THE EFFECT OF INTERNAL THERMAL GRADIENTS ON THE RELIABILITY OF SURFACE MOUNTED FULL-HISTORY TIME-TEMPERATURE INDICATORS

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ABSTRACT

A simple analytical expression aimed at assessing the theoretical reliability of a full-history time-temperature indicator placed on the surface of a food item as a predictor of the remaining shelf-life in the presence of heat transfer limitations within the food is obtained. Such expression, which depends on three dimensionless parameters only, can be written as a univariate function of a single parameter containing the thermal properties of the food via a suitable algebraic scaling. The derivation of the relevant formulae is based on the integration of a generic quality function across the slab-shaped food item under the assumption that the temperature on the surface of the food undergoes a sinusoidal variation with time. The analysis reported is useful because it provides a quick estimate of the effect of the thermal diffusivity of the food on the relative error associated with the use of a TTI when the activation energies of the food and the indicator are matched (as should happen in the idealistic case) under realistic environmental conditions of storage.

INTRODUCTION

It is generally agreed that the most important environmental parameter leading to quality changes during refrigerated and frozen food handling is the cumulative effect of storage time and temperature (Van Arsdel *et al*. 1969; Jul 1984; Labuza 1982). In order to assess the degree of quality loss of perishable foods, full-history time-temperature indicators (TTI's) have been developed; reviews by Schoen and Byrne (1972) and Kramer and Farquhar (1976) provided comprehensive information on patented and commercially available indicators able to monitor variations in temperature with time. These indicators are physicochemical systems which exhibit an easily monitored irreversible change in a physical property in response to the combined cumulative effect of time and temperature (Wells and Singh 1988b). The TTI's must be small, inexpensive, and easily attachable to the surface of the food or its package (Taoukis and Labuza 1989a). The usefulness of TTI's as tools for the detection of food quality changes during storage has been emphasized by Mistry and Kosikowski (1983) and Singh and Wells (1985). The information provided by TTI's on the amount of food quality left can be used to improve and tightly control the food distribution, to optimize the food product rotation at the retail level, and to replace and/or complement the open date labeling at the consumer point (Taoukis and Labuza 1989a). Confined systems undergoing a temperature-sensitive, irreversible chemical reaction or a diffusionally-controlled transformation are particularly adequate for monitoring the extent of deterioration and remaining shelf life of a food product provided that they mimick the kinetic behavior of the food quality loss in terms of similar activation energies (Taoukis and Labuza 1989a).

The use of TTI's as food quality monitors has a potentially important application in the area of perishable inventory management (Wells and Singh 1988a). Usually food items are stored in large refrigerated chambers with forced air circulation or kept in small refrigerators at home. The temperature control that has been traditionally employed in either type of storage system is an on-off thermostat triggered by a signal generated by a thermocouple. This thermostat acts as a switch in the circuit of the compression/expansion refrigeration cycle; it switches on the electric current for the compressor when the air temperature rises above a given value, and opens the circuit when the temperature falls below another, but lower, given value (Webb 1964). Such a behavior generates a measurable dead band between the set point and the two extreme states (also known as lockup or differential gap), which, although often due primarily to limitations in sensitivity of the temperature probe, avoids needless chattering of the output manipulated variable caused by noise on the temperature input signal (Shinskey 1988). Hence, on-off controllers allow the temperature to cycle in a sinusoidal fashion with an amplitude equal to the dead band and a period which is a direct function of the time constant associated with the whole controlled temperature room or refrigerator (Shinskey 1988). Despite these limitations, the on-off controller is of extremely wide application because it offers a number of advantages over alternative device controllers such as being relatively inexpensive, usually accurate and always very reliable, easily installed and adjusted, and prone to little or virtually no maintenance (Smith 1980). The most reasonable errors in food storage that are likely to occur on the long run are, therefore, those due to the aforementioned temperature fluctuations.

The effect of sinusoidal oscillations on the performance of TTI's has been the subject of a number of studies (Riboh and Labuza 1982; Chen *et al*. 1983; Labuza and Bergquist 1983; Taoukis and Labuza 1989b). In most of these studies, however, heat transfer limitations within the food itself were not taken into account. Since the TTI placed on the top a food item will respond only to the temperature fluctuations at the top of said food item, large errors may result when the actual, overall degree of quality loss of the food is compared with its counterpart as predicted from the response of the indicator. The problem then arises as how to estimate the error involved in the common use of TTI's when the thermal inertia of the food plays a role in the temperature profile within the boundaries of the food.

It is the purpose of this paper to present the basis of a mathematical procedure that may lead to a systematic assessment of the accuracy of a TTI as a predictor of the degree of food quality loss as a function of the thermal properties of the food material and the environmental conditions of storage.

MATHEMATICAL METHODS

Loss of shelf-life in a food product is usually evaluated by the measurement of a characteristic quality parameter, which can consist of a physical, chemical, microbiological, or sensory index. The change with time, t, of a quality parameter, Y, of a food item can be usually expressed as (Taoukis and Labuza 1989a)

$$-\frac{dY}{dt} = k_{o,F} \exp\left\{-\frac{E_{act,F}}{RT\{t\}}\right\} \Psi\{Y\} \tag{1}$$

whereas the change of a suitable property, X, of the indicator can equivalently be modelled as

$$-\frac{dX}{dt} = k_{o,I} \exp\left\{-\frac{E_{act,I}}{RT\{t\}}\right\} \Xi\{X\} \tag{2}$$

Here R is the universal gas constant, and Ψ and Ξ are known functions of Y and X, respectively, while $k_{o,I}$ and $k_{o,F}$ are the preexponential factors, and $E_{act,I}$ and $E_{act,F}$ the activation energies of the Arrhenius model associated with the indicator and the food, respectively.

Following the approach initially suggested by Taoukis and Labuza (1989a), the change of the quality function (or measurable property) during a known variable temperature exposure $T\{t,z=L\}$ at the surface of a slab-shaped food item can be calculated from Eq. (2) via

$$F\{X\{t,L\}\} = -\int_{X\{0,L\}}^{X\{t,L\}} \frac{d\varsigma}{\Xi\{\varsigma\}} = k_{o,I} \int_0^t \exp\left\{-\frac{E_{act,I}}{RT\{\xi,L\}}\right\} d\xi \tag{3}$$

for the indicator, and similarly from Eq. (1) via

$$f\{Y\{t,L\}\} = -\int_{Y\{0,L\}}^{Y\{t,L\}} \frac{d\varsigma}{\Psi\{\varsigma\}} = k_{o,F}\int_0^t \exp\left\{-\frac{E_{act,F}}{R\,T\{\xi,L\}}\right\} d\xi \tag{4}$$

for the food if it were subject to exactly the same temperature history of the indicator. Here L denotes the half-thickness and z the spatial coordinate along the slab, whereas F is a function of X only and f is a function of Y only.

Defining an effective temperature, $T_{eff}\{L\}$, as the constant temperature at the surface of the food which, upon exposure to, for the same period of time, results in the same property change of a surface-mounted indicator as exposure to the variable temperature distribution, one may write

$$F\{X\{t, L\}\} = k_{o,I}\exp\left\{-\frac{E_{act,I}}{R\,T_{eff}\{L\}}\right\} t \tag{5}$$

If the surface of the food were exposed for the same period of time to the aforementioned constant temperature T_{eff}, then the approximate change in the quality parameter of the surface layer of food would be obtained from

$$f_{app}\{Y\{t,L\}\} = k_{o,F}\exp\left\{-\frac{E_{act,F}}{R\,T_{eff}\{L\}}\right\} t \tag{6}$$

The value of f_{app} will be equal to the value of f as obtained from Eq. (4) if and only if the activation energies of the food quality function and the indicator property are the same. According to the general philosophy underlying the use of TTI's, F (or a known function thereof) is measured, T_{eff} is computed employing Eq. (5), and f_{app} is calculated from Eq. (6); f_{app} is then used as an estimator of the true value of f. In order to isolate the effect of non-isothermal conditions throughout the food on the reliability of the TTI response, it will be assumed hereafter that $E_{act,I} = E_{act,F}$. Hence, Eq. (6) may be rewritten as

$$f\{Y\{t,L\}\} = k_{o,F}\exp\left\{-\frac{E_{act,F}}{R\,T_{eff}\{L\}}\right\} t \tag{7}$$

Rearrangement of Eq. (5) gives

$$T_{eff}\{L\} = \frac{E_{act,F}}{R\,\ln\left\{\dfrac{k_{o,I}\,t}{F\{X\{t,L\}\}}\right\}} \tag{8}$$

Combination of Eq. (7) and (8) yields

$$f\{Y\{t,L\}\} = \frac{k_{o,F}}{k_{o,I}} F\{X\{t,L\}\} \tag{9}$$

Assuming a variable temperature at the surface of the slab of the form

$$T\{t,L\} = T_m + a\{L\}\sin\left(\frac{2\pi t}{\tau}\right) \tag{10}$$

where T_m is the median temperature, a the amplitude, and τ the period of the sinusoidal fluctuation, Eq. (3) becomes (Taoukis and Labuza 1989b; Labuza 1984; Hicks 1944)

$$F\{X\{t,L\}\} = k_{o,I}\, t \exp\left\{-\frac{E_{act,F}}{R\,T_m}\right\} I_o\left\{\frac{a\{L\}\,E_{act,F}}{R\,T_m(a\{L\}+T_m)}\right\} \tag{11}$$

where I_o is a modified zero order Bessel function (Abramowitz and Stegun 1968). Upon use of Eq. (11) in Eq. (9), one gets

$$f_{pred}\{Y\{t\}\} = f\{Y\{t,L\}\} = k_{o,F}\, t \exp\left\{-\frac{E_{act,F}}{R\,T_m}\right\} I_o\left\{\frac{a\{L\}\,E_{act,F}}{R\,T_m(a\{L\}+T_m)}\right\} \tag{12}$$

where f_{pred} is the value of f to be expected if no resistance to heat transfer existed within the boundaries of the food. On the other hand, the actual quality function of the food, f_{true}, can be obtained by integrating the quality function over the whole volume of the food item (i.e., A.L, where A is the cross sectional area of the slab) according to

$$f_{true}\{Y\{t\}\} = \frac{A\displaystyle\int_0^L k_{o,F}\int_0^t \exp\left\{-\frac{E_{act,F}}{R\,T\{\xi,\varsigma\}}\right\} d\xi\, d\varsigma}{A\displaystyle\int_0^L d\varsigma} = \tag{13}$$

$$\frac{k_{o,F}\, t \exp\left\{-\frac{E_{act,F}}{R\,T_m}\right\}}{L}\int_0^L I_o\left\{\frac{A_r\{\varsigma\}\,a\{L\}\,E_{act,F}}{R\,T_m(A_r\{\varsigma\}\,a\{L\}+T_m)}\right\} d\varsigma$$

where advantage was taken from the symmetry of the slab and from the fact that the ultimate response of a linear system at a generic $0 < z < L$ to a sustained sinusoidal input at $z = L$ with amplitude $a\{L\}$ is a sine wave with the same frequency, and with an amplitude $a\{z\}$ equal to $A_r\{z\}a\{L\}$ (Stephanopoulos 1984).

Combining Eq. (12) and (13), one finally obtains an estimate of the relative error resulting from not taking heat transfer limitations into account, Er*, as given below

$$Er^* = \frac{f_{pred}\{Y\{t\}\} - f_{true}\{Y\{t\}\}}{k_{o,F}\, t \exp\left\{-\frac{E_{act,F}}{R\, T_m}\right\}} = I_o\left\{\frac{a^*\, E^*_{act,F}}{a^* + 1}\right\} - \int_0^1 I_o\left\{\frac{A_r\{\varsigma\}\, a^*\, E^*_{act,F}}{A_r\{\varsigma\}\, a^* + 1}\right\} d\varsigma \qquad (14)$$

where the dimensionless parameters are defined as follows

$$a^* = \frac{a\{L\}}{T_m} \qquad (15)$$

$$E_{act,F}{}^* = \frac{E_{act,F}}{R\, T_m} \qquad (16)$$

and

$$z^* = \frac{z}{L} \qquad (17)$$

The differential equation describing the one-dimensional unsteady heat conduction through a finite homogeneous layer reads

$$\frac{\partial T}{\partial t} = \frac{k}{\rho\, C_P}\frac{\partial^2 T}{\partial z^2} \qquad (18)$$

where k is the thermal conductivity, ρ is the mass density, and C_p is the isobaric specific heat capacity of the food material. The group $k/\rho C_p$ is usually known as thermal diffusivity, and will hereafter be denoted as α. Equation (18) is subject to the boundary condition.

$$@\, z = 0\ ,\ \forall_{t \geq 0}\ ,\ \frac{\partial T}{\partial z} = 0 \qquad (19)$$

and to the initial condition

$$@\, t = 0\ ,\ \forall_{0 \leq z \leq L}\ ,\ T = T_m \qquad (20)$$

Applying Laplace transforms with respect to time, $\mathcal{L}_t$, to Eq. (18)–(20), one gets (Stephenson 1973; Webb 1964)

$$G\{s\} = \frac{\mathcal{L}_t\{T\{t,z\}\}}{\mathcal{L}_t\{T\{t,L\}\}} = \frac{\cosh\left\{\sqrt{\frac{s\, L^2}{\alpha}}\, z^*\right\}}{\cosh\left\{\sqrt{\frac{s\, L^2}{\alpha}}\right\}} \qquad (21)$$

where s the independent complex variable in the Laplace domain and G{s} is the transfer function relating the behavior at a generic z to the behavior at z = L at any time t (Webb 1964). The values for A_r are simply given by the modulus of $G\{s=2\pi i/\tau\}$, where i is the imaginary unit. Recalling Eq. (21), one then obtains

$$G\left\{\frac{2\pi i}{\tau}\right\}=\frac{\cosh\left\{\sqrt{\pi\zeta}\,(1+i)\,z^*\right\}}{\cosh\left\{\sqrt{\pi\zeta}\,(1+i)\right\}} \tag{22}$$

where the dimensionless parameter ζ is defined by the following relationship

$$\zeta=\frac{L^2}{\alpha\,\tau} \tag{23}$$

Use of the mathematical properties of the hyperbolic functions with complex arguments in the above equation coupled with some algebraic work finally leads to

$$A_r\{z^*\}=\sqrt{\frac{\cosh^2\left\{\sqrt{\pi\zeta}\,z^*\right\}\cos^2\left\{\sqrt{\pi\zeta}\,z^*\right\}+\sinh^2\left\{\sqrt{\pi\zeta}\,z^*\right\}\sin^2\left\{\sqrt{\pi\zeta}\,z^*\right\}}{\cosh^2\left\{\sqrt{\pi\zeta}\right\}\cos^2\left\{\sqrt{\pi\zeta}\right\}+\sinh^2\left\{\sqrt{\pi\zeta}\right\}\sin^2\left\{\sqrt{\pi\zeta}\right\}}} \tag{24}$$

Equation (14) leads to results plotted in Fig. 1.i–iv as Er^* vs $E_{act,F}^*$ for a number of values of a^* and various orders of magnitude of ζ with physical interest. The integration was performed by an adaptative double precision FORTRAN routine using the Gauss 10-point and the Kronrod 21-point rules (Doncker 1978). The modified Bessel function of the first kind, $I_o\{\upsilon\}$, was approximated by $\exp\{\upsilon\}.\Sigma_{r=0,\infty}\, a_r.T_r\{\upsilon/2\text{-}1\}$, where T_r is a Chébyshev polynomial of the first kind (Abramowitz and Stegun 1968). For large ζ, $A_r\{z^*\}$ was approximated by the asymptotic expression $\exp\{-2(1-z^*)\surd(\pi.\zeta)\}$.

It is apparent from observation of the log-log plots denoted as Fig. 1.i–iv that the approximately straight lines in each plot are parallel to each other. Furthermore, the slope of these lines remains unchanged irrespective to the value of ζ. Therefore, the slope of $\log\{Er^*\}$ vs $\log\{E^*_{act,F}\}$ must be a constant, say β_1. On the other hand, each line of each plot can be obtained from the previous one by a translation along the vertical axis of a distance proportional to $\log\{a^*\}$. Hence, the vertical intercept of the lines follows a linear dependence on $\log\{a^*\}$ characterized by a vertical intercept $Z\{\zeta\}$ and a constant slope β_2. The above conclusions allow one to obtain the following empirical expression:

$$\log\{Er^*\}=\left(Z\{\zeta\}+\beta_2\log\{a^*\}\right)+\beta_1\log\left\{E^*_{act,F}\right\} \tag{25}$$

Using linear regression of the slopes of the lines in Fig.1.i-iv vs $\log\{E^*_{act,F}\}$ and linear regression of the intercepts of the same lines vs $\log\{a^*\}$, one found that

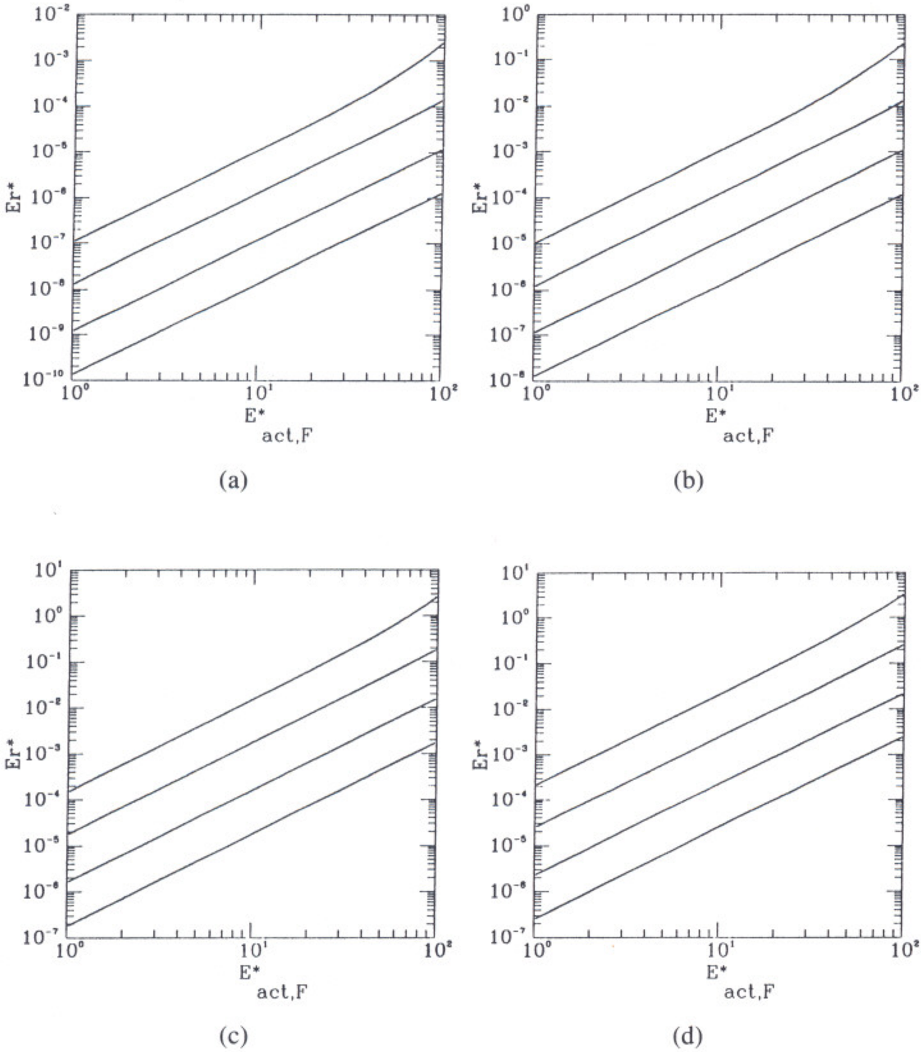

FIG. 1. LOGARITHMIC PLOT OF Er* AS A FUNCTION OF E_{act,F^*} FOR
(a) $\zeta = 10^{-2}$, (b) $\zeta = 10^{-1}$, (c) $\zeta = 10^{0}$, and (d) $\zeta = 10^{4}$.
From top to bottom: $a^* = 0.03$, $a^* = 0.01$, $a^* = 0.003$, and $a^* = 0.001$.

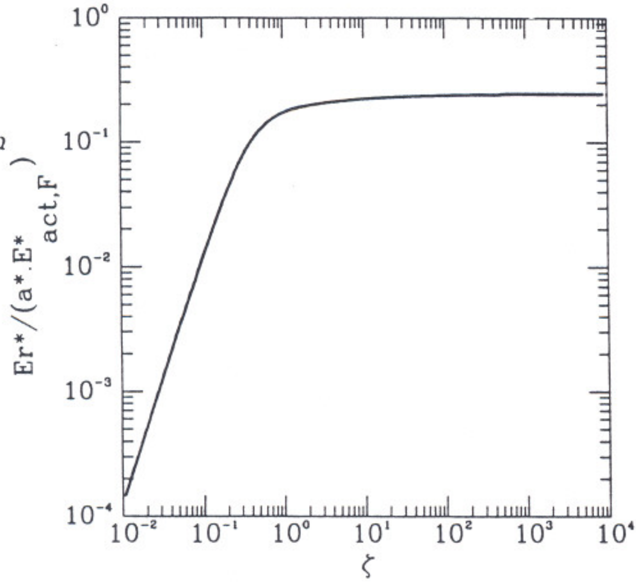

FIG. 2. LOGARITHMIC PLOT OF $Er^*/(a^*.E_{act,F^*})^2$ AS A FUNCTION OF ζ

both values of β_1 and β_2 were approximately equal to 2. Use of this finding in the above equation finally gives

$$\log\left\{\frac{Er^*}{a^{*2}\,.\,E^{*2}_{act,F}}\right\} = Z\{\zeta\} \tag{26}$$

The results of Eq. (26) are depicted in Fig. 2. Inspection of this figure leads one to the conclusion $Er^*/(a^*.E_{act,F}{}^*)^2$ becomes a very weak function of ζ at large ζ [i.e., $Er^*/(a^*.E_{act,F}{}^*)^2 \sim 0.230$]; for very small ζ, one finds that $Er^*/(a^*.E_{act,F}{}^*.\zeta)^2 \sim 1.20$. Taking advantage of these asymptotic behaviors, one can finally propose the following empirical overall relationship between Er^*, a^*, $E^*_{act,F}$, and ζ:

$$\frac{Er^*}{a^{*2}\,.\,E^{*2}_{act,F}} = \frac{0.230\,\zeta^2}{0.192 + \zeta^2} \tag{27}$$

The applicability of the foregoing analysis is emphasized in the practical situation described below.

NUMERICAL EXAMPLE

Consider the case of pasteurized homogenized milk to be stored at 5°C in a large refrigerated chamber as one-quarter, plastic coated paper cartons containerized in 140 cm wide pallet loads. The pallets are laid side by side in the horizontal direction, and top to bottom in the vertical direction so as to form long 140 cm wide independent piles. The refrigerated air contacts each of these piles on the largest two exposed vertical surfaces. The deadband of the temperature on-off controller is such that the temperature fluctuates with an amplitude of 5°C, whereas the regular usage of the chamber leads to a period of 10 min. The physical properties of the milk were obtained from Geankopolis (1983), whereas the activation energy for sensory changes arising from microbial activity in the milk was obtained from Labuza (1982). These flavor changes follow a first order kinetic decay pattern. Assuming that Y is the organoleptic score given to milk (initial score is arbitrarily set to 40, and milk becomes unacceptable after the score drops to 36), the value for the preexponential factor was obtained from a shelf-life vs. temperature plot (Labuza 1982). The shelf-life at the nominal storage temperature is 15 days (Labuza 1982).

The indicator selected was LifeLines™ Freshness Monitor, model 57 (from LifeLines Technologies, Morristown, NJ 07960) which is to be displayed at the outer, plastic-covered surfaces of the pallets directly exposed to the refrigerated air. The physicochemical behavior of this TTI consists on the polymerization of acetylenic molecules which lead to a change of the optical density of the material resulting in the darkening of the indicator (which can be measured with a reflectance probe). The estimated activation energy of this indicator was reported by Wells and Singh (1988a).

Using the above information, the relevant data for the analysis are as follows: $T_m = 278$ K, $L = 0.70$ m, $a(L) = 5$, $\tau = 600$ s, $\rho = 1.03 \times 10^3$ kg.m^{-3}, $C_P = 3.85 \times 10^3$ J.kg^{-1}.K^{-1}, $k = 0.538$ J.m^{-1}.s^{-1}.K^{-1}, $E_{act,F} = 9.12 \times 10^4$ J.mol^{-1}, $k_{o,F} = 1.36 \times 10^{10}$ s^{-1}, $\theta_s = 1.296 \times 10^6$ s, and $E_{act,I} = 8.91 \times 10^4$ J.mol^{-1}. Hence, $\alpha = 1.36 \times 10^{-7}$ m^2.s^{-1}. The dimensionless parameters of interest are found to be $\zeta = 6.02 \times 10^3$, $a^* = 0.0180$, and $E_{act,I}^* \sim E_{act,F}^* = 39.5$. Using Eq. (27), the foregoing value of ζ corresponds to $Er^*/(a^*.E_{act,F}^*)^2 = 0.230$, which in turn leads to $Er^* = 0.116$.

Recalling the definition of Er^* [see Eq. (14)] and the values of $k_{o,F}$ and $E_{act,F}^*$, one obtains that $f_{pred}\{Y\{\theta_s\}\}$-$f_{true}\{Y\{\theta_s\}\} = 0.0143$. Since the food decays according to a first order pattern, then at the end of the anticipated shelf-life $f_{pred}\{Y\{\theta_s\}\} = \ln\{Y\{O\}/Y_{pred}\{\theta_s\}\}$ and $f_{true}\{Y\{\theta_s\}\} = \ln\{Y\{O\}/Y_{true}\{\theta_s\}\}$. Therefore, one may write $\ln\{Y\{O\}/Y_{pred}\{\theta_s\}\}$-$\ln\{Y\{O\}/Y_{true}\{\theta_s\}\} = 0.0143$. On the other hand, the quality threshold corresponds to stating that $f_{true}\{Y\{\theta_s\}\} = \ln\{Y\{O\}/Y_{true}\{\theta_s\}\} = \ln\{40/36\} = 0.105$. Using this piece of information, one finds that the relative error involved in the use of the indicator is $[f_{pred}\{Y\{\theta_s\}\}$-$f_{true}\{Y\{\theta_s\}\}]/f_{true}\{Y\{\theta_s\}\} = 0.0143/0.105 = 13.6\%$, which means that the quality function of the food at the end of the anticipated shelf-life as calculated solely from information provided by the surface-mounted indicator is considerably larger than the actual value of the quality function. In other words, given the definition of the quality functions as explicit in Eq. (1)–(2), the food would become unacceptable for consumption later than would be predicted by the TTI.

DISCUSSION

The analysis reported above established the theoretical reliability of full-history, time temperature indicators placed on the top of a packaged food item (or on the top of a pile of containerized food items) as shelf-life monitors of the whole food material on the assumption that the classical models for the mechanism of heat transfer and temperature dependence of the food quality and indicator property apply. The food item was assumed to possess slab geometry; this requirement is met by some foods considered individually, and by most foods packed together in large pallets. Similar analyses can be developed for other types of geometry at the expense of more involved expressions for A_r. Furthermore, the pattern of the temperature change might not always be well described by a sine wave (with constant amplitude and period) as assumed. The main goal of the analysis was, however, to provide a quick estimate of the error arising from ignoring the effect of the thermal diffusivity of the food on the temperature profile inside the said food using a reasonable and common type of temperature fluctuation.

It should be emphasized here that the analysis was developed on the assumption that k is a very weak function of temperature (at least in the temperature range of interest) when compared with the corresponding dependence of the kinetic constant associated with the food deterioration (measured by the activation energy), which usually is a good approximation. Although the food may be in a liquid form, no forced convection is expected unless the packages are deliberately shaken in a vigorous way from the outside. On the other hand, although free convection may occur inside the liquid due to temperature gradients, this phenomenon is seldom important because the gradients are not usually large. Even in the worst case corresponding to non-negligible free convection, the equation describing heat transfer inside the fluid in the absence of end effects is of the same form as Eq. (18) (Bird *et al*. 1960), so the analysis reported remains valid in general. The indicator is to be placed on the outside of the packaging material, which has a thermal conductivity different from the food counterpart. However, the conductivities are often of the same order of magnitude (Bird *et al*. 1960), and the thickness of the packaging material is typically one to two orders of magnitude smaller than the thickness of the food material itself. Hence, the contribution of the packaging material to the overall resistance to heat transfer is negligible in most cases.

In the developed application scheme, there is an important underlying assumption; that the effective temperature of the food is equal to the effective temperature of the TTI for a given temperature distribution, which is true when the activation energies of the food and the TTI are equal (Taoukis and Labuza 1989b). Therefore, $E_{act,I}$ was taken as approximately equal to $E_{act,F}$ throughout the analysis, thus paralleling the correct choice of indicator. If the activation energies of the food quality and the indicator property differ by, say, 40 kJ.mol^{-1}, then for most types of temperature variation patterns on the surface of the food the error in quality estimation of the surface food layer will be of the order of 15% (Taoukis and Labuza 1989a). On the other hand, the average relative error in estimating the activation energies from experimental data is also ca. 10–20% (Taoukis and Labuza 1989a). Although a tag reliability of 15% is acceptable in most cases (Labuza and Kamman 1983), it should be noted that an extra 15% of error arising from heat transfer limitations within the food (as obtained in the numerical example) will start defeating the purpose of the TTI as an accurate monitor of food quality. Hence, special attention is to be paid to the error arising from small thermal diffusivities in the process of selection or design of a TTI for a given application.

It is interesting to note that although the error associated with ignoring heat resistance effects of the food material depends only on three dimensionless parameters (i.e., ζ, a^*, and $E_{act,F}^*$), these parameters can be further combined in a trivial way to yield a univariate, known dependence on ζ. Therefore, Fig. 2, or, equivalently, Eq. (27), becomes the most important tool in error estimation. Inspection of Fig. 2 leads one to the conclusion $Er^*/(a^*.E_{act,F}^*)^2$ becomes a very weak function of ζ for ζ larger than, say, 10; in this upper range the bulk of the food remains at T_m at virtually all times, whereas sinusoidal variations occur only at the vicinity of the surface. For $\zeta<0.1$, one finds that there is virtually no difference between the time-dependent temperature profile on the surface and at any other location within the food. Hence, the major effect of ζ on Er^* occurs at the intermediate range $0.1<\zeta<10$.

The relation denoted as Eq. (26) breaks down for a^* higher than, say, 0.03 and $E_{act,F}^*$ higher than, say, 100. In general, $10^{-1}<k<2.5\times10^{0}$ J.m^{-1}.s^{-1}.K^{-1} (Geankopolis 1983), $9\times10^{2}<\rho<1.1\times10^{3}$ kg.m^{-3} (Geankopolis 1983), $10^{3}<C_p<4.5\times10^{3}$ J.kg^{-1}.K^{-1} (Geankopolis 1983), $10^{-2}<L<10^{0}$ m, $10^{-1}<a<10^{1}$ K, $10^{2}<\tau<10^{4}$ s, $2.5\times10^{2}<T_m<3.0\times10^{2}$ K, and $2\times10^{3}<E_{act,F}<3.3\times10^{5}$ J.mol^{-1}(Taoukis and Labuza 1989a). These values provide working ranges for the dimensionless parameters approximately given by $3.6\times10^{-3}<\zeta<4.9\times10^{5}$, $3.3\times10^{-4}<a^*<4\times10^{-2}$, and $8\times10^{-1}<E_{act,F^*}<1.6\times10^{2}$. Therefore, for most practical applications the values of the dimensionless parameters do not fall above the aforementioned upper limits for $a^*$and E_{act,F^*}, and the simplified analysis keeps its validity.

The reported approach proves particularly useful for refrigerated or frozen foods (especially the emerging extended shelf life foods for which strict temperature control is critical) provided that the necessary kinetic data for the food and the indicator are available. In all cases the response of the TTI is faster than the loss of the quality of the food considered as a whole; hence the error in the prediction will lie on the conservative side. This underprediction of the residual shelf life may, however, be an economic concern since in cases of considerably large values of a^*, $E_{act,F}^*$, and ζ the TTI will signal the end of the food's shelf-life much earlier than it actually occurs.

It should be emphasized here that with respect to food quality, a number of reactions at the surface will cause rejection of the food and thus the knowledge of the interior temperature variation with time may not be necessary. This would be true for processes that require molecular oxygen to occur such as surface lipid oxidation, nonenzymatic browning, and mold growth. The analysis developed meets its full applicability for degradative reactions which tend to occur uniformly throughout the bulk of the food rather than preferentially at an interface. Examples of these type of reactions include lipase-catalyzed release of free fatty acids, protease-catalyzed breakdown of polypeptides, and growth of anaerobic bacteria.

The above analysis was aimed at developing a numerical method for the *a priori* assessment of the approximate magnitude of the error implicit in ignoring thermal gradients within the food when using surface-mounted TTI's. In order to completely establish reliability, real shelf life data will be required. Examples of these type of analyses have been reported by the Swedish Institute for Food Conservation (SIK) for pallet loads of frozen foods, with a moving freezing/thawing front for application to the I-POINT® tags (from I-Point Biotechnologies A. B., Reston, VA) in the early 1970's. On the other hand, further theoretical research on the effect of different container shapes on the reliability of surface mounted TTI's is warranted because the slab shape is currently limited mostly to dry foods (which very few companies are willing to put TTI's on) and frozen or refrigerated packages. The major features of the method reported are its (1) mechanistic background, (2) general applicability, and (3) numerical simplicity, all of which are likely to make it a useful tool for the food technologists.

NOMENCLATURE

Roman Symbols

a	= amplitude of absolute temperature sinusoidal variation (K)
A	= cross sectional area of slab (m)
a^*	= normalized amplitude of absolute temperature sinusoidal variation(--)

a_r = constant (--)
A_r = ratio of amplitude of sine wave at a generic location within the food to the amplitude counterpart at the surface of the food (--)
C_p = isobaric specific heat capacity of food ($J.kg^{-1}.K^{-1}$)
$E_{act,F}$ = activation energy for the food quality parameter ($J.mol^{-1}$)
$E_{act,I}$ = activation energy for the indicator parameter ($J.mol^{-1}$)
$E_{act,F*}$ = normalized activation energy for the food quality parameter (--)
$E_{act,I*}$ = normalized activation energy for the indicator parameter (--)
Er^* = normalized error of indicator prediction arising from assuming no heat transfer limitations within the food (--)
f = function of Y only ($mol.m^{-3}.s^{-1}$ for zero order, s^{-1} for first order, $m^3.mol^{-1}.s^{-1}$ for second order, etc.)
F = function of X only ($mol.m^{-3}.s^{-1}$ for zero order, s^{-1} for first order, $m^3.mol^{-1}.s^{-1}$ for second order, etc.)
f_{app} = predicted quality function of the food on the assumption that $E_{act,I} = E_{act,F}$ ($mol.m^{-3}.s^{-1}$ for zero order, s^{-1} for first order, $m^3.mol^{-1}.s^{-1}$ for second order, etc.)
f_{pred} = predicted quality function of the food in the absence of heat transfer limitations ($mol.m^{-3}.s^{-1}$ for zero order, s^{-1} for first order, $m^3.mol^{-1}.s^{-1}$ for second order, etc.)
f_{true} = true quality function of the food in the presence of heat transfer limitations ($mol.m^{-3}.s^{-1}$ for zero order, s^{-1} for first order, $m^3.mol^{-1}.s^{-1}$ for second order, etc.)
G = transfer function in the Laplace domain (--)
i = imaginary unit (--)
I_o = modified zero order Bessel function (--)
k = thermal conductivity of food ($J.m^{-1}s^{-1}.k^{-1}$)
$k_{o,F}$ = preexponential factor for the food quality parameter ($mol.m^{-3}.s^{-1}$ for zero order, s^{-1} for first order, $m^3.mol^{-1}.s^{-1}$ for second order, etc.)
$k_{o,I}$ = preexponential factor for the indicator parameter ($mol.m^{-3}.s^{-1}$ for zero order, s^{-1} for first order, $m^3.mol^{-1}.s^{-1}$ for second order, etc.)
L = half-thickness of the slab (m)
R = universal gas constant ($J.mol^{-1}.K^{-1}$)
s = complex, independent variable in the Laplace domain (s^{-1})
t = time elapsed after food product manufacturing (s)
T = absolute temperature (K)
T_{eff} = effective absolute temperature (K)
T_m = median of absolute temperature sinusoidal variation (K)
T_r = Chébishev polynomial of the first kind
X = suitable property of indicator ($mol.m^{-3}$)
Y = quality parameter of food ($mol.m^{-3}$)

Y_{pred} = predicted quality parameter of the food in the absence of heat transfer limitations ($mol.m^{-3}$)
z = spatial coordinate (m)
z^* = normalized spatial coordinate (--)

Greek symbols

α = thermal diffusivity ($m^2.s^{-1}$)
β_1, β_2 = constants (--)
θ_s = expected shelf life of food (s)
ρ = mass density of food ($kg.m^{-3}$)
τ = period of sinusoidal temperature fluctuation (s)
υ = dummy variable
ς = dummy variable of integration
ξ = dummy variable of integration
Ξ = function of X only (-- for zero order, $mol.m^{-3}$ for first order, $mol.m^{-3}$ for second order, etc.)
Ψ = function of Y only (-- for zero order, $mol.m^{-3}$ for first order, $mol.m^{-3}$ for second order, etc.)
ζ = dimensionless parameter (--)
Z = function of ζ only (--)

Special symbols

L_t = Laplace transform with respect to time (--)
$\forall_x$ = for all values of x

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