To cite this article:
Arias-Mendez A., Vilas C., Alonso A.A., Balsa-Canto E. Time-temperature integrators as predictive temperature sensors.*Food Control*, 2014, 44:258-266. DOI:https://doi.org/10.1016/j.foodcont.2014.04.001

Time-temperature integrators as predictive temperature sensors

Ana Arias-Mendez[a], Carlos Vilas[a], Antonio A. Alonso[a], and Eva Balsa-Canto*[a]

[a]Process Engineering Group, IIM-CSIC, Eduardo Cabello 6, 36208 Vigo, Spain.

Abstract

This work presents the idea of the *predictive Time Temperature Integrator sensors (pTTIs)* as a means to recover and to predict safety and quality evolution in thermal processing. *Predictive TTIs* combine a rigorous and computationally efficient model of the process with standard TTIs. The calibration of the *pTTIs* requires several steps, including the definition of the model, the appropriate means for its simulation and the use of adequate parameter estimation and optimal experimental design techniques to recover food and package thermo-physical properties.

Results show how a limited number of experiments and standard TTIs are required to calibrate *predictive sensors*. Possible uses include the prediction of microbial lethality and quality attributes, recovery of processing conditions considering eventual perturbations or optimal process design.

Calibration and uses are illustrated here with examples related to the tunnel pasteurization of highly viscous liquid foods.

Keywords: Thermal processing, Time-temperature integrators, Predictive sensors, Reduced order models, Parameter estimation, Optimal experimental design

1 Introduction

Food thermal processing persists as one of the most widely used methods for food preservation. The product is treated at a given temperature for a

*Corresp?onding author: ebalsa@iim.csic.es

Postprint submitted to Food Control

given period of time to minimize public health hazards due to the presence of pathogenic microorganisms and to extend product shelf-life.

As the number of processes, products and packaging types increases, food companies are faced with the challenge of satisfying safety constraints. Different time-temperature combinations could be used to achieve safety. However, the related time-temperature histories would affect the quality of the product in different ways. This has led to a common practice of over-processing food products to guarantee safety but at the expense of higher product quality deterioration.

Anyhow, consumers demands go beyond the basic requirements of safety and shelf-stability. Therefore more emphasis is to be placed in high quality and added value products. This calls for appropriate process validation and optimization techniques (Awuah et al, 2007).

However, designing thermal processes requires a deep understanding of the heating process of the given product, the impact on the target microorganism and quality factors. The thermal treatment will depend on the thermophysical characteristics, shape and size of the food product and container; the type and thermal resistance of the microorganisms that are likely to be present in the product and the kinetics of quality degradation.

To achieve such understanding is of critical importance to have access to adequate sensors: i) temperature probes to follow temperature evolution throughout the process; ii) microbiological techniques to study the thermal inactivation kinetics and iii) chemical and biochemical techniques to assess quality loss. It is important to remark here that microbial, chemical and biochemical techniques are used off-line.

Microbial destruction typically follows a first order kinetics. Microbial counting data can, then, be used to determine the two key parameters that characterize microbial lethality: D (the heating time required to reduce microbial population in a 90%) and z (the temperature change that results in a 10-fold change in D). Similarly D and z values can be determined to characterize loss of nutrients, for example.

Differences between the D and z values of microorganisms and quality factors can be exploited to optimize thermal processes. In this regard, model based approaches have been exploited in the context of the thermal sterilization of packaged solid food products, see for example Banga et al (1991); Holdsworth (1996); Banga et al (2003); Miri et al (2008) among others.

In fact, thermocouples can be used to follow temperature evolution on-line for solid food products, enabling the possibility of implementing model based real time optimization strategies capable of handling process perturbations and uncertainties (Alonso et al, 2013).

Unfortunately, direct registration of the time-temperature profile is not possible in other thermal processes. In continuous processes or rotating retorts, for instance, thermocouples are impractical, and their size may also be an issue (Marra and Romano, 2003). To overcome that difficulty, time temperature integrators (TTIs) were introduced to validate pasteurization processes. A TTI is a mechanical, chemical or enzymatic system that indicates the cumulative time-temperature history of the associated product by means of an irreversible change during the thermal treatment. The change is usually expressed as a visible response, in the form of a mechanical deformation or color modification. The use of enzymes, more specifically amylases, has been suggested since their breakdown by heat shows first order reaction kinetics with z values similar to those of the target microorganisms (Hendrickx et al, 1995; Van Loey et al, 1996; Guiavarc'h et al, 2002, 2005). Similarly TTIs can be designed so as to assess the degradation of particular quality factors (see Bobelyn et al (2006); Vaikousi et al (2009); Ellouze and Augustin (2010) among others). The time-temperature history of the product is, therefore, not necessary to determine the impact of thermal treatments with respect to the specific product attribute the TTI is designed for.

Potential limitations of the TTIs have to do with the fact that they are usually located in the surface of the product and the relationship between the surface and the product temperature varies from product to product and depends on the process, the thermo-physical properties of the product, the type of package, etc. In addition, different microorganisms and quality factors require different TTIs. In fact, many recent works suggest different possibilities (see, for example, Tucker et al (2002); Guiavarc'h et al (2005); Mehauden et al (2007); Tucker et al (2009); Ellouze and Augustin (2010)). Finally, the use of TTI measurements for process design, requires extensive experimentation any time the product or the package is to be changed, with the associated implications in terms of time-to-market and economic cost.

In order to surmount these difficulties, this work addresses the following questions: i) Is it possible to document the evolution of temperature in the interior of food from measurements of TTIs? and, as a consequence, ii) is it possible to use a single type of TTIs to validate the process and analyze quality loss? We argue that the answer to both questions is positive provided that we combine a rigorous model of the temperature evolution during thermal processing with TTIs. Of course, to calibrate the models we may also use TTIs. So that, with a reduced number of optimally designed experiments, it is possible to retrieve the thermo-physical properties of food product and container, and therefore the evolution of temperature and quality factors.

We regard the combination of TTIs with a rigorous, yet computationally efficient, model of the process as *pTTIs* since they may document the thermal history of the process and make predictions, provided it is possible to remove the TTIs at different stages in a multistage process. In addition, they can be used to design product-package specific optimal operating conditions.

The proposed methodology is general and applicable to any type of food product and any type or size of container. However, for illustrative purposes, we consider here the case of pasteurization in tunnels which is used to treat soups, soft drinks, beer, sausages and other foods previously prepacked in closed bottles or cans.

Table 1: Nomenclature

Symbol	Parameter	Units	Value
a_μ	Viscosity coefficient	[ ]	2.596×10^{-4}
b_μ	Viscosity coefficient	[ ]	0.06219
c_μ	Viscosity coefficient	[ ]	4.135
C_p	Specific heat	$[\frac{J}{Kg^0C}]$	4100
g	Gravity acceleration	$[\frac{m}{s^2}]$	9.81
h	Heat transfer coefficient	$[\frac{W}{^0Cm^2}]$	100
k	Thermal conductivity	$[\frac{W}{^0Cm}]$	0.7
P_c	Lethality at cold point	$[s]$	
r	Package radial coordinate	$[m]$	
R	Package radius	$[m]$	0.04
R_g	Ideal gases constant	$[\frac{kJ}{kmolK}]$	8.3
Z	Package height	$[m]$	0.09
t	Time	$[s]$	
T	Temperature	$[K]$	
T_{ref}	Kinetic parameter	$[^0C]$	70
z	Package height coordinate	$[m]$	
Z_{ref}	Kinetic parameter	$[^0C]$	7.5
Greek letters			
α	Thermal diffusivity	$[\frac{m^2}{s}]$	1.7872×10^{-7}
β	Thermal dilatation coefficient	[ ]	0.0002
μ	Viscosity	$[sPa]$	$Eqn.(4)$
ρ	Density	$[\frac{Kg}{m^3}]$	950
Subscripts			
ff	Falling film		
ini	Initial		
$prod$	Product		

To cite this article:
Arias-Mendez A., Vilas C., Alonso A.A., Balsa-Canto E. Time-temperature integrators as predictive temperature sensors.*Food Control*, 2014, 44:258-266. DOI:https://doi.org/10.1016/j.foodcont.2014.04.001

2 Material and methods

2.1 Process and product description

In this work we consider the tunnel pasteurization of highly viscous liquid foods such as tomato or carrot puree in cylindrical food jars, see Figure 1.

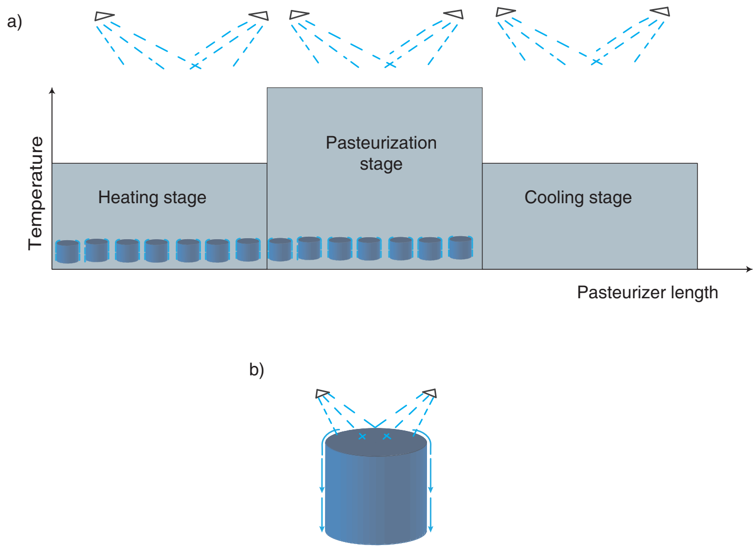

Figure 1: Typical industrial tunnel pasteurization equipment: a) traditional configuration of the tunnel itself and b) detail of the package typically employed

The containers are loaded at one end of the pasteurizer and passed under sprinkles of water as they move along the conveyor belt. Temperature of the water changes in the main three different zones (see Figure 1(a)) so as to achieve the required lethality (Horn et al, 1997). The heat transfer occurs between the hot water film, usually called falling film, and the package surface, and from the package to the food product. Heat transfer within the food product is driven by heat *conduction* and *convection*, which induces a temperature gradient within the food product. Safety will be then assessed by means of the lethality as evaluated in the coldest point, whereas quality is typically quantified as a surface or volumetric measure.

However, eventual temperature deviations in one or more of the heating zones considered during the pasteurization process may end up with products which do not comply with the safety requirements or with lower quality of the final product than expected (due, for instance, to over-processing). In such scenarios it is of remarkable importance to be able to guarantee the proper process operation or at least to be capable of quantifying the relevance of such perturbations in the final product specifications.

To cite this article:
Arias-Mendez A., Vilas C., Alonso A.A., Balsa-Canto E. Time-temperature integrators as predictive temperature sensors.*Food Control*, 2014, 44:258-266. DOI:https://doi.org/10.1016/j.foodcont.2014.04.001

2.2 Time-temperature integrators

Time-temperature integrators (TTIs) considered in this work are prepared using silicon tubes of 15 *mm* length, 2 *mm* bore and 0.5 *mm* wall. Tubes are filled with an enzyme with the following kinetic characteristics T_{ref} = 70 °C and z_{ref} = 7.5, equivalent to those of the target microorganisms (see details about the definition of T_{ref} and z_{ref} in the following section). It should be remarked that any other TTIs could have been selected.

TTIs will be placed inside the food package and fixed to the jar walls.

2.3 Process model

The evolution of temperature and velocity within the food product during the pasteurization is described by means of conservation laws. The package (Figure 1) is assumed to be homogeneously heated therefore axial symmetry allows to consider a 2D geometry, Figure 2. The process can be mathematically described as follows (Erdogdu et al, 2010):

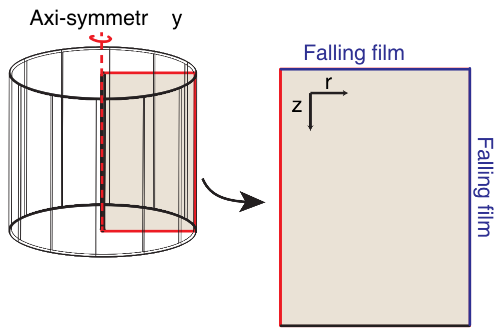

Figure 2: Definition of the geometry for model simulation

Continuity equation:

$$\frac{\partial u}{\partial z} + \frac{v}{r} + \frac{\partial v}{\partial r} = 0, \tag{1}$$

being r and z being the spatial coordinates (radius and height of the package) while v and u are the velocity field components, i.e., $w = [u, v]^T$.

Momentum conservation:

$$\rho_{prod}\Big(\frac{\partial v}{\partial t} + u\frac{\partial v}{\partial z} + v\frac{\partial v}{\partial r}\Big) = -\frac{\partial p}{\partial r} + \mu_{prod}\Big(\frac{\partial}{\partial r}\Big(\frac{1}{r}\frac{\partial rv}{\partial r}\Big) + \frac{\partial^2 v}{\partial z^2}\Big), \tag{2}$$

$$\rho_{prod}\Big(\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial z} + v\frac{\partial u}{\partial r}\Big) = -\frac{\partial p}{\partial z} + \mu_{prod}\Big(\frac{1}{r}\frac{\partial}{\partial r}\Big(r\frac{\partial u}{\partial r}\Big) + \frac{\partial^2 u}{\partial z^2}\Big) + \widehat{\rho} g, \tag{3}$$

where p is the pressure, ρ_{prod} corresponds with the food stuff density, g is the gravity constant, T represents the temperature distribution inside the food, μ_{prod} stands for the viscosity expressed as a function of the temperature (Erdogdu et al, 2010)

$$\mu_{prod} = a_\mu T^2 - b_\mu T + c_\mu, \tag{4}$$

and the density $\widehat{\rho}$ is usually expressed in terms of the fluid temperature as follows:

$$\widehat{\rho} = \rho_{ref}(1 - \beta(T - T_{ref})), \tag{5}$$

with β being the thermal dilatation coefficient. ρ_{ref} and T_{ref} are given reference values.

Energy conservation:

$$\frac{\partial T}{\partial t} + v\frac{\partial T}{\partial r} + u\frac{\partial T}{\partial z} = \alpha_{prod}\Big(\frac{1}{r}\frac{\partial}{\partial r}\Big(r\frac{\partial T}{\partial r}\Big) + \frac{\partial^2 T}{\partial z^2}\Big). \tag{6}$$

The system in Eqns.(1-6) is subject to the following **initial and boundary conditions**:

- Initially the food stuff is at rest ($v = 0$) and at uniform temperature $T_{ini} = T_0$.

- The velocity field components (u, v) are zero in the package walls, i.e.:

$$u_{|_{z=0}} = u_{|_{z=Z}} = u_{|_{r=R}} = 0, \tag{7}$$
$$v_{|_{z=0}} = v_{|_{z=Z}} = v_{|_{r=R}} = 0. \tag{8}$$

- Symmetry conditions are imposed in the symmetry axis ($r = 0$):

$$\left.\frac{\partial T}{\partial r}\right|_{r=0} = \left.\frac{\partial u}{\partial r}\right|_{r=0} = \left.\frac{\partial v}{\partial r}\right|_{r=0} = 0. \tag{9}$$

- The package bottom is touching the transportation belt assumed to be an insulating material:

$$\left.\frac{\partial T}{\partial z}\right|_{z=0} = 0. \tag{10}$$

- At the right and upper sides, the package is in direct contact with the falling film of heating fluid:

$$k_{prod}\left.\frac{\partial T}{\partial r}\right|_{r=R} = h_{jar}\Big(T_{ff}(t) - T(R, z, t)\Big), \tag{11}$$

$$k_{prod}\frac{\partial T}{\partial z}\bigg|_{z=Z} = h_{jar}\Big(T_{ff}(t) - T(r,Z,t)\Big), \tag{12}$$

with T_{ff} being the temperature of the falling film, h_{jar} the jar heat transfer coefficient and k_{prod} the product thermal conductivity.

2.3.1 Pasteurization value

The *thermal death time* method relates parameter D with the temperature. Defining the lethality as the relation between the current and a reference treatment, i.e. $dP^0/dt = D_{ref}/D$, the following equation is obtained:

$$\frac{dP^0}{dt} = 10^{\frac{Tc(t)-T_{ref}}{z_{ref}}}, \tag{13}$$

where T_c is the temperature at the coldest point. Parameters T_{ref} and z_{ref} represent the kinetic coefficients for the target pathogen which coincide (or are close to) the TTIs characteristic values.

2.3.2 Quality attributes

The quality degradation of a food product, can also be modelled by the thermal death time equation in every point of the food product. In this work, the superficial retention is used as a measure of the quality of the food:

$$Ret = 10^{-\frac{1}{D_{ref}}\int_0^{t_f}\frac{Ts(t)-T_{ref}}{z_{ref}}dt}, \tag{14}$$

where T_s is the temperature at the different points in the surface of the food, and parameters T_{ref}, D_{ref} and z_{ref} depend on the type of nutrient considered.

2.4 Calibration of the *predictive TTIs*

To calibrate the predictive TTIs the following elements will be necessary: i) model simulation methods, ii) parameter estimation techniques and iii) experimental data.

2.4.1 Model simulation

Models as the one presented in Eqns.(1-14) are typically solved using spatial discretization based techniques -such as the finite element method (FEM)-. However, it has been recognised that reducer order models like those obtained by means of the *proper orthogonal decomposition* (POD) approach, are accurate yet computationally efficient alternatives more suited to optimization and real-time applications (Balsa-Canto et al, 2002).

For the sake of clarity, mathematical details about the derivation of a reduced order model using the POD method are included in A. Only the main practical steps are summarized here:

1. Obtain a set of snapshots that characterizes the spatio-temporal distribution of the variable of interest (temperature, velocity, etc). In our case all the snapshots are obtained from a FEM based simulation of system Eqns.(1-14) under different possible experimental conditions and product and package parameter values.

2. Computation of the POD basis. The snapshots are then used to compute the so-called POD basis as described in (García et al, 2007).

3. Projection. Projection is carried out by multiplying the original system by the POD basis and integrating the result over the spatial domain. Note that the FEM structure may be exploited to numerically perform the projection (García et al, 2007).

As a result a reduced set of ordinary differential equations is finally obtained.

2.4.2 Parameter estimation

The parameter estimation problem consists of finding the unknown model parameters that minimize the distance between model predictions and experimental measurements as measured by the log-likelihood function:

$$J_{PE} = \sum_{k=1}^{n_{exp}} \sum_{i=1}^{n_l} \frac{\left(P_{k,i}^{TTI}(\theta)_k - P_{k,i}^{m}\right)^2}{\sigma_{k,i}^2}, \tag{15}$$

where n_{exp} and n_l are the number of experiments and TTIs, respectively and σ the experimental noise standard deviation. θ represents the set of model unknown parameters that must be estimated. In this work we have chosen those parameters which are difficult to measure and whose values depend on the fluid composition, package specifications, heating fluid characteristics, etc. and therefore they cannot be found in the literature. Such parameters are h_{jar}, α_{prod}, β, a_μ, b_μ and c_μ. $P_{k,i}^{TTI}$ represents the lethality achieved at the end of the process under experimental conditions k as measured by the TTI located at i position. Finally P^m corresponds to the model predictions computed as follows:

$$\frac{dP^m}{dt} = 10^{\frac{\hat{T}(t)-T_{ref}}{Z_{ref}}}, \tag{16}$$

where $\bar{T}$ regards the mean temperature within the corresponding TTI:

$$\bar{T} = \int_{V_{TTI}} T(r,z)\,\mathrm{d}V_{TTI}, \tag{17}$$

with V_{TTI} being the volume of the TTI tubes.

A number of constraints must be considered in the task of searching for the minimum value of J_{PE} in Eqn.(15):

- Model equations which provide us with the values of P^m for a given set of parameters θ.
- Parameters a, b and c must comply with the physical requirement that the viscosity of the product is positive, i.e., $\mu_{prod} > 0$.
- Physically meaningful bounds for the parameters.

The solution of the parameter estimation problem will be the parameter values that are able to reproduce the experimental data as close as possible (θ^*) together with the corresponding confidence intervals which provide information about the reliability of the estimates.

The confidence interval of a given parameter $\boldsymbol{\theta}_i^*$ can be computed by means of the *Fisher information matrix* ($\mathcal{F}$) and the Crammer-Rao inequality(Ljung and Glad, 1994; Walter and Pronzato, 1997) as follows:

$$\pm t^{\gamma}_{\alpha/2}\sqrt{\mathbf{C_{ii}}} \tag{18}$$

where $\mathbf{C}$ corresponds to the inverse of the Fisher Information Matrix:

$$\mathcal{F} = E_{P^m|\boldsymbol{\theta}^*}\left\{\left[\frac{\partial J_{PE}(\boldsymbol{\theta})}{\partial\theta}\right]\left[\frac{\partial J_{PE}(\boldsymbol{\theta})}{\partial\theta}\right]^T\right\}, \tag{19}$$

and $t^{\gamma}_{\alpha/2}$ is given by Students t-distribution, $\gamma = N_d - n_\theta$ corresponds to the number of degrees of freedom and α is the (1-α) 100% confidence interval selected, typically 95% is used.

The correlation by pairs of parameters can be assessed by means of the correlation matrix as computed by:

$$\mathbf{C_r} = \frac{\mathbf{C_{ij}}}{\sqrt{C_{ii}C_{jj}}}, \tag{20}$$

in such a way that two parameters $\boldsymbol{\theta}_i$ and $\boldsymbol{\theta}_j$ are highly correlated if $\mathbf{C_{rij}} = \pm\mathbf{1}$ and uncorrelated if $\mathbf{C_{rij}} = \mathbf{0}$. And the mean correlation can be computed as follows:

$$\mathbf{C_{r_m}} = \frac{\sum_{\mathbf{i=1}}^{\mathbf{i=n_\theta-1}} \sum_{\mathbf{j=i+1}}^{\mathbf{j=n_\theta}} \mathbf{C_{rij}}}{\sum_{\mathbf{k=1}}^{\mathbf{k=n_\theta-1}} \mathbf{k}}, \tag{21}$$

with n_θ the number of unknown parameters.

2.4.3 Optimal experimental design

The objective of *optimal experimental design* (OED) is to find the experimental set-up that maximizes the information provided by the experiments for the purpose of parameter estimation as encoded, for example, in the *Fisher information matrix* ($\phi(\mathcal{F})$) (Walter and Pronzato, 1997). The problem can be stated as a dynamic optimization problem as follows:

Find the number of experiments and experimental conditions -falling film temperature profile, experiment duration and number and location of TTIs- so as to minimize $J_{OED} = \phi(\mathcal{F})$ subject to the system dynamics, maximum and minimum processing temperatures and a maximum number of TTIs with specific locations as shown in Figure 3.

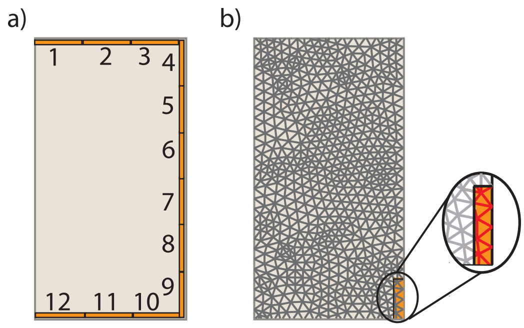

Figure 3: Conditions for OED: a) Allowed positions for TTIs inside the jar numbered from 1 to 12, b) Mesh used for the purpose of FEM based computation of the TTI mean temperature Eqn.(17)

Several possibilities exist to define the scalar function $\phi(\mathcal{F})$. In this work the ratio between the determinant and the minimum eigenvalue was used so as to achieve a compromise confidence-correlation (García, 2008).

Parameter estimation and optimal experimental design problems were solved using the AMIGO toolbox (Balsa-Canto and Banga, 2011). It should be remarked that this tool offers the possibility of selecting several optimizers including global optimization methods to deal with the usual multimodal character of these problems. In particular the metaheuristic approach eSS (Egea et al, 2009) was selected to perform the optimization tasks due to its robustness and efficiency.

2.5 Predictive TTIs examples of use

By complementing direct measurements of quality and safety factors with mathematical physico-chemical models, the *pTTI* concept provides a full picture of the process history and its effects on the product. Among other capabilities we remark:

- A complete documentation of the process itself.

  When the results of the pasteurization process are those expected in terms of final lethality of the product, *pTTIs* can provide a full documentation of the process, since they allow the reconstruction of product temperature and fluid velocity distributions and profiles which are at the basis of the estimation of other unmeasured quality or safety parameters.

- Detection and prevention of deviations of process conditions.

  In the presence of disturbances that may include changes of process temperature profiles or undocumented product specifications for instance, *pTTIs* allow, via optimization, to infer possible causes of process deviations (perturbations) thus contributing to enhance on-line process diagnosis, at least on a batch to batch basis.

  The optimization problem to recover the actual conditions of the process under the presence of perturbations can be formulated as:

$$\begin{aligned} &\min_{T_{ff}(t)} \phi = \sum_{i=1}^{p} \left(\frac{P_i^{TTI} - P_i^m}{P_i^{TTI}} \right)^2 \\ \text{Subject to} \quad & \\ & f(T, u, w, T_{ff}, t_p, \xi, t) = 0, \\ & T^L(t) \le T(t) \le T^U(t), \end{aligned} \tag{22}$$

  where t_p is the duration of the process itself, f stands for the model equations (1-14) and $T_{ff}(t)$ is the actual temperature of the falling film within the pasteurizer which may be discretized by using the control vector parameterization approach (CVP). Finally, ϕ refers to the distance from the expected (P_i^m) to the measured (P_i^{TTI}) final lethality.

3 Results and discussion

3.1 Model simulation

The finite element method, with a mesh of 725 discretization points, was employed to numerically solve the system of Eqns.(1-14). This implies solving

To cite this article:
Arias-Mendez A., Vilas C., Alonso A.A., Balsa-Canto E. Time-temperature integrators as predictive temperature sensors.*Food Control*, 2014, 44:258-266. DOI:https://doi.org/10.1016/j.foodcont.2014.04.001

2900 differential equations. A reduced order model with 40 ODEs was achieved by means of the POD technique. The reduced order model is able to accurately describe the system. Differences between FEM and POD based simulations remain bellow the 2% for a validation example, as shown in Figure 4.

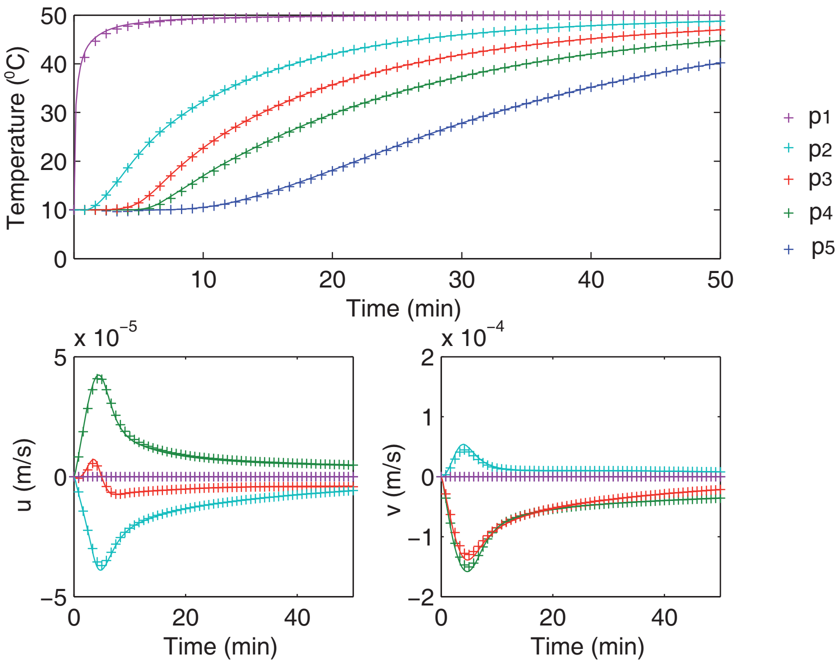

Figure 4: Dynamic evolution of the temperature and velocity fields at five spatial locations distributed along the diagonal of the spatial domain ($p_1 = (0,0), p_2 = (0.011, 0.022), p_3 = (0.019, 0.045), p_4 = (0.029, 0.067), p_5 = (0.04, 0.09)$). Continuous lines correspond to the FEM simulation while marks represent the solution of the POD based model.

3.2 Parameter estimation

The starting point for parameter estimation was a factorial plan consisting of three experiments. The experiments were designed to provide information about both heating and cooling dynamics, as follows:

- Four TTIs were used and placed at the locations 3, 7, 10 and 12 as shown in Figure 3.
- The process duration was 60 minutes for all experiments and lethality (P^{TTI}) was measured at the end of the process.

- Constant falling film temperature profiles were considered: T_{ff} = 72 °C, T_{ff} = 65 °C and T_{ff} = 20 °C, for the first, second and third experiments, respectively.

- Initial conditions for the first two experiments were T_0 = 20 °C and $P^0(0) = 0\,min$. The third experiment started from T_0 = 70 °C and $P^0(0)$ = 1 min[1].

Uniformly distributed error with a maximum of 20% standard deviation was included in the *in-silico* experimental data to emulate experimental error.

Parameters were normalized to one using a reference value. The solution of the corresponding parameter estimation problem is: $\bar{h}_{jar}$ = 0.92, $\bar{\alpha}_{prod}$ = 0.97, $\bar{\beta}$ = 1.33, $\bar{a}_{\mu}$ = 0.84, $\bar{b}_{\mu}$ = 0.94 and $\bar{c}_{\mu}$ = 0.87. The optimal solution is far from the expected optimum (all parameters equal to 1). Besides the mean confidence interval is 254% and the maximum confidence interval is 545%. The high confidence intervals reveal reduced sensitivity of model predictions to parameter values under the experimental conditions. In addition, the correlation between parameters is also rather significant (C_{r_m} = 0.71).

In order to improve the quality of parameter estimates a sequential optimal experimental design was performed. The underlying idea is to add an experiment at a time so as to progressively converge to the parameters real value and to reduce the confidence intervals. Table 3 presents a summary of results, showing how the use of the factorial plan (FP) plus four optimally designed (OD) experiments results in a 2.3% maximum confidence interval.

Table 2: Parameter estimation results (optimal value of the parameters and mean and maximum value of the confident intervals,CI) for the sequence of optimally designed experiments.

	h_{jar}	α_{prod}	β	a_{μ}	b_{μ}	c_{μ}	mean CI	max CI
FP+1OD	1.02	0.88	2.74	1.19	0.81	1.20	94%	210%
FP+2OD	1.01	0.97	1.55	1.17	0.81	1.03	45%	104%
FP+3OD	1.01	0.98	1.47	0.96	0.85	1.07	12%	27%
FP+4OD	1.01	0.99	1.02	1.08	1.00	1.01	1%	2.3%

The optimal experiments achieved as well as the corresponding parameter correlation matrix are shown in Figure 5.

All designed experiments make use of a time varying temperature profile, three of them correspond to a heating process while one corresponds to a cooling process. Temperature switching times as well as the optimal sensor

[1]Initial temperature different from the ambient and $P^0(0)$ different from zero are achieved by perfectly mixed precooking process

To cite this article:
Arias-Mendez A., Vilas C., Alonso A.A., Balsa-Canto E. Time-temperature integrators as predictive temperature sensors.*Food Control*, 2014, 44:258-266. DOI:https://doi.org/10.1016/j.foodcont.2014.04.001

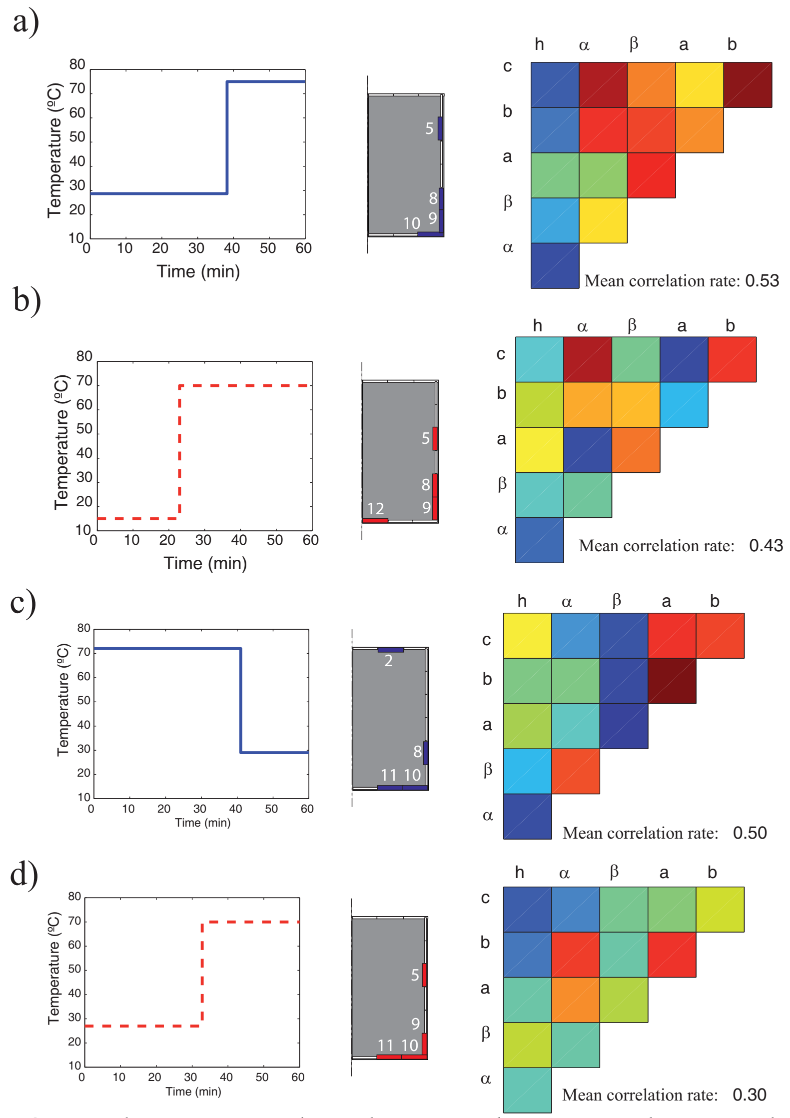

Figure 5: Optimal experimental conditions and corresponding correlation matrix. a) First optimally designed (OD) experiment and correlation matrix (CM) for FP+1OD. b) Second OD experiment and CM for FP+2OD. c)Third OD experiment and CM for FP+3OD. d) Fourth OD experiment and CM for FP+4OD

locations change from one experiment to the other. Note that the maximum allowed number of sensors (4) is used in all experiments and their locations are such that all package walls are visited, although mostly towards the bottom of the package.

Figure 5 also shows how the parameters tend to decorrelate with the addition of optimally designed experiments. This facilitating the convergence to

To cite this article:
Arias-Mendez A., Vilas C., Alonso A.A., Balsa-Canto E. Time-temperature integrators as predictive temperature sensors.*Food Control*, 2014, 44:258-266. DOI:https://doi.org/10.1016/j.foodcont.2014.04.001

the optimal solution.

3.3 Examples of use

In this section we present two practical scenarios of use of *pTTIs*.

3.3.1 Prediction of quality attributes

To asses the quality of *pTTIs* as quality sensors we considered a new experimental set-up and compared the results achieved with *pTTIs* with those obtained with two standard TTIs. Results reveal good predictive capabilities of the *pTTI* with errors within the expected experimental error (Figure 6).

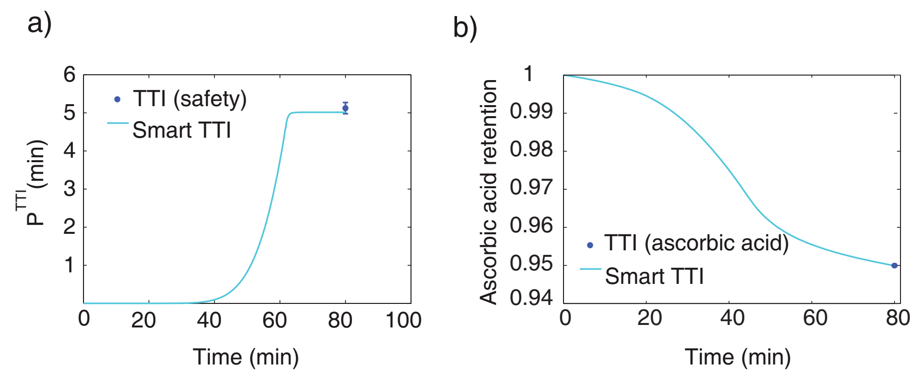

Figure 6: Comparison of the TTI measurements and *pTTI* predictions: a) microbial lethality and b) acid ascorbic retention. In the dynamic of the acid ascorbic degradation the next values of the kinetic parameters have been considered, $z_{ref} = 7.5$ and $D_{70} = 1354$

It should be noted that *pTTIs* enable the possibility of documenting the temperature and velocity distribution as well as quality and safety dynamics throughout the process. Figure 7 presents the distribution of temperature and velocity of the product at a given time.

3.3.2 Process reconstruction in the presence of perturbations

The objective is to recover, from standard TTI measurements, the “real” falling film temperature profile, in the presence of perturbations, through the solution of the dynamic optimization problem stated in Eqns.(22).

In the example it is possible to infer perturbed temperature profiles using four pTTIs (see Table 3). The profiles recovered from the process lead to very small discrepancies between real and predicted lethalities (see Figure 8).

To cite this article:
Arias-Mendez A., Vilas C., Alonso A.A., Balsa-Canto E. Time-temperature integrators as predictive temperature sensors.*Food Control*, 2014, 44:258-266. DOI:https://doi.org/10.1016/j.foodcont.2014.04.001

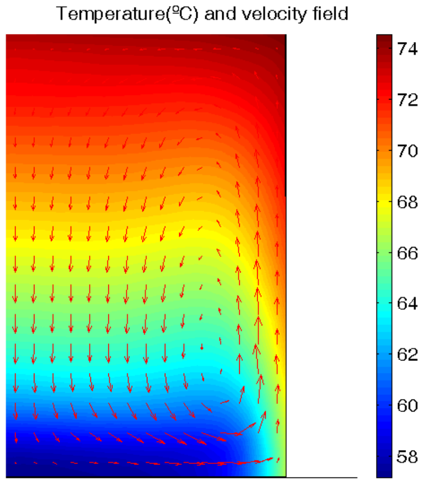

Figure 7: Distribution of the product temperature and velocity field at a given time as predicted by the *pTTI*

Table 3: Results of the recovering problem using the pTTI structure.

	T(heating)	T(pasteurization)	T(cooling)
Ideal process conditions	50^0C	75^0C	30^0C
Recovered conditions	50.03^0C	74.99^0C	29.4^0C

4 Conclusions

This work presented the idea of *predictive time temperature integrators* as a means to recover and to predict safety and quality evolution in thermal processing. The underlying idea is to combine a rigorous but computationally efficient model of the process with standard TTIs.

The calibration of the *pTTIs* and their practical uses were illustrated with an example related to thermal pasteurization of food products in tunnels. The results showed how with a reduced number of experiments and TTIs, it is possible to calibrate the *pTTI* to accurately recover the evolution of temperature in the interior of the food product and, therefore, the microbial lethality and the deterioration of quality attributes. Remark that for *pTTIs* to assess quality attributes the kinetics of quality deterioration must be known and therefore further experiments may be required for this purpose.

The use of *pTTIs* brings new possibilities for process monitoring and optimization: i) a unique type of *pTTIs* may be used to validate the process and to follow quality loss ii) and allow the recuperation of process conditions un-

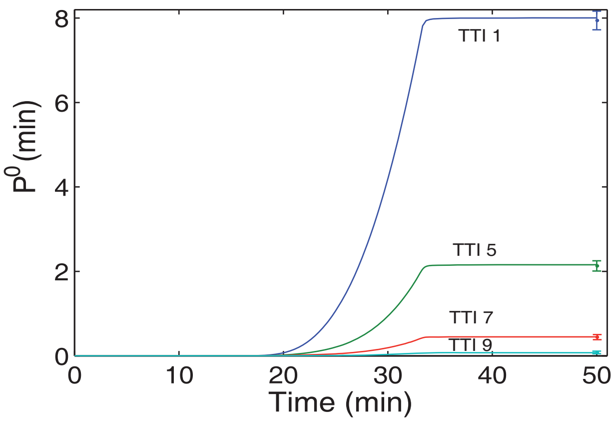

Figure 8: Real and recovered lethality profiles obtained by solving the optimization problem. Lines stand for the measured values obtained after performing the experiment, and dots for the values estimated with the recovered temperatures

der unexpected perturbations; iii) they facilitate the design of product-package specific operating conditions which guarantee food safety, while minimizing the impact on quality related factors and iv) their computational efficiency enables the possibility of taking decisions in real time, provided TTIs can be retrieved at different stages of the process.

Acknowledgements

This work has been funded by the Spanish Ministerio de Economía y Competitividad, MINECO (Is-for-Quality, AGL2012-39951-C02-01) and by the Spanish National Research Council (CSIC) intramural project CONTROLA (PIE201270E075). A. Arias-Méndez acknowledges financial support from the JAE-CSIC program and all the support received from Profs. Fryer and Bakalis during her short stay at the Chemical Engineering School, University of Birmingham .

A The proper orthogonal decomposition

In this section we present the basics of the *proper orthogonal decomposition* (POD) technique using the pasteurization model to illustrate the different steps. A more detailed descriptions can be found in Sirovich (1987); García et al (2007).

The first step is to approximate the dependent variables T and $w = [u, v]^T$

by a truncated Fourier series of the form:

$$T(\xi,t) \approx \sum_{i=1}^{N_T} m_{T_i}(t)\phi_{T_i}(\xi), \tag{23}$$

$$w(\xi,t) \approx \sum_{i=1}^{N_w} m_{w_i}(t)\phi_{w_i}(\xi), \tag{24}$$

where ξ represents the spatial coordinates z and r. The basis functions in the sets $\{\phi_{T,i}(\xi)\}_{i=1}^{N_T}$ and $\{\phi_{w,i}(\xi)\}_{i=1}^{N_w}$ are orthogonal and contain the spatial dependency of the solution, while the sets $\{m_{T,i}(t)\}_{i=1}^{N_T}$ and $\{m_{w,i}(t)\}_{i=1}^{N_w}$ collect the time dependent coefficients. Instead of computing $T(\xi,t)$ and $w(\xi,t)$ directly, we will compute the basis functions and the time dependent coefficients. Then, variables $T(\xi,t)$ and $w(\xi,t)$ can be reconstructed using Eqns.(23) and (24).

The POD basis are obtained using experimental data (either *in silico* or *in vitro*). Such experimental data (snapshots) must characterize the spatio-temporal distribution of the variable of interest (temperature, velocity, etc). In our case all the snapshots are obtained from a FEM based simulation of system (1)-(12) under different possible experimental conditions (T_{ff}, T_0) and using different values for the unknown parameters. The snapshots are then used to compute, solving an eigenvalue problem, the so-called POD basis as described in Sirovich (1987); García et al (2007).

The time dependent coefficients $\{m_{x,i}(t)\}_{i=1}^{N_x}$ with $x = T, w$ are computed by projecting the original PDE system into POD basis. In practice this is performed by multiplying the original PDE system by the POD basis and integrating the result over the spatial domain (García et al, 2007):

$$\int_V \phi_{T,i}\frac{\partial T}{\partial t}d\xi = \int_V \phi_{T,i}(\alpha\Delta T - w\nabla T)d\xi, \tag{25}$$

$$\rho\int_V \phi_{w,i}\frac{\partial w}{\partial t}d\xi = \int_V \phi_{w,i}\left(\mu\Delta w - \rho w\nabla w - \nabla P + \rho g\left(1-\beta(T-T_0)\right)\vec{z}\right)d\xi, \tag{26}$$

with $i = 1, ..., N_x$ and $\vec{z}$ being a unitary vector with the direction of the spatial coordinate z. Eqn.(26) with $w = [u, v]^T$ is equivalent to Eqns (2)-(3).

Using relations (23)-(24) and after some algebraic manipulations, Eqns.(25) - (26) can be rewritten as:

$$\frac{d\mathbf{m}_T}{dt} = \left(\alpha_{prod}A_T + B_T + \alpha_{prod}D_T\right)m_T, \tag{27}$$

$$\rho\frac{d\mathbf{m}_w}{dt} = \left(\mu A_w + \rho B_w + \mu D_w\right)m_w - \rho g\beta C_{T,w}m_T + \rho g(1+\beta T_0), \tag{28}$$

where each component of matrices A_x, B_x, $C_{T,w}$ and D_x are of the form:

$$A_x(i;j) = \int_V \nabla\phi_{x,i}\nabla\phi_{x,j}d\xi; \qquad B_x(i;j) = \int_V \phi_{x,i}(w\nabla\phi_{x,j})d\xi.$$

$$C_{T,w}(i;j) = \int_V \phi_{w,i}\phi_{T,j}d\xi; \qquad D_x(i;j) = \int_{\partial V} \phi_{x,i}\nabla\phi_{x,j}d\xi.$$

with ∂V denoting the boundary of V. The vector of time dependent functions $\mathbf{m}_x$ is of the form: $\mathbf{m}_x = [m_{x,1}, m_{x,2}, \cdots, m_{x,N}]^T$.

At this point both the basis functions and the time dependent coefficients are known so the field can be recovered using equations (A.4)-(A.5). Note that the accuracy of the approximation can be improved arbitrarily by increasing the number of elements N_x in the basis set Φ_x.

References

Alonso AA, Arias-Méndez A, Balsa-Canto E, García M, Molina J, Vilas C, Villafín M (2013) Real time optimization for quality control of batch thermal sterilization of prepackaged foods. Food Control 32(2):392 – 403

Awuah G, Ramaswamy H, Economides A (2007) Thermal processing and quality: Principles and overview. Chemical Engineering and Processing 46:584–602

Balsa-Canto E, Banga JR (2011) AMIGO, a toolbox for advanced model identification in systems biology using global optimization. Bioinformatics 27:2311–2313

Balsa-Canto E, Alonso AA, Banga JR (2002) A novel, efficient and reliable method for thermal process design and optimization. part i: Theory. J Food Engineering 52:227–234

Balsa-Canto E, Rodríguez-Fernández M, Banga JR (2007) Optimal design of dynamic experiments for improved estimation of kinetic parameters of thermal degradation. J Food Engineering 82:178–188

Banga J, Versyck KJ, Van Impe J (2002) Computation of optimal identification experiments for nonlinear dynamic process models: an stochastic global optimization approach. Ind & Eng Chem Res 41:2425–2430

Banga JR, Martín RP, Gallardo JM, Casares JJ (1991) Optimization of thermal processing of conduction-heated canned foods: Study of several objective functions. J Food Engineering 14(1):25–51

Banga JR, Balsa-Canto E, Moles C, Alonso AA (2003) Improving food processing using modern optimization methods. Trends in Food Science and Technology 14(4):131–144

Bernaerts K, Servaes R, Kooyman S, Versyck K, Van Impe J (2002) Optimal temperature input design for estimation of the square root model parameters: parameter accuraty and model validity restrictions. Int J Food Microbiol 73:145–157

Bobelyn E, Hertog M, Nicolai B (2006) Applicability of an enzymatic time temperature integrator as a quality indicator for mushrooms in the distribution chain. Postharvest Biology and Technology 42(1):104–114

Boz Z, Erdogdu F (2013) Evaluation of two-dimensional approach for computational modelling of heat and momentum transfer in liquid containing horizontal cans and experimental validation. Food and Bioproducts Processing 91(1):37 – 45

Egea J, Balsa-Canto E, García M, Banga JR (2009) Dynamic optimization of nonlinear processes with an enhanced scatter search method. Industrial and Engineering Chemistry Research 48(9):4388–4401

Ellouze M, Augustin J (2010) Applicability of biological time temperature integrators as quality and safety indicators for meat products. International Journal of Food Microbiology 138:119–129

Erdogdu F, Uyar R, Palazoglu TK (2010) Experimental comparison of natural convection and conduction heat transfer. Journal of Food Process Engineering 33:85–100

García MR (2008) Identification and real time optimisation in the food processing and biotechnology industries. Departamento de Matemática Aplicada II, Universidade de Vigo, Galicia, Spain

García MR, Vilas C, Banga JR, Alonso AA (2007) Optimal field reconstruction of distributed process systems from partial measurements. Industrial and Engineering Chemistry Research 46(2):530–539

Guiavarc'h Y, Van Loey A, Zuber F, Hendrickx ME (2002) Validation and use of an enzymatic time temperature integrator to monitor thermal impacts inside a solid/liquid model food. Biotechnology prog 18(5):1087–1094

Guiavarc'h Y, Van Loey A, Hendrickx ME (2005) Extended study on the influence of z-value(s) of single and multicomponent time–temperature integrators on the accuracy of quantitative thermal process assessment. J Food Prot 68:384–395

Hendrickx M, Maesmans G, De Cordt S, Noronha J, Van Loey A, Tobback P (1995) Evaluation of the integrated time-temperature effect in thermal processing of foods. Crit Rev Food Sci Nutr 35(3):231–262

Holdsworth SD (1996) Thermal Processing of Packaged Foods. Chapman & Hall

Horn C, Franke M, Blakemore F, Stannek W (1997) Modelling and simulation of pasteurization and staling effects during tunnel pasteurization of bottled beer. Food and Bioproducts Processing 75(1):23 – 33

Ljung L, Glad T (1994) On global identifiability of arbitrary model parameterizations. Automatica 30(2):265–276

Marra F, Romano V (2003) A mathematical model to study the influence of wireless temperature sensor during assessment of canned food sterilization. J Food Engineering 59(2–3):245 – 252

Mehauden K, Cox P, Bakalis S, Simmons M, Tucker G, Fryer PJ (2007) A novel method to evaluate the applicability of time temperature integrators to different temperature profiles. Innovative Food Science & Emerging Technologies 8(4):507–514

Miri T, Tsoukalas A, Bakalis S, Pistikopoulos EN, Rustem B, Fryer PJ (2008) Global optimization of process conditions in batch thermal sterilization of food. J Food Engineering 87(4):485–494

Sirovich L (1987) Turbulence and the dynamics of coherent structures. Part I: Coherent structures. Quaterly of Appl Math pp 561–571

Tucker G, Lambourne T, Adams J, Lach A (2002) Application of a biochemical time temperature integrator to estimate pasteurisation values in continuous processes. Innovative food science and emerging technologies 3:165–174

Tucker G, Hanby E, Brown H (2009) Development and application of a new time-temperature integrator for the measurement of P-values in mild pasteurisation processes. Food and Bioproducts Processsing 87(C1):23–33

Vaikousi H, Biliaderis C, Koutsoumanis K (2009) Applicability of a microbial time temperature indicator (tti) for monitoring spoilage of modified atmosphere packed minced meat. International Journal of Food Microbiology 133(3):272–278

Van Loey A, Hendrickx ME, De Cordt S, Haentjens T, Tobback PP (1996) Quantitative evaluation of thermal processes using time-temperature integrators. Trends in Food Science and Technology 7:16–26

Walter E, Pronzato L (1997) Identification of parametric models form experimental data. Springer, Masson