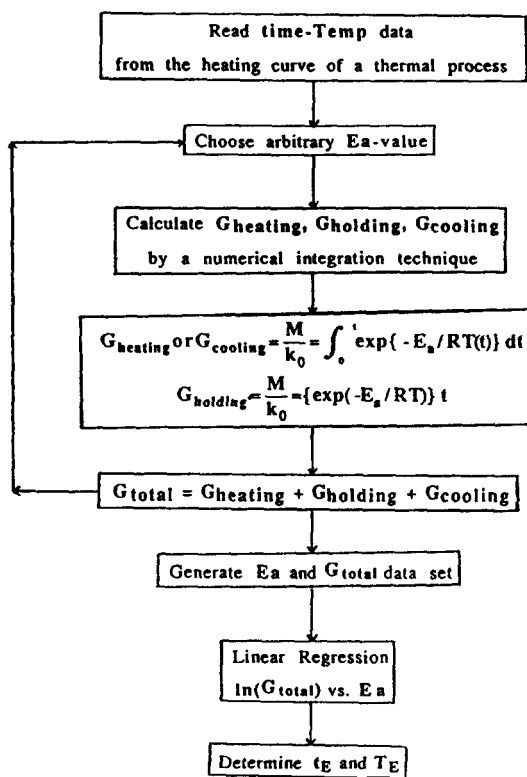


Fig. 1. Procedure for calculating the equivalent time and temperature using time-Temperature data for a defined thermal process

thermometer (Type 2809, Omega Engineering, Inc., Stamford, CONN.) with a 30 gauge thermocouple (T-type) which was located at the center of the sample. The output signal from the digital thermometer was recorded continuously with a digital chart recorder (model L-4000, Linseis Inc., Princeton, NJ).

Calculation of the equivalent point

Based on the time-temperature data of each heat treatment, the equivalent time and the equivalent temperature were calculated by the procedure shown in Fig. 1. Integrating the thermal effect is the most important step in this procedure. For the integration, the general Simpson's rule was used and computer programs for this calculation were written in BASIC language.

Analysis of kinetic data

The kinetic data obtained by both theoretical calculation and experimentation were analyzed using

the proposed method, i.e. plotting $\ln(M/t_E)$ vs. $1/T_E$ according to eqn (10).

Results and Discussion

To generate the theoretical kinetic data for the selected reactions (Table 1), heating time-temperature conditions were chosen to cover a wide range of concentration changes as shown in Table 2. Concentration changes for the reactions with the heating conditions were calculated using eqn. (5). The results are also shown in Table 2. In all cases, concentrations were expressed as the fractional ratio (C/C_0). In browning reaction, the degree of browning is increased as the reaction continues, therefore the initial concentration (C_0) was assumed zero. On the other hand, both reactions of sucrose hydrolysis and loss of lysine are destruction reactions, so C_0 was assumed unit.

The theoretical kinetic data shown in Table 2 were plotted as proposed in this paper. The results are shown in Fig. 2-4. The kinetic parameters (E_a and k_0) can now be found from the slope and the intercept of the straight lines in the Figures by a least squares fit. In this way, both kinetic parameters (E_a and k_0) were determined with one step calculation. The resulting kinetic parameters estimated by the method were as follows:

Browning Reaction (zero order):

$$E_a = 123.9 \text{ kJ/mol}, k_0 = 2.937 \times 10^{18} \text{ day}^{-1} \\ (R^2 = 1.000)$$

Sucrose hydrolysis (first order):

$$E_a = 99.2 \text{ kJ/mol}, k_0 = 3.704 \times 10^{13} \text{ hr}^{-1} \\ (R^2 = 1.000)$$

Loss of Lysine (second order):

$$E_a = 108.6 \text{ kJ/mol}, k_0 = 7.017 \times 10^{13} \text{ hr}^{-1} \\ (R^2 = 1.000)$$

For each reaction, the estimated values are almost identical with the theoretical values (Table 1). This result proves the validity of the proposed method.

The applicability of the method was tested using experimental data for sucrose hydrolysis. For generation of experimental data, TDT tubes containing sucrose solution were heated by immersing into the oil bath for predetermined time at 100 to 130°C by raising 10°C. The heating patterns at each heating temperature are shown in Fig. 5. Thermal

Table 2. Time-temperature conditions and the resulting concentrations for the selected reactions

Browning Reaction ^{a)}			Sucrose Hydrolysis ^{b)}			Loss of Lysine ^{b)}		
Temp. (°C)	time (day)	Conc. (C/Co)	Temp. (°C)	time (min)	Conc. (C/Co)	Temp. (°C)	time (hr)	Conc. (C/Co)
25	50	0.029	100	12	0.907	100	3	0.883
35	50	0.148	110	12	0.799	110	3	0.751
45	30	0.457	120	12	0.610	120	3	0.560
55	10	0.565	130	12	0.350	130	3	0.358
65	4	0.866	140	12	0.117	140	3	0.203

^{a)}Formation reaction (concentration indicates C/Co, where Co = 0).

^{b)}Destruction reactions (concentration indicates C/Co, where Co = 1).

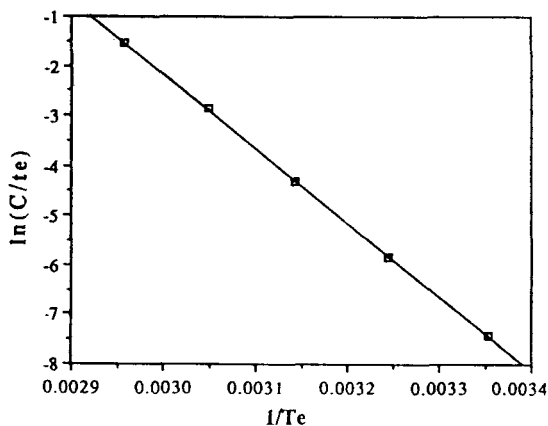


Fig. 2. Arrhenius type plot of simulated data for browning of nonhygroscopic whey ($a_w = 0.44$) plotted by zero order kinetic model

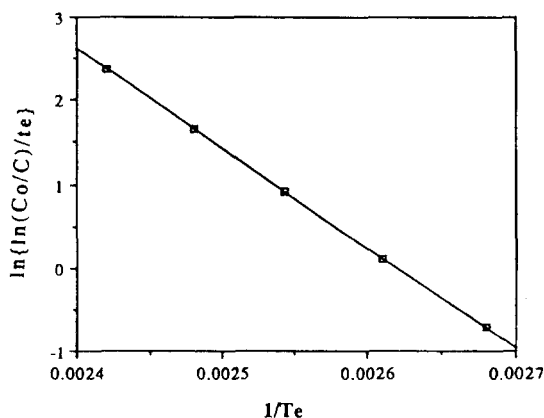


Fig. 3. Arrhenius type plot of simulated data for acid catalyzed sucrose (2%) hydrolysis plotted by first order kinetic model

lags between heating medium and sample were depend on heating temperature. The thermal lag time of heating at 100 °C was about 210 sec, while those at 110 and 120 °C were about 160 sec. The equivalent time and temperature were calculated at each heating condition by the procedure shown in Fig. 1. The results are shown in Table 3. Here, immersion time indicates the time elapsed from immersing the TDT tube into the oil bath to the end of heating, i.e. it includes the heating and the holding part. Table 3 also includes the remaining sucrose concentration after heat treatment. These experimental data were analyzed by the first order kinetic model and the results are shown in Fig. 6. A linear regression of these data yields following kinetic parameters:

$$E_a = 104.74 \pm 1.87 \text{ kJ/mol}, k_0 = 5.62 \times 10^{14} \text{ hr}^{-1} \\ (R^2 = 0.997)$$

Although these values show slightly higher than Lou's result⁽²⁷⁾, they agrees fairly well with other literature values⁽²⁹⁻³¹⁾. Especially, it is important to note that the kinetic parameter values coincide with those of Rhim *et al.*⁽²⁹⁾, who used the same analytical method for measuring sucrose concentration, but different approach of kinetic data generation, i.e. the linearly increasing temperature method. This result proves that this procedure can be used successfully for generating kinetic data without being involved with the problem of thermal lag correction. In addition, this procedure has more advantageous features compared with the conventional method of kinetic data generation. As pointed out by Swartzel⁽¹⁴⁾, this procedure allows to examine a variety of effects on kinetics of target material and provides means of kinetic data generation for thermal destruction at processing conditions simulating actual conditions. Especially, this method is suitable for

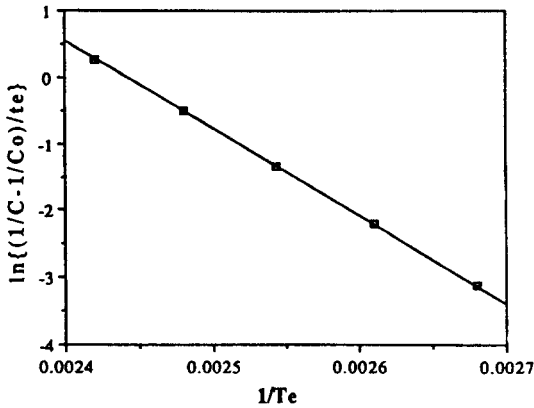


Fig. 4. Arrhenius type plot of simulated data for lysine loss in heated milk plotted by first order kinetic model

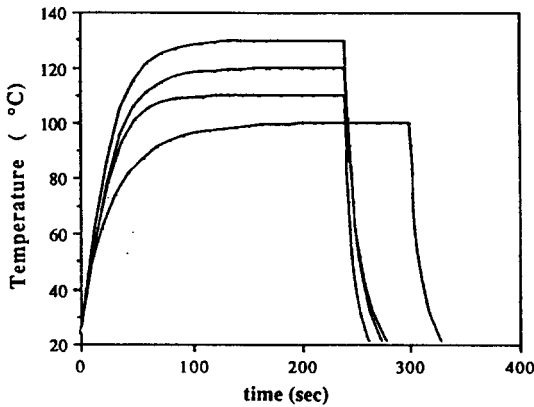


Fig. 5. Representative time-temperature relationships of sucrose solution (2%) in a TDT tube heated at 100-130°C

thermal evaluation of canning industry in determining single point sterilization or continuous sterilization at ultra high temperature, because only data on the initial and the final concentration and time-temperature profile are needed for applying this procedure. One precaution for applying of this method is to use the time-temperature conditions to cover as wide concentration changes (5-95%) as possible. However, it is not the constriction only for this method. This precaution is universally applied to any of kinetic data generation methods.

Therefore, we recommend this procedure not only for generating kinetic data in the laboratory but also for the thermal evaluation of the canning process as well as the continuous flow thermal pro-

Table 3. The equivalent time and temperature and sucros concentration at each heating condition

Temp. ^{a)} (°C)	Time ^{b)} (min)	t _E ^{c)} (sec)	T _E ^{d)} (°C)	Conc. (mmol/l)
100 ^{e)}	4	190.41	98.00	53.27
	7	367.79	99.11	50.37
	12	666.87	99.53	45.83
110 ^{e)}	3	—	—	51.59
	9	501.00	109.55	39.07
	13	740.85	109.67	32.85
120 ^{f)}	3	137.69	117.61	45.86
	10	555.35	119.27	20.91
	13	735.17	119.38	15.02
130 ^{f)}	3	137.10	127.84	34.80
	9	495.52	129.26	7.30
	13	735.32	129.41	2.75

a) Temperature of heating medium

b) Immersion time

c) Equivalent time

d) Equivalent temperature

e) Co = 56.64 mmol/l

f) Co = 56.76 mmol/l

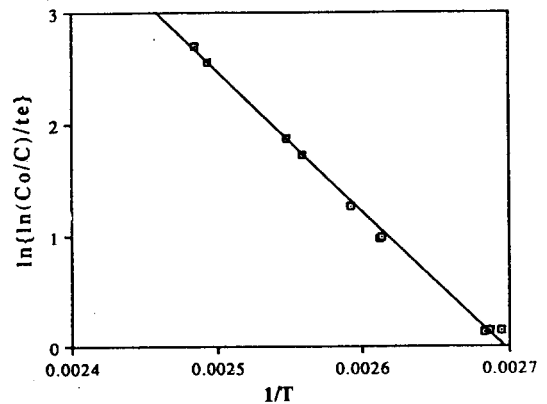


Fig. 6. Arrhenius type plot for experimental data for acid (0.0005 N HCl) catalyzed hydrolysis of 2% sucrose solution

cessing of fluid and possibly including particulate materials.

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Kinetic Parameters 결정을 위한 Equivalent Point Method의 이용

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본 고에서는 Equivalent time과 Equivalent temperature를 활용하여 Kinetic parameters를 결정하는 새로운 방법을 제안하였다. 본 방법의 타당성을 두 가지의 Kinetic data 즉, 계산치와 실험치를 이용하여 예시하였다. 계산치는 그 Kinetics가 잘 알려진 세 가지 화학반응에 대해 임의의 등온가열조건을 적용하여 계산하였고 실험

치는 2% 설탕용액을 사용하여 0.0005 N 염산용액을 사용하여 가수분해가 일어나는 정도를 효소반응을 이용하여 측정하였다. 본 방법에 의해 결정된 활성화 에너지와 Frequency factor는 각각 104.74 ± 1.87 KJ/mol과 $5.26 \times 10^{14} \text{ hr}^{-1}$ 이었으며 이들 값은 보고된 결과와 잘 일치되었다.