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PAPER

A theoretical procedure for using multiple response time–temperature integrators for the design and evaluation of thermal processes

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Time–temperature integrators (TTI) offer a sound alternative to in situ *and physical–mathematical methods for thermal process design and evaluation. In the present work, the use of multi-component TTI systems, in cases where a single-component TTI with a particular* z *value is not available, was investigated.*

A procedure in using double or triple response TTI systems to evaluate the impact of a thermal process on a particular target heat labile substance was proposed and evaluated, based on a large number of product time–temperature profiles. Parameters to be considered in using a multi-component TTI included the z *values of the TTI, in relation to the target* z *value, as well as the reference temperature used for the calculations. Guidelines for proper selection of the parameters involved are given.*

Although, generally, triple response TTIs performed better compared with double response TTIs, the results of double response TTIs were also satisfactory, and for practical applications, the use of a double response TTI might be sufficient. © *1998 Elsevier Science Ltd. All rights reserved.*

Keywords: thermal processing; sterilisation; time–temperature integrators; TTI; multiple response TTI; multiple component TTI

NOMENCLATURE

Latin letters

C	concentration (or activity) of a heat labile substance, g ml^{-1}, or any other appropriate unit
D_T	time at constant temperature, T, required to reduce the level of an attribute, of a heat labile substance or device, by a factor of 10 (s)
F_T^z	(or simply F) time at constant temperature, T, required to reduce, to a given value, the level of an attribute of a heat labile substance or device whose thermal resistance is characterized by z (s unless otherwise explicitly stated)
F_o	the F value for $T_{ref} = 250$°F and $z = 18$°F
f, g	response functions, variable units
k_T	reaction rate constant at constant temperature, T (s^{-1}) for first order reactions

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T temperature (°C unless otherwise explicitly stated)
t time (s)
X response variable, variable units
z temperature interval required to achieve a decimal change of the D_T value (°C unless otherwise explicitly stated)

Greek letters

α, β empirical coefficients defined in equation (6), equation (7), or equation (8), various units

Subscripts

a initial condition
b final condition
base base value used for subsequent calculations
max maximum value (for product temperature)
RT heating medium
ref reference value
target target value

Symbols

Δ difference

INTRODUCTION

The integrated time–temperature effect of a thermal process on the destruction of a heat labile substance can be evaluated by *in situ*, physical–mathematical, or TTI (time–temperature integrator) methods (Hendrickx *et al.*, 1995). The *in situ* method involves measurements of the concentration change, after processing, of the substance of interest itself (eg, microbial spores) present in the food. It is the direct method of evaluating a thermal process and no knowledge of the destruction kinetics or of any other parameter is required. Despite its accuracy, the *in situ* method can be very laborious, and is often limited by the detection limit of the methods of analysis. The physical–mathematical evaluation of the destructive effects of a thermal process is based on degradation kinetics and the temperature dependence of the kinetic parameters for the given substance, and the temperature experienced by that substance during a given heat treatment. In using the physical–mathematical approach, the difficulty in determining the thermal and physical parameters associated with some particular processes (eg, during aseptic processing of liquid/particulate foods) might necessitate conservative assumptions which can guarantee safety, but will probably result in processes far from the optimal design as far as product quality is concerned.

The use of TTIs, coming to alleviate the limitations of the other two methods, involves measurements of the concentration, or some other attribute, before and after processing of a heat sensitive substance or device, either present in the product or introduced into the food sample, chosen so as to mimic the thermal degradation of the substance of interest. The requirement is for an easily measurable irreversible, time–temperature dependent, change that can be attributed to a biological, chemical, or physical phenomenon (Taoukis and Labuza, 1989).

The basic assumption in using TTIs for thermal process evaluation is that the activation energies, or the z values, of the TTI and the substance of interest are the same (Taoukis and Labuza, 1989; Hendrickx *et al.*, 1995). The design of such TTIs is not easy (Van Loey, 1996). Guidelines for conservative (in terms of product safety) use of TTIs, with z values different from the ones characterizing the substance of interest, have been proposed by Van Loey *et al.* (1995). Converting results from one z value to another has been suggested by Pflug and Christensen (1980); however, the proposed procedure requires knowledge of the heat penetration parameters for the process and product involved.

The use of TTI systems with multiple responses, ie, multi-component TTIs with each component having its own activation energy (or z value), and correlation of the responses of these multi-TTI systems with the thermal degradation of the product of interest (which product is characterized by an activation energy different from the characteristic activation energies of the multi-TTI system) has been proposed as an alternative to single component TTIs (Swartzel *et al.*, 1991; Hendrickx *et al.*, 1995). Analysis of such systems is not yet considered satisfactory (Maesmans *et al.*, 1993). The objective of this work was to develop a procedure in using multi-component TTI systems for thermal process design and evaluation.

BASIC CONSIDERATIONS

Following the classical thermobacteriological approach (TDT approach, Ball and Olson, 1957; Stumbo, 1973), the governing equation for the design and the evaluation of a thermal process is given here by equation (1) (Stoforos *et al.*, 1997a)

$$F_{T\text{ref}}^{z} = \int_{t_a}^{t_b} 10^{(T-T\text{ref})/z}\,dt = \frac{f(X_a,X_b)}{k_T} \qquad (1)$$

The integral for the F value calculation employs the traditional z value concept. However, the following analysis is not restricted to the assumptions associated with the TDT approach (eg, first order destruction kinetics) with regard to the F value calculation through physical–mathematical procedures. The F value concept, arriving from the definition of equivalent processes, is valid for reactions of any order and for different models used to express the temperature dependency of the reaction rate constant. The appropriate integral expression for F

value calculations for thermal destruction phenomena following *n*th order kinetics, and using the Arrhenius model instead of the *z* value model for temperature dependency is given by Hendrickx and coworkers (1995).

Equation (1) refers equally to the substance of interest as well as to the TTI attribute, the possible difference being the magnitude of the parameter involved (ie, the *z* value) as well as the response function $f(X_a, X)$.

The last part of equation (1) allows calculation of the *F* value of a process by measuring the response, *X*, of a heat-induced change at the beginning and at the end of the process. The response *X* can be the spore concentration (*in situ* method) or any other appropriate variable (TTI method). The general form of the response function, $f(X_a, X)$, must be such that, for responses under constant processing temperatures, it can be written in the form of

$$f(X_a, X) = k_T t \quad (2)$$

or preferably, in the form of

$$f(X_a, X) = g(X_a) - g(X) = k_T t \quad (3)$$

explicitly indicating that the response function is the result of an integration over a finite interval. Such response functions could include the first order reduction of enzyme activity in an enzymatic TTI, that is,

$$f(X_a, X) = \ln(C_a) - \ln(C) \quad (4)$$

or the response function of 3M Monitor Mark®, a commercial TTI used for self life monitoring (Taoukis and Labuza, 1989) given by

$$f(X_a, X) = X^2 \quad (5)$$

where *X* is the distance covered by a dyed fatty acid ester diffusing along a porous wick at a time–temperature dependent rate (note that $X_a = 0$). A 'thermal processing' TTI based on the same diffusion principle was commercialized by 3M Company in the late 1980s for microwave heated foods (Monitor Mark® microwave doneness indicator, Anonymous, 1987).

Alternatively, knowing the temperature experienced by a substance during a given process, one can calculate the *F* value of the process for the substance, characterized by a particular *z* value, by performing the integration in the first part of equation (1), (physical–mathematical method). As stated earlier, a similar equation, employing the activation energy, instead the *z* value concept, can be used. Ideally (for error free experimental data), in view of equation (1), all procedures (ie, the *in situ*, the TTI, and the physical–mathematical methods) should produce the same result. Therefore, from the response of a fully characterized single-component TTI (ie, the response function and the kinetic parameters of the TTI are available) one can evaluate the *F* value of the process for any substance characterized by the same, as the TTI, *z* value, provided that both the TTI and the substance of interest have undergone through the same time–temperature exposure.

METHODOLOGY

The proposed procedure was based on the hypothesis that for relative small differences between the *z* value of the heat labile substance of interest and the *z* value of the TTI, the difference in the *F* values for the substance of interest and the TTI, ΔF, is proportional to the correspondent difference of the *z* values, Δz. Taking into account that $\Delta F = 0$ when $\Delta z = 0$, we have

$$\Delta F = \alpha \Delta z \quad (6)$$

The parameter α in equation (6) can be determined from two *F* values (F_1 and F_2) calculated from the responses of two TTIs (or from a double response TTI system) each one of them characterized by different *z* value (z_1 and z_2) as $\alpha = (F_2 - F_1)/(z_2 - z_1)$. Having thus calculated the parameter α, for a given thermal treatment, then, by using the *F* value associated with the one *z* value (z_{base}) of the TTI and equation (6), one can calculate the *F* value for a target substance with a particular z_{target} value.

The limits and the validity of equation (6) can be examined through observations of the linearity of the *F v z* function. This was done graphically for selected cases (*Figure 1*).

Focusing our attention to the first part of equation (1), it becomes clear that the *F* value of a process is a function of the *z* value and the time–temperature profile experienced by the target substance, and the reference temperature used for calculating and reporting the results. One should expect all these parameters to influence our assumption about linearity associated with equation (6). Plots of *F v z* as a function of reference temperature, for selected temperature profiles, are shown on *Figure 1*. The *F* values were calculated through the integral presented in equation (1), after having specified a particular $T(t)$ curve, for a number of *z* values.

In *Figure 1*(a), a theoretical (based on the empirical formulas presented by Hayakawa, 1970) time–temperature profile for a conduction heating product, curve T_{1a} of *Figure 2*, was used. The maximum product temperature associated with this particular profile was $T_{max} = 115.50°C$, and the designed process gave an F_o value of 6.12 min. Several reference temperatures, above and below the maximum product temperature, were investigated, including the T_{ref} of 121.11°C (ie, of 250°F) traditionally used in the thermal process literature and practice. Based on *Figure 1*(a), some general observations can be made.

It becomes obvious that the use of a T_{ref} below the product maximum temperature attained during

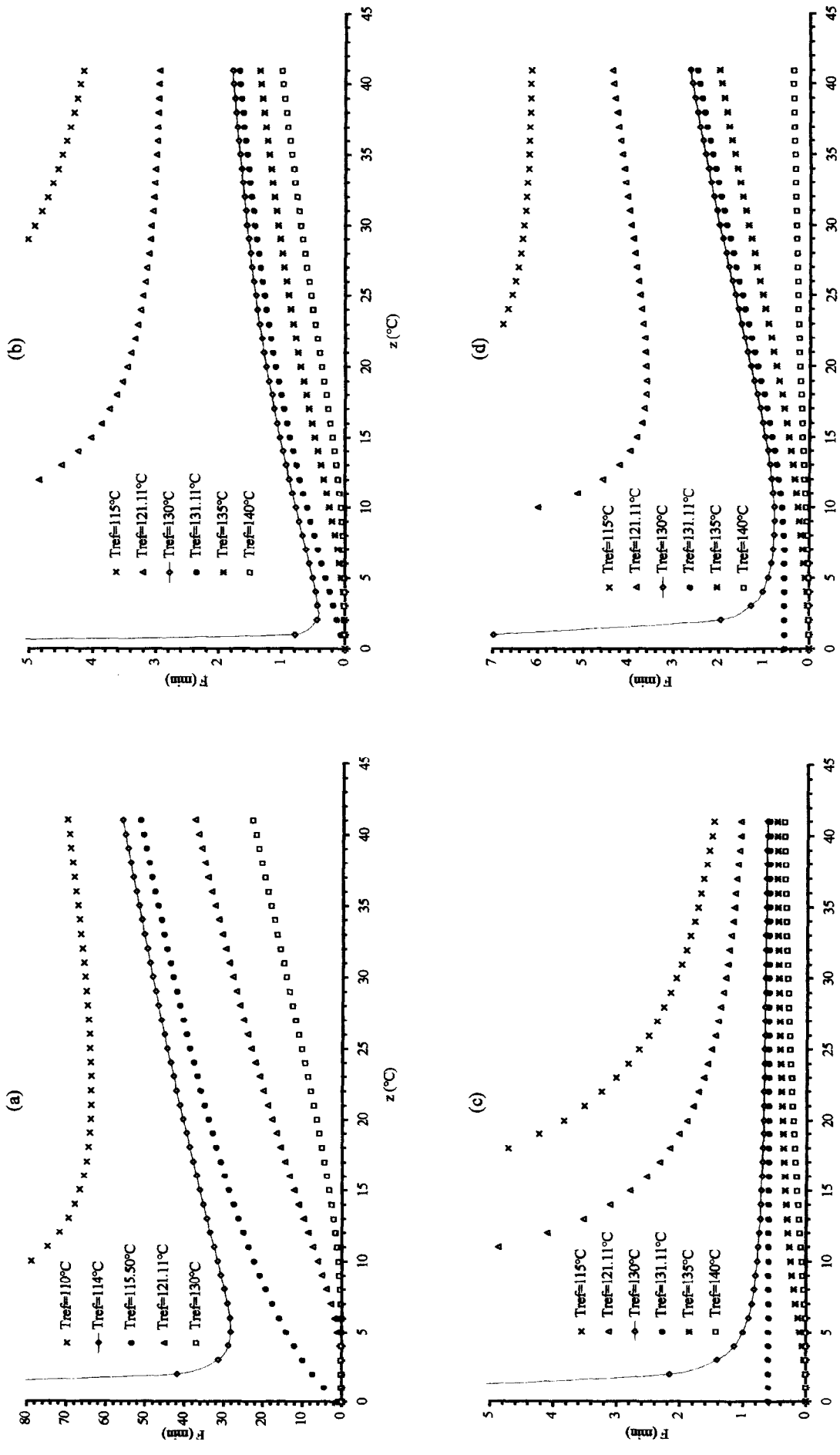

Figure 1 Effect of the reference temperature on the F v z relationship for selected product time–temperature profiles. (a) Theoretical time–temperature profile for a conduction heating product, curve T_{1a} of *Figure 2*; (b) linearly increasing temperature profile, curve T_7 of *Figure 2*; (c) constant temperature profile, curve T_6 of *Figure 2*; (d) step increasing temperature profile, curve T_5 of *Figure 2*.

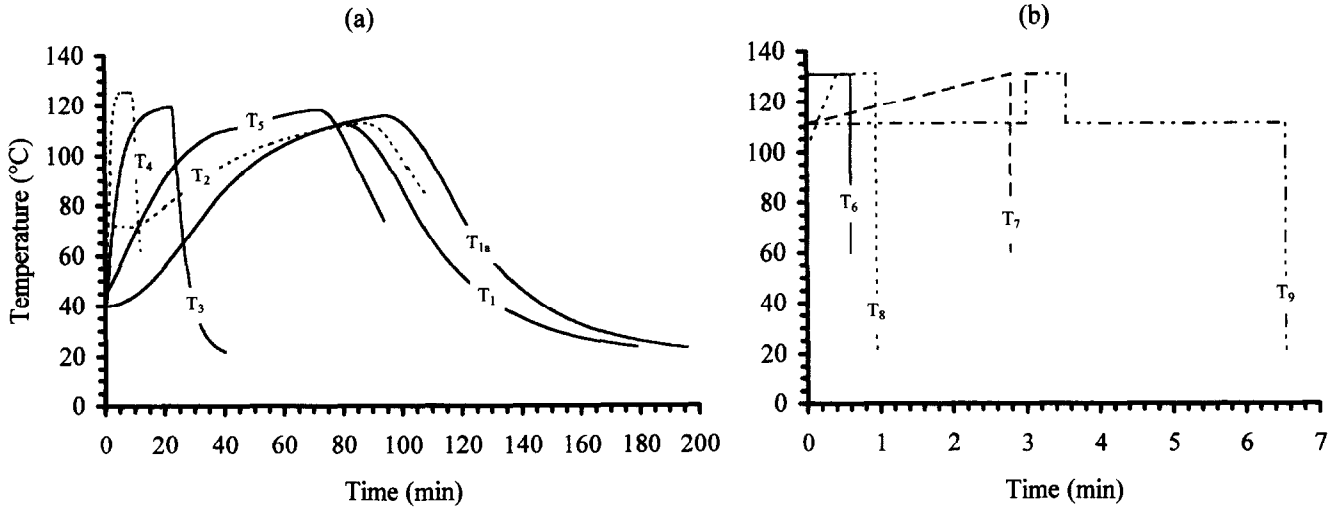

Figure 2 Product temperature curves studied. (a) Typical temperature profiles for conduction: T_1 and T_{1a} (theoretical), T_2 (experimental), T_5 (experimental under process deviation, in terms of retort temperature, conditions), and convection: T_3 (theoretical), T_4 (experimental), heating products. (b) Challenging temperature profiles: T_6 (constant), T_7 (linearly increasing), T_8 (constant followed by linearly increasing), and T_9 (step).

processing, is not advisable when working in the low z value ranges. Thus, for example, for the particular temperature profile studied, the use of equation (6) with a $T_{ref} = 114°C$ and z values below 5°C can produce erroneous results. Further reduction in T_{ref} will limit the workable z range to higher values. So, the use of a $T_{ref} = 110°C$, will be valid only for z values higher than about 20°C. When a multiple response TTI system is used to assess product safety, then a z_{target} value of 10°C, a value referring to *Clostridium botulinum*, is usually used (Pflug and Odlaug, 1978) and one should be careful in using low reference temperatures. On the other hand, for product quality evaluation (z values in the higher range of 25–45°C, Lund, 1977) one can be more flexible in selecting an appropriate reference temperature.

Additionally, when working with T_{ref} values higher than the maximum product temperature, a seemingly good linearity is achieved. However, it should be noticed that the F values associated with these T_{ref} values are low, and therefore, a small deviation from linearity of the F v z curve, can actually produce high relative errors. Similar observations were made when using different product temperature profiles. *Figures 1*(b)–*1*(d) illustrate the effect of reference temperature for three specific product temperature profiles, for which the application of multi-component TTIs was found (Maesmans *et al.*, 1993) to produce erroneous results. Specifically, *Figure 1*(b) uses a linearly increasing temperature profile, curve T_7 of *Figure 2* ($F_0 = 6$ min, $T_{max} = 131.11°C$), *Figure 1*(c) refers to a constant temperature profile, curve T_6 of *Figure 2* ($F_0 = 6$ min, $T_{max} = 131.11°C$ = constant), and *Figure 1*(d) employs a step increasing temperature profile from 111.11°C to 131.11°C, curve T_9 of *Figure 2* ($F_0 = 6$ min, $T_{max} = 131.11°C$) the contribution of the period that the product was at the 111.11°C temperature being the 10% of the total F_0 of the process. As expected, for the constant temperature profile case (*Figure 1*(c)) the use of a T_{ref} equal to the constant product temperature produces error-free results. Large deviations from this T_{ref} can lead to prediction errors especially in the low z range ($z < 10°C$). The use of the traditional reference temperature of 121.11°C with these profiles of high T_{max} (131.11°C), and with a z_{target} value of 10°C, is obviously inappropriate, according to the preceded analysis.

The effect of reference temperature in predicting F_0 values from different, double response TTI systems characterized by the indicated z_1 and z_2 values, for the particular T_{1a} temperature profile discussed earlier, is presented in *Table 1*. The results of the calculations are presented as the percent error, ie, $\%\text{error} = ((F_{exact} - F_{predicted})/F_{exact}) \times 100$. The exact F values, F_{exact}, were calculated through the integral presented in equation (1), while the predicted F values, $F_{predicted}$, were calculated as described earlier through equation (6) from a particular double response TTI system and for a z_{target} value of 10°C. The T_{ref} of 114°C gave the best results overall. Based on *Figure 1*(a) and the discussion made so far, this was the expected result since this T_{ref} is close to the T_{max} of 115.50°C, and the working z range (including the z_1 and z_2 of the TTI, and the z_{target} value) was high enough, ie, within the requirements of the T_{ref} of 114°C (in most cases greater than 5°C). Furthermore, it should be mentioned here that the contribution of the time period that the product was above 114°C to the F_0 value of the total process was only 16.6%.

From the above discussion, we can conclude that the selection of the reference temperature is very important. In general, one should choose a T_{ref} close to the maximum temperature attained by the product. However, for the cases where the use of TTIs is more justifiable, data for the product temperature history are not available. Nevertheless, an educated guess should be made having the processing temperature as the basis to start. Discrepancies from the expected F

values observed by Maesmans *et al.* (1993) are totally attributed to the inappropriate reference temperature employed for the calculations.

For the cases for which the approximation given by equation (6) is not considered adequate, the predictions for F values can be improved by including higher order terms in equation (6). For example, by including a second order term, we obtain

$$\Delta F = \alpha\Delta z + \beta(\Delta z)^2 \quad (7)$$

Equation (7) needs a triple response TTI (in order for the parameters α and β to be determined). Obviously, F value predictions can be further improved by including even higher order terms in equation (7). However, this would require multiple TTI systems of at least quadruple response, thus possibly limiting the practical application of TTIs. As an alternative, one could use a different correlation function between F and z. Limiting our analysis to triple response TTIs, and based on preliminary results (where various relations of different combinations of F, $1/F$ and $\ln F$ *v* z and $1/z$ were tested) the following function was further investigated

Table 1 Percent error in predicting F_0 values from different, double response TTI systems (characterised by the z_1 and z_2 values) for the T_{1a} temperature profile of *Figure 2*. Effect of reference temperature. (Dark and light grey areas indicate the cells, for each TTI, with the least and the second least percent error)

z_1	z_2 (z_{base})	Reference Temperature					
(°C)	(°C)	110°C	114°C	115.50°C	121.11°C	125°C	130°C
4	6	326.0	11.7	-6.4	24.8	54.1	77.5
4	8	103.1	3.9	-2.8	9.8	25.8	43.8
4	34	-207.4	-5.3	15.3	-9.0	-94.9	-336.0
4	41	-218.6	-5.2	17.2	-5.7	-96.9	-366.3
5	12	-29.0	-1.1	1.9	-4.3	-17.3	-40.3
5	15	-54.5	-2.0	4.1	-7.4	-36.6	-96.4
5	20	-76.8	-2.3	7.1	-8.3	-56.1	-170.7
5	30	-96.4	-2.1	10.9	-4.8	-70.8	-257.4
6	8	28.8	1.3	-1.7	4.8	16.3	32.5
6	14	-26.2	-0.9	2.6	-4.2	-23.4	-63.7
6	38	-56.7	-0.3	9.8	2.2	-52.5	-228.9
8	12	-4.8	-0.1	0.6	-0.9	-5.8	-16.6
8	15	-9.0	-0.2	1.4	-1.2	-11.9	-38.5
8	38	-16.8	0.4	4.4	3.4	-20.4	-106.9
9	11	-1.1	0.0	0.2	-0.2	-1.4	-4.2
12	15	4.9	-0.1	-1.2	0.0	8.5	34.6
15	20	12.4	-0.8	-4.6	-4.7	21.8	126.2
15	25	14.2	-1.3	-6.1	-8.4	22.1	155.1
15	30	15.3	-1.7	-7.2	-11.8	20.3	171.9
20	25	19.6	-2.7	-10.4	-19.5	23.0	242.0
20	30	21.0	-3.4	-12.2	-26.0	17.2	263.3
26	34	25.4	-5.6	-18.0	-47.9	-6.1	315.6
26	41	26.6	-6.5	-20.1	-57.4	-21.1	312.5
34	41	29.1	-8.3	-24.6	-78.5	-54.4	305.6

$$\frac{1}{F - F_{base}} = \frac{\alpha}{\frac{1}{z} - \frac{1}{z_{base}}} + \beta \quad (8)$$

The base F_{base} and z_{base} values appearing in equation (8) simply refer to one of the components of a triple response TTI taken as the basis for the subsequent calculations. The F and z values in equation (8) are either the F_1 or F_2 and the z_1 or z_2 values of the other two left components of the TTI when equation (8) is used for estimation of the parameters α and β, or the F_{target} and the z_{target} values when equation (8) is used for predicting the process F value for a particular target substance.

Based on the preceding analysis, the use of double or triple response TTI systems was evaluated. A number of TTIs, with z values ranging from 4°C to 41°C was examined. Note that single response TTIs with z values from 7.8°C to 26°C have been reported in the literature (Van Loey, 1996). Concerning the product time–temperature profiles studied, this included experimental curves (Stoforos, 1995; Stoforos *et al.*, 1997b) as well as theoretical predictions (based on the empirical formulas presented by Hayakawa, 1970) for both conduction and convection heating foods. For the theoretical profiles, processing times have been so chosen, such as process F values of approximately 2 min, 6 min, and 10 min were achieved. In *Figure 2*(a), selected theoretical (curves T_1, $F_0 = 2.36$ min, and T_{1a}, $F_0 = 6.12$ min) and experimental (curve T_2, $F_0 = 3.43$ min) product temperature profiles for conduction heating products used in the subsequent Results and Discussion section, are presented. An experimental temperature profile for a conduction heating product under process deviation, in terms of retort temperature, conditions is also included in *Figure 2*(a) (curve T_5, $F_0 = 10.88$ min). Furthermore, *Figure 2*(a) shows some of the theoretical (curve T_3, $F_0 = 6.02$ min) and the experimental (curve T_4, $F_0 = 15.70$ min) product temperature profiles for convection heating products used in the analysis. The proposed procedure was also tested under several specific product temperature profiles, likely to challenge the procedure. A selection of such profiles (all with $F_0 = 6.00$ min) for constant (curve T_6), linearly increasing (curve T_7), constant followed by linearly increasing (curve T_8), and step increasing (curve T_9) product temperatures, is presented in *Figure 2*(b).

The exact F values, corresponding to each temperature profile, were calculated through the integral presented in equation (1), for the particular z values of the double or triple response TTI system under investigation, and for a z_{target} value of 10°C. The so calculated F values of the TTI system, were used, through equation (6) equation (7), or equation (8), to predict the F value for a z_{target} value of 10°C. Results are reported as the percent deviation of the predicted, as it compares with the exact F values for

a z_{target} value of 10°C, that is, as %error = $((F_{exact} - F_{predicted})/F_{exact}) \times 100$. The calculations were occasionally repeated for different T_{ref} values.

RESULTS AND DISCUSSION

The results presented below are restricted to the product temperature profiles illustrated on *Figure 2*, and the TTI systems appearing on *Tables 2* and *3*. Nevertheless, similar results were obtained for all additional temperature profiles and TTI systems examined.

As discussed thoroughly earlier, the selection of the reference temperature for performing the calculations involved, is critical. This is illustrated on *Table 2* for the T_1 and the T_6 temperature profiles. In general, of the two reference temperatures shown, the lower one gave better results (*Table 2*). We should mention here that the results presented in *Tables 2* and *3*, are not necessarily the best ones as far as the selection of T_{ref} is concerned. Nevertheless, the T_{ref} values used in obtaining the results presented in *Tables 2* and *3* were logical values based on our knowledge about the thermal processes the product time–temperature profiles were coming from. Indicatively, we cite the retort temperature (at its maximum value) and the maximum product temperature attained for the T_1–T_9 profiles used: for T_1, $T_{RT} = 120$°C and $T_{max} = 112.4$°C; for T_2, $T_{RT} = 115.8$°C and $T_{max} = 112.4$°C; for T_3,

Table 2 Percent error in predicting F_0 values from different, double response TTI systems (characterised by the z_1 and z_2 values) for the temperature profiles, T_1–T_9 of *Figure 2*, studied. (Numbers in parentheses refer to T_{ref} (in °C) used in the calculations)

z_1 (°C)	z_2 (°C)	T_1 (121.1)	T_1 (116.7)	T_2 (116.7)	T_3 (121.1)	T_4 (126.1)	T_5 (121.1)	T_6 (135.0)	T_6 (132.0)	T_7 (135.0)	T_8 (135.0)	T_9 (135.0)
9	11	−1.2	0.0	0.1	0.3	0.2	0.2	0.5	0.2	−0.3	0.4	−0.5
7	13	−10.9	−0.3	0.3	2.9	1.6	1.5	4.5	1.8	−2.4	3.7	−4.3
5	15	−31.1	−2.0	−0.2	8.2	5.1	3.5	12.2	5.7	−7.7	9.9	−10.3
11	12	1.9	−0.1	−0.2	−0.5	−0.3	−0.4	−0.9	−0.3	0.3	−0.7	1.3
14	16	12.7	−2.6	−3.5	−4.9	−2.2	−4.8	−7.7	−2.1	−0.7	−6.6	16.0
8	9	3.0	0.2	0.0	−0.7	−0.4	−0.3	−1.1	−0.5	0.8	−0.9	0.7
4	6	49.4	14.0	11.4	−11.9	−11.5	3.0	−12.9	−14.6	21.1	−9.5	−2.4
5	20	−47.3	−0.6	2.3	13.7	8.0	7.8	20.6	8.7	−8.6	17.1	−23.6
5	30	−59.8	3.8	8.7	20.7	11.3	15.4	31.0	11.9	−2.9	26.4	−40.4
15	20	17.5	−6.1	−7.7	−8.5	−3.7	−9.4	−13.1	−3.3	−5.0	−11.5	29.6

Table 3 Percent error in predicting F_0 values from different, double or triple response TTI systems (characterised by the z_1, z_2 and z_{base} values) for the temperature profiles, T_1–T_9 of *Figure 2*, studied. Comparison of the various models (Eqs. (6)–(8)) used. (Numbers in parentheses refer to T_{ref} (in °C) used in the calculations)

z_1 (°C)	z_2 (°C)	z_{base} (°C)	T_1 (116.7)	T_2 (116.7)	T_3 (121.1)	T_4 (126.1)	T_5 (121.1)	T_6 (135.0)	T_7 (135.0)	T_8 (135.0)	T_9 (135.0)	Model
5	12	15	−1.2	−1.0	0.1	0.2	−0.5	−0.3	−2.1	−0.1	1.1	Eq. (8)
5	12	15	−1.2	−1.0	0.7	0.7	−0.4	0.9	−2.0	0.6	1.9	Eq. (7)
	12	15	−0.9	−1.3	−2.3	−1.1	−2.0	−3.6	0.3	−3.1	6.7	Eq. (6)
5	12		−1.5	−0.7	3.7	2.4	1.1	5.4	−4.2	4.4	−3.0	Eq. (6)
5		15	−2.0	−0.2	8.2	5.1	3.5	12.2	−7.7	9.9	−10.3	Eq. (6)
8	12	15	−0.3	−0.3	0.1	0.1	−0.1	−0.1	−0.7	0.0	0.0	Eq. (8)
8	12	15	−0.3	−0.2	0.2	0.2	−0.1	0.4	−0.6	0.3	0.5	Eq. (7)
8	12		−0.1	0.2	1.3	0.7	0.7	2.0	−1.0	1.6	−2.0	Eq. (6)
	12	15	−0.9	−1.3	−2.3	−1.1	−2.0	−3.6	0.3	−3.1	6.7	Eq. (6)
8		15	0.3	0.9	2.8	1.5	1.9	4.4	−1.6	3.7	−5.7	Eq. (6)
5	20	30	−5.6	−5.4	2.2	2.0	−2.4	−1.9	−15.1	0.8	−11.5	Eq. (8)
5	20	30	−5.0	−4.0	6.7	4.7	0.1	10.2	−14.3	7.7	−6.9	Eq. (7)
5	20		−0.6	2.3	13.7	8.0	7.8	20.6	−8.6	17.1	−23.6	Eq. (6)
	20	30	−22.8	−29.5	−21.3	−8.4	−30.3	−31.3	−37.1	−29.7	60.3	Eq. (6)
5		30	3.8	8.7	20.7	11.3	15.4	31.0	−2.9	26.4	−40.4	Eq. (6)
15	20	30	0.5	1.5	−1.9	−1.2	0.1	0.7	9.1	−1.3	20.9	Eq. (8)
15	20	30	−0.5	−0.5	−4.2	−2.1	−2.5	−7.0	5.7	−5.4	19.3	Eq. (7)
15	20		−6.1	−7.7	−8.5	−3.7	−9.4	−13.1	−5.0	−11.5	29.6	Eq. (6)
	20	30	−22.8	−29.5	−21.3	−8.4	−30.3	−31.3	−37.1	−29.7	60.3	Eq. (6)
15		30	−11.6	−15.0	−12.8	−5.3	−16.4	−19.2	−15.7	−17.6	39.8	Eq. (6)
6	8	38	2.4	2.1	−0.5	−0.5	1.1	0.7	4.6	0.0	−0.6	Eq. (8)
6	8	38	2.4	2.0	−1.9	−1.6	0.6	−2.7	4.6	−2.0	−1.7	Eq. (7)
6	8		2.0	1.2	−3.4	−2.4	−0.6	−4.8	4.6	−3.8	0.8	Eq. (6)
	8	38	4.9	7.2	8.2	3.8	8.7	12.5	5.1	11.2	−19.5	Eq. (6)
6		38	7.5	12.5	18.3	9.2	16.8	27.7	5.6	24.3	−37.3	Eq. (6)
8	6	4	−6.5	−5.6	−0.1	0.3	−2.6	−1.6	−9.2	−1.4	2.3	Eq. (8)
8	6	4	−4.0	−3.9	0.9	2.2	−2.4	−0.8	−3.7	−1.0	2.5	Eq. (7)
8	6		2.0	1.2	−3.4	−2.4	−0.6	−4.8	4.6	−3.8	0.8	Eq. (6)
	6	4	14.0	11.4	−11.9	−11.5	3.0	−12.9	21.1	−9.5	−2.4	Eq. (6)
8		4	5.0	3.8	−5.5	−4.6	0.3	−6.9	8.7	−5.3	0.0	Eq. (6)

T_{RT} = 120°C and T_{max} = 119.5°C; for T_4, T_{RT} = 125.6°C and T_{max} = 125.6°C; for T_5, T_{RT} = 122.5°C and T_{max} = 118.2°C; for T_6–T_9, T_{max} = 131.1°C.

In the remaining of the text, reference to a double response TTI characterized by z_1 and z_2, or to a triple response TTI characterized by z_1, z_2, and z_3, and used for F value predictions of a substance with z_{target} value, will be made as $(z_1-z_2-(z_{target}))$ or $(z_1-z_2-z_3-(z_{target}))$, respectively. The z values will be presented in an ascending order, while the z_{target} value will be placed in parenthesis. So, for example, a double TTI with z_1 = 9°C and z_2 = 11°C, used for F value predictions of a substance with a z_{target} = 10°C, will be referred to as TTI (9–(10)–11).

The range of the z values employed, including the z values of the TTI as well as the target z value, affected directly the accuracy of the predictions. As expected, smaller z range resulted in smaller percent error (*Table 2*) all other parameters being equivalent. Thus, the error in using the (9–(10)–11) TTI was smaller than that of the (7–(10)–13) TTI, and the latter smaller than that of the (5–(10)–15) TTI (*Table 2*). The same was observed by comparing TTIs (8–9–(10)) and (4–6–(10)), TTIs ((10)–11–12) and ((10)–14–16), or TTIs (5–(10)–20) and (5–(10)–30) of *Table 2*.

For the same spread of the z values employed, interpolation (z_{target} being between the z values of the TTI) gave better results than extrapolation (z_{target} being outside the z range of the TTI). This can be seen by comparing the results of TTIs (7–(10)–13), ((10)–14–16), and (4–6–(10)), or TTIs (5–(10)–15) and ((10)–15–20) of *Table 2*. In general combinations of the form $((z_{target})-z_1-z_2)$ gave better results than $(z_1-z_2-(z_{target}))$ type TTIs (eg, compare TTIs ((10)–11–12) and (8–9–(10)), and TTIs ((10)–14–16) and (4–6–(10)), *Table 2*). That is, when extrapolating, it was better to have TTIs with z values higher than the z_{target} value. This fact might be of practical significance, given that a variety of biological and chemical TTIs with z values larger than 10°C exists (Van Loey, 1996).

For TTIs characterized by different z value spread, general conclusions could not be made. The superiority of one or the other TTI was related to the particular product temperature profile examined. Thus, for example, the TTI (5–(10)–20) with wider z spread compared with TTI ((10)–15–20), but with the z_{target} value included between its z values, gave better predictions for the T_1, T_2, T_5, and T_9, but worse for the T_3, T_4, T_6, T_7, and T_8 profiles (*Table 2*).

In most cases, triple response TTIs performed better compared with double response TTIs. Here, we refer not only to cases were the added third z value of the triple TTI was between the two z values of the double TTI, but also to cases where the additional z value was outside the range of the original z values (*Table 3*). Finally, for triple response TTIs, equation (8) gave comparable results with equation (7), the most noticeable point being the better performance of equation (8) for the constant temperature profile T_6 (*Table 3*).

In general, the results were considered satisfactory, in view of the expected error in determining the required F value of a thermal process in order to achieve commercial sterilisation of low-acid foods (of the order of 20%, Pflug, 1987) and the experimental error associated with using single response TTIs (for example, over 15% for chemical TTIs, Williams and Adams, 1997).

Ending this section, we should mention that in the preceding analysis and the results shown, a z_{target} value of 10°C was employed. However, the methodology can be also used with different z_{target} values that refer not only to safety, but also to product quality.

CONCLUSION

The proposed procedure in using multiple response TTI systems to evaluate the impact of a thermal process on a particular target heat labile substance, produced satisfactory results and can serve as an alternative for the cases where a single-component TTI with a particular z value is not available. Important parameters to be considered in using a multi-component TTI, for each particular case, include the z values of the TTI, in relation to the target z value, as well as the reference temperature used for the calculations.

In selecting a multi-component TTI one should bear in mind that smaller z ranges (including the z values of the TTI as well as the target z value) give better results and that, if possible, the z_{target} value should lie between the z values of the TTI. If the latter is not attainable, it is better to have TTIs with z values higher than the z_{target} value, in a way such that the z range is shifted towards higher z values, where the T_{ref} can be more freely chosen. As far as the selection of the reference temperature is concerned, one should choose a T_{ref} close to the maximum temperature attained by the product, based on knowledge of the processing conditions and the product characteristics.

In general, triple response TTIs performed better compared with double response TTIs. Nevertheless, the results of double response TTIs were also satisfactory, as long as the above stated rules were followed. The cost of TTI, together with the desired accuracy, should be considered when selecting the TTI system to be used in a particular application.

The proposed methodology can be also used with different z_{target} values that refer not only to safety, but also to product quality, and for different (than thermal) processes (eg, shelf life monitoring). Due to the higher z values involved in such cases, differences between predicted and actual data are expected to be minimal.

The preceded analysis was based on a large number of time–temperature curves. Further theo-

retical analysis might provide more specific, exact, guidelines concerning the selection of the appropriate z range and the reference temperature to be employed. Finally, we should indicate that the error involved in experimental measurements of process F values, using single response TTI must be taken in account, in an error analysis, when using multi-component TTI.

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