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Thermal processing and quality: Principles and overview

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Abstract

The food processing industry has matured over the years with an impressive record on safety and a vibrant marketplace for new product development. Consumer demands for high-quality products has inspired researchers and the food industry to explore alternative methods as replacement for traditional processing methods. The food industry is poised to adopt cost effective technologies that offer better quality and safe products. Given the impressive safety record associated with traditional systems, one may be tempted to conclude that there is little room for advancement and innovation to meet current consumer demands. Process optimization will continue to evolve to enhance quality and overall energy utilization either in traditional or novel systems. The need for efficient operations will certainly drive system automation, control and monitoring systems that can handle complex mathematical routines in real-time. Such systems would certainly require vigorous validation and verification for industry to embrace them. It truly sounds illogical for industry to re-evaluate existing process schedules based on studies that demonstrate non-linearity of survival curves. However, the need to optimize quality and operating costs could potentially prompt re-evaluating existing systems to capture additional benefits. New processing concepts such as the application of variable retort temperature have received attention from processing experts and promises to improve both the economy and quality of thermally processed foods.

Keywords: Thermal processing; Inactivation kinetics; Quality optimization; Alternative technologies and on-line control

1. Introduction

The concept of thermal processing, which primarily involves in-container sterilization of foodstuff has come a long way since Bigelow and Ball developed in 1920, the first scientific basis for calculating the minimum safe sterilization process. In all its forms of application, thermal processing persists as the most widely used method of preserving and extending the useful shelf-life of foods. The concept of in-container sterilization (canning) involves the application of a high-temperature thermal treatment for a sufficiently long time to destroy microorganisms of public health and spoilage concerns. The hermetic seal maintains an environment in the container that prevents the growth of other microorganisms of higher resistance and most importantly, prevents recontamination and pathogens from producing toxins during storage.

Today, the demand for processed foods goes beyond the fundamental requirements of safety and shelf-stability. More emphasis is being placed on informatively labeled, high-quality, and value-added foods with convenient end use. Improvements in quality and safety of processed foods have been achieved through regulatory requirements on manufacturers, and national or international legislature that recommend and/or enforce performance standards or methods for achieving safety and quality assurance. Equally important is the fact that the need for affordable, yet, high value-added products has been driven by the consumer.

Conventional canning operations have the tendency to induce permanent changes to the nutritional and sensory attributes of foods. Therefore, recent developments in food processing operations have aimed at technologies that have the potential to substantially reduce damage to nutrients and sensory components by way of reduced heating times and optimized heating temperatures.

Over four decades ago, thin-profile and agitated retorting were developed to promote rapid heating to minimize the impact

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of heat on quality attributes. The retortable pouch has re-emerged as a packaging alternative for both conventional and aseptically processed foods. Aseptic processing and packaging was developed to minimize the heat severity even further by rapid heating and cooling of the food prior to packaging under aseptic conditions to further sustain the nutrient and quality of the food. Quite recently, alternative or novel food processing methods (both thermal and non-thermal) have emerged and are being explored to produce safe and better quality foods. These alternative technologies which include but are not limited to: high-pressure processing, pulsed electric field, pulsed X-ray or ultraviolet light, ohmic heating, radio frequency, microwave, pulsed light, and oscillating magnetic fields could potentially replace conventional thermal processes for some products. The food industry is actively involved in these developments, and poised to adopt new technological alternatives that offer competitive advantages. Each of these alternatives has to be challenged in terms of microbiological capabilities, safety, efficiency and overall quality for acceptance as a mainstream technology. This paper focuses on the fundamental principles of thermal processing with emphasis on quality enhancement as it relates to both conventional and alternative technologies that employ heat.

2. Principles of thermal processing

Thermal destruction of microorganisms is traditionally established to take place following a first order semi-logarithmic rate. Therefore, theoretically, a sterile product cannot be produced with certainty no matter how long is the process time [1]. Targeting a product that is completely void of microorganisms would render the product unwholesome or inferior in quality. Industrially, thermal processes are designed by processing authorities to provide commercially sterile or shelf-stable products. Commercial sterility (as defined by the United States Food and Drug Administration (FDA)) or shelf-stability (U.S. Department of Agriculture (USDA)) refers to conditions achieved in a product by the application of heat to render the product free of microorganisms that are capable of reproducing in the food under normal non-refrigerated conditions of storage and distribution. Designing a sound thermal process requires extensive understanding of process methods, the heating behavior of the product and its impact on a target microorganism. Thus, the severity of any thermal process [1] must be known and depend on factors such as: (i) the physical characteristics of the food product including thermo-physical properties, shape and size of the container holding the product, (ii) the type and thermal resistance of the target microorganisms that are likely to be present in the food, and (iii) the pH, water activity (a_w) and salt content of the food.

Changes in the intrinsic properties of food, mainly salt, water activity and pH are known to affect the ability of microorganisms to survive thermal processes in addition to their genotype. Due to health-related concerns on the use of salt, there is increased demand to reduce salt levels in foods [2]. The United States Food and Drug Administration (FDA) has classified foods in the federal register (21 CFR Part 114) as follows: (i) acid foods, (ii) acidified foods and (iii) low acid foods. Acid foods are those that have a natural pH of 4.6 or below. Acidified foods (e.g., beans, cucumbers, cabbage, artichokes, cauliflower, puddings, peppers, tropical fruits and fish) are low acid foods to which acid(s) or acid foods are added with a water activity greater than 0.85 and a finished equilibrium pH of 4.6 or below. Low-acid foods have been defined as foods, other than alcoholic beverages, with a finished equilibrium pH greater than 4.6 and a water activity greater than 0.85. Scientific investigations [3] have revealed that spores of *Clostridium botulinum* will not germinate and grow in food below pH 4.8. To provide sufficient buffer, a pH of 4.6 has generally been accepted as the point below which *C. botulinum* will not grow to produce toxin. Thus, a pH of 4.6 represents a demarcating line between low and high acid foods. During thermal processing of low acid foods (pH $\geq$ 4.6), attention is given to *C. botulinum*: the highly heat resistant, rod-shaped, spore-former that thrives comfortably under anaerobic conditions to produce the *botulism* toxin. Commercial sterility is achieved when *C. botulinum* spores are inactivated to satisfy regulatory requirements. However, other heat resistant spores (generally referred to as *thermophiles*) such as *Clostridium thermosaccolyaticum*, *Bacillus stearothermophilus*, and *Bacillus thermoacidurans* have the potential to cause spoilage and economic losses when processed cans are stored under "abuse" storage conditions of temperature. However, *thermophiles* would be of no consequence provided one can guarantee that processed cans would be stored at temperatures below 30 °C.

2.1. Establishing a thermal process

Thermal processes are established based on two premises: (i) the heat resistance of microorganisms for each specific product formulation and composition, and (ii) the heating rate of the specific product. Procedures used to experimentally evaluate the thermal resistance kinetics of microorganisms are summarized in [4]. In addition, the USDA has designed "The Pathogen Modeling Program" as a research and instructional tool for estimating the effects of multiple variables on the growth, survival and inactivation of foodborne pathogens in liquid foods (http://www.arserrc.gov/mfs/pathogen.htm). The program, which is based on mathematical modeling of experimental data, can serve as a useful resource for understanding the impact of pH and temperature among others, on relevant pathogens to the food industry. Users of such programs should be reminiscent of the conditions for which such models apply and their limitations since food matrices are complex and can influence microbial resistances in different ways. Determination of the heating rate of a product is accomplished from a detailed analysis of parameters (both product and system) that have the potential to affect the heating behavior of the product. The two factors described above are well established for conventional thermal processes, and therefore, could be used as a benchmark for establishing and validating scheduled emerging technologies that generate heat in the product.

2.2. Thermal inactivation kinetics

Thermal inactivation kinetics of microorganisms are obtained by first establishing a survivor curve, which is a logarithmic

plot of the number of microorganisms surviving a given heat treatment at a given temperature against the heating time. This pre-supposes that microbial destruction generally follows a first order reaction. Two key parameters (D and z values) are then determined from the survivor and resistance curves, respectively. The D-value represents a heating time that results in 90% reduction of the existing microbial population. This is expressed mathematically as follows:

$$D = \frac{t_2 - t_1}{\log(A) - \log(B)} \quad (1)$$

where A and B represent the survivor counts following heating for times t_1 and t_2 minutes. The first order reaction rate constant (k) is obtained from the expression $k = 2.303/D$. The temperature sensitivity (z-value) which represents the temperature change that results in a 10-fold change in the D-value, is represented mathematically as follows:

$$z = \frac{T_2 - T_1}{\log(D_1) - \log(D_2)} \quad (2)$$

where D_1 and D_2 are D values at temperatures T_1 and T_2, respectively. These are shown in Fig. 1. An alternative to the D–z model for describing temperature dependence is the classical Arrhenius equation (referred to as the k–E_a model), which relates the reaction rate constant (k) to the reciprocal of the absolute temperature (T) as follow:

$$\log\left(\frac{k_1}{k_2}\right) = \left[\frac{-E_a}{2.303R}\right]\left[\frac{T_2 - T_1}{T_2 T_1}\right] \quad (3)$$

where E_a is the activation energy and R is the gas constant. Both the D–z and k–E_a models have been used extensively to describe temperature effect in kinetic data analysis. It should be recognized however that both concepts are at variance since the D–z model relates k directly to temperature while the k–E_a model relates inversely to temperature. It has been demonstrated that the inter-conversion of factors (E_a and z) from one concept to the other outside the temperature limits over which experimental data were gathered can lead to discrepancies. Good conversions of literature data with minimum errors were obtained using the relationship [5]:

$$E_a = \frac{2.303 T_{min} T_{max}}{z} \quad (4)$$

where T_{min} and T_{max} represent the minimum and maximum temperatures, respectively.

The D–z model predicts greater lethality values than the k–E_a model for temperatures below $T_{ref} = 121.1\,^{\circ}C$ and vice versa. However, some experts recommend the D–z concept for monitoring and validating sterilization processes [6]. Alternative technologies can use similar concepts in establishing kinetic parameters.

It is important to note that non-isothermal heating conditions may be associated with some heat treatments that need to be accommodated when evaluating kinetic data. Typically, the food constituent experiences a transient temperature regime, which makes it more complex than isothermal procedures. Hence, a lag correction factor is properly applied to the heating time to account for the heating lag [7–9] associated with non-isothermal heating conditions. For instance, numerical integration of lethalities for *Escherichia coli* (*E. coli*) inoculated in agar [10], apple juice [11], pectin methylesterase (PME), *Saccharomyces cerevisiae* and *Lactobacillus plantarum* in fruit juices [12] have been used for predicting thermal inactivation effects during microwave heating. Apparently, novel technologies (both thermal and non-thermal) need extensive kinetic data for key pathogens of concern and appropriate surrogates in establishing their effectiveness and significance in preserving foods. Selected kinetic data based on the assumption that microbial inactivation follows a first order reaction are shown in Table 1.

Deviations from the first order reaction (commonly referred to as the *mechanistic* approach) have been reported extensively in the literature that indicates that the semi-logarithmic survival curves of some organisms may have an upward or downward concavity. In other words the semi-logarithmic curve may have a "shoulder" and/or "tail". The tailing could result from (i) a small number of large clumps of cells in a population, (ii) differences in cell heat resistances and (iii) variations in life cycle or potential heat adaptation [13–16]. The presence of shoulders has been attributed to microbial populations that consist of several sub-populations (with each population have its own inactivation kinetics), clumping of cells and poor heat transfer or multiple targets within a cell.

The *vitalistic* approach is based on the assumption that the exponential decay of microorganisms could be explained by dif-

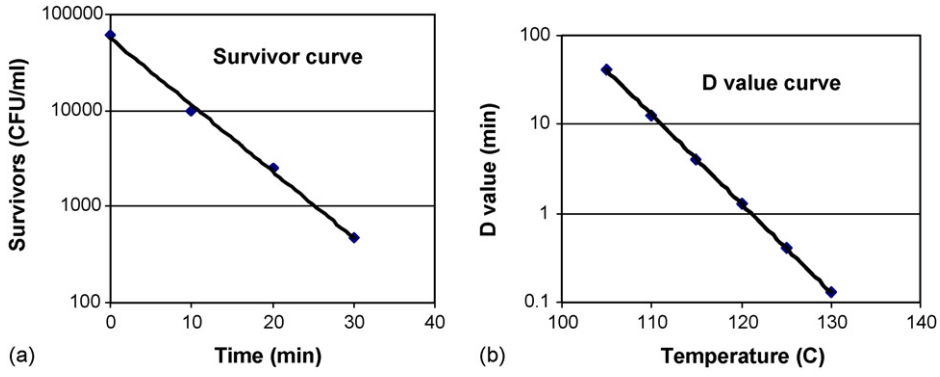

Fig. 1. (a and b) Typical survivor and D-value curves.

Table 1
Kinetic data on thermal destruction of microbial spores

Organism	Temperature range (°C)	pH	T_{ref} (°C)	D (s)	z-Value (°C)
Bacillus stearothermophilus					
TH 24 aqueous	120–160	–	120	1000	7.3
TH 24 milk	120–160	–	160	0.32	11.2
ATCC 7953 water	121	–	121	33.6	8.0
ATCC phosphate buffer	111–125	7	121	126	8.5
NCA 1518 skim milk	128–140	–	128	134	7.8
NCIB 8710 phosphate buffer	100–140	7	121	210	12.1
FS 128 buffer	110–135	7	110	10^4	7.7
FD 7954 water	105–120	–	121	138.2	10.43
Bacillus subtilis					
5230 aqueous	105–132	6.6	121	6.0	8.3
5230 aqueous	100–110	–	100	698	7.6
5230 aqueous	124–140	–	121	30.3	14.1
9372 aqueous	100–148	120	0.003	3.7	
A skim milk	112.5–135	–	112.5	20	8.8
Clostridium botulinum					
Type C aqueous	93–104	–	104	60	5.6
Type A aqueous	115.6–121	–	121	1.2	10
213 phosphate buffer	120–140	7	120	8.75	10
213B carrot	104–116	–	107	143.9	11.3
213B corn	104–116	–	110	92.1	11.1
A35B phosphate buffer	105–115.5	6.8	121	19.2	10.8
Clostridium thermosaccharolyticum					
S9 McIlvaine spore form	99–127	–	121	51	14.7
S9 acid spore form	99–127	–	121	192	9.76
S9 water	124–132	–	132	4.4	6.89
S9 molasses	124–132	–	132	3.3	10.2
Tree bark compost	115.5–127	–	121	4080	11.5
Putrefactive anaerobe					
PA 3679 white corn purée	110–127	4.5	121	230	8.8
PA 3679 distilled water	115.5–143.3	–	115.5	39	10.4
PA 3679 aqueous	110–132.2	–	121	48	9.8

Adapted from Holdsworth [21].

ferences in resistance or inactivation kinetics. This approach has been challenged to ignore the rigorous stochastic basis for inactivation transformation with the assumption that biological variability in resistances can explain observed behavior correctly [17].

Some researchers are of the view that the non-linearity associated with some semi-logarithmic curves is unlikely to result from a mixed population or experimental artifacts as traditional explanation claims. An alternative explanation to non-linearity is that the survival curve is a cumulative form of a temporal distribution of lethal events [18]. Furthermore, the semi-logarithmic survival curves are reflections of the heat resistance distributions having a different mode, variance and skewness, but not of different mortality kinetics of different orders [18]. The concept of having survival curves to follow a distribution of events has been referred to as the *probabilistic* approach. The *probabilistic* approach is also challenged due to complications arising from spore inactivation. Spores could be in a dormant state that cannot be readily inactivated. To initiate growth, these spores need to be activated. The inactivation of viable, dormant spores differs from that of activated spores [19]. Therefore, observed effects represent a mixture of kinetics of spore activation and of spore inactivation. Other researchers who argue against the *probabilistic* approach are of the view that arbitrary use of frequency distribution equations such as the Weibull model represents an extensive jump in logic that cannot be rigorously justified [20].

Using a log-linear model for a non-linear survival curve will have serious implications and potential health-related risks when the D-value is underestimated (i.e., when the survival curve has a downward concavity). In other words, a scheduled process determined with underestimated D-values may not provide commercial sterility. A log-logistic model demonstrated this [21] and indicated that processes below 111 °C that were deemed to be equivalent to a 121 °C process (that was developed with kinetic data from the log-linear model) delivered less reduction in *C. botulinum* 213B spores. For over-estimated D-values on the other hand, the product will be over-cooked with inferior sensory and nutritional attributes. Therefore, the D–z concept becomes problematic when experimental semi-logarithmic curves indicate non-linearity [22].

Several alternative models to the *mechanistic* approach as well as opposing views in terms of the behavior/survival of microorganisms exposed to lethal agents have been reported in

the literature with supporting experimental data to demonstrate validity. However, it is becoming increasingly evident that a single "fit-all-data" model may not be unique in describing the complex behavior of microorganisms to external agents (such as temperature, salt, pH, etc., and their interactions). The bottom line will be the need for models that are robust in design, simple to use, flexible in terms of its use in process deviation analysis, and above all, provide appropriate levels of public safety.

Although limitations associated with the *mechanistic* approach have been reported, it should be mentioned that the impressive food safety record in the industry somewhat supports is use. Similarly, inoculated pack studies and the absence of failures support the classical log-linear model. Proponents against the classical first order equation could also argue that the additional safety margins built into scheduled processes may have contributed to the impressive safety record enjoyed by the canning industry.

Given current information on the nature of survival curves, the impact of emerging/novel technologies on (i) the behavior of microorganisms, (ii) the sensitivity of the methodology used determining microbial survival, and (iii) the need to optimize processes would certainly change the way inactivation kinetics data are analyzed and reported by researchers.

2.3. Kinetic models describing non-linearity in survival curves

An attempt to cover all non-linear models (with a detailed description of all related formulae, assumptions and potential limitations) falls outside the scope of this review. However, an attempt will be made to cover some of the models while references for others are cited.

Lambert [23] used the motifs of chemical reaction kinetics to develop the empirical $\log R$–fa_t double Arrhenius model that was used to describe the inactivation curves of published data. The five-parameter empirical $\log R$–fa_t model is defined as:

$$\log R = M[1 - \exp(-10^{[P_2-(P_1/T)]}t^{[P_3-(P_4/T)]})] \quad (5)$$

where $\log R$ is the decimal reduction in microbial numbers, T the temperature in Kelvin, M the maximum log reduction achievable, t the time, and P_1 to P_4 represent experimentally derived factors. The $\log R$–fa_t model provided excellent description of data for *Salmonella anatum* at 55 °C, *Pseudomonas viscos*e at 48 °C, *Streptococcus faecalis* at 60 °C, *C. botulinum* spore at 101–121 °C, and *Bacillus stearothermophilus* spores at 105–121 °C [23].

The Weibull model has been used extensively and described as one of the key models with capability to describe the non-linearity associated with semi-logarithmic survival curves. The model is basically a statistical model of distribution of inactivation times, with the classical first order equation (*mechanistic* approach) representing a special case when the shape factor (n) equals to unity [16]. The Weibull model is given as [13,16,24]:

$$\log_{10} S = -bt^n \quad (6)$$

where S (N_t/N_o) is the survival ratio at time t, and b, n are constants. When the shape factor (n) is less than unity ($n<1$) the semi-logarithmic curve will have upward concavity. At $n>1$, the curve will have a downward concavity. The validity of the Weibull model in terms of fitting experimental data could be tested by (i) performing a double logarithmic plot of [ln(−ln S)] against [ln t] for linearity, (ii) studying the residuals for random distribution and (iii) using the χ^2-test [16]. Estimated b and n values could be used to calculate the distributions mean, mode, variance, the coefficient of skewness as well as the sensitivities/resistance frequency curve using the following equation [18]:

$$\frac{d\Psi}{dt} = bnt^{n-1}\exp(-bt^n) \quad (7)$$

where Ψ is the fraction of organisms at any given time t. If the constants b and n are determined using Eq. (6), then the generated distribution of resistances may result in an exaggerated fraction of the most resistant survivors, especially when the distribution curve is strongly skewed to the right [16,18]. The temperature sensitivity of both b and n for several vegetative organisms has been evaluated which shows that the temperature dependence of the shape factor (n) was not clear-cut [16]. The scale parameter (b) on the other hand showed a temperature dependence that could well be defined by an exponential relationship [16]. The shape factor (n) in most cases was found to be greater than unity which suggested that the remaining cells have the tendency to become weaker when heating time increases [16]. It is prudent to emphasize that the temperature dependence of the shape factor (n) needs to be explored for process determination purposes if the Weibull model is adopted.

Using survival data from the literature, the shape factor (n) and scale parameter (b) were modeled as follows for *C. botulinum* at temperatures greater than 100 °C ($T \geq 100$ °C) [25]:

$$n(T) = \frac{1 - (T - 100)}{0.696 + 1.44(T - 100)} \quad (8)$$

$$b(T) = -14.1 + 0.005T^{1.73} \quad (9)$$

The authors used the above models and computer-simulated heating curves to demonstrate how the Weibull model could be used to assess the efficacy of the heating stage in a sterilization process. Similar relationships for *Listeria monocytogenes* were reported by [26]. Regression model can accommodate situations where n and b depend on factors, such as pH, temperature, salt concentration, water activity and pressure.

For non-isothermal heating conditions, Peleg et al. [26] presented a modified version of the Weibull model in the form of a differential equation that accounted for time–temperature dependent b and n values. For non-isothermal treatment or any lethal agent of varying intensity, the actual survival curve can be obtained from the isothermal curves on conditions that growth and damage repair does not occur during the heating process, and the momentary inactivation rate is only a function of the momentary agent intensity and survival ratio [22,26].

The Whiting and Buchanan model, which describes the sigmoidal trend associated with survival curves was coupled to both heat and mass transfer equations in evaluating the inactivation of *Enterococcus faecium* during bologna sausage cooking [27]. The authors found the Whiting and Buchanan model to provide realistic results when compared to the first order kinetic model which over-estimated lethality at the sausage core. Thermal inactivation models including that of Sapru et al. [28], Shull et al. [29], Rodriguez et al. [30], and the first order kinetic equation were compared by [19]. The Sapru model could potentially replace the conventional (first order) model for predicting and validating lethalities that incorporate activation and inactivation of dormant spores as well as inactivation of activated spores [19]. The authors indicated that the Sapru model is important for processes of shorter duration such as thin-bodied liquids in continuous agitated retorts, and liquids in heat exchangers and holding tube during ultra high-temperature processing. Linton et al. [31] used a modified Gompertz equation to model non-linear survival curves for *Listeria monocytogenes* Scott A at three pH and NaCl levels and concluded that the Gompertz equation agreed closely to experimental data. The modified Gompertz equation (Eq. (10)) consisted of three parameters that were estimated using the non-linear regression procedure [31]:

$$\log S = C\mathrm{e}^{-e(A+Bt)} - C\mathrm{e}^{-eA} \tag{10}$$

The coefficients A, B and C were developed as polynomial equations that included temperature, pH and NaCl concentration. Using this approach, the authors were able to evaluate the interactive effects of pH, temperature and NaCl concentration on the survival of *Listeria monocytogenes*. In another related study using the modified Gompertz model for *L. monocytogenes* in infant formula, Linton et al. [32] recommended the need to re-evaluate the 4D reduction in *L. monocytogenes* for minimally thermal processed foods since microbial response to heat does not always conform to the first order kinetic equation. In a recent study using data from the work of [32], Xiong et al. [33] compared the prediction performance of the modified Gompertz equation to the Baranyi model and concluded that the Baranyi model can predict commonly observed survival curves involving the initial lag phase, linear and tailing, as well as sigmoidal curves. It performed better and is more robust than the modified Gompertz model [33]. For other models and their applications, the reader is referred to the work by [34–36].

2.4. Lethality requirements for thermal processes

Traditionally, estimated kinetic data (using the classical first order equation) are linked to the time–temperature history at a pre-defined location (cold spot) within the product to evaluate the sterilizing value or otherwise "process lethality" (F_o), which forms the basis for a sound thermal process [37]:

$$F_o = \int_0^t 10^{(T-T_o)/z}\mathrm{d}t \tag{11}$$

where t, z, T and T_o represent the time (min), temperature sensitivity of the target microorganism, temperature at any given time, and reference processing temperature, respectively. The reference temperature is conveniently chosen to be 121.1 °C (250 °F) for low acid foods.

Two approaches could be used to evaluate the impact of time–temperature combinations on process lethality: (i) target lethality (F_o) at the coldest spot of the product as defined by Eq. (11), and (ii) an integrated lethality (F_s) which represents the volume average of microbial survival [4]. Process integrated lethality (F_s) is evaluated as:

$$F_s = D_o \log\left[\frac{1}{V}\int_0^V 10^{\left[-(1/D_o)\int_0^t 10^{(T-T_o)/z}\mathrm{d}t\right]}\mathrm{d}V\right] \tag{12}$$

where V is the volume in cubic meters, D_o the D-value at the reference temperature T_o, and z is the temperature sensitivity for the target microorganism. The ultimate goal in achieving commercial sterility is to ensure that the ratio of F_o to F_{req} (required lethality) is at least, equal to unity. Low acid foods must experience the minimum "bot cook" ($F_o = 3$ min) which is 12D cycle reduction based on kinetic data for *C. botulinum* [38]. However, processes are designed to consider both public health (12D) and spoilage organisms. The reason for this is the occurrence of more heat-resistant spoilage organisms that are not of public health concern [39], but could cause economic losses. Pasteurization, which is a relatively mild heat treatment in which food is heated to temperatures below 100 °C, is used to minimize public health hazards and to extend the useful shelf-life of foods for several days. Again, the required lethality to be achieved is dependent on the organism of public health concern. For example, milk pasteurization is based on 12D cycle reductions in the numbers of *Coxiella burnetti* [40], while whole egg is heat treated to provide a 9D cycle reductions based on *Salmonella seftenberg* [41]. Since the logarithmic of the survival ratios used in establishing the D-values in the past usually covered 5–7 decimal reductions, the question of extrapolating data to 12 decimal reductions has been raised [35].

Different time–temperature combinations, and obviously different processing methods, systems or techniques could be employed to achieve required lethality. Such systems and related time–temperature histories would affect the quality of the end product to different extents. Therefore, minimum changes to the sensory and organoleptic attributes of food products are always sort through process optimization routines to determine system appropriateness using kinetic data for the most heat sensitive nutrient. The time–temperature history of a product undergoing thermal treatment will depend on several factors that include but are not limited to: (i) the processing system (conventional (static or agitating retorts, hydrostatic retorts)) or aseptic systems, (ii) the heating medium (steam, water immersion, water spray, or steam/air mixtures), (iii) product characteristics including consistency, solid/liquid ratio, and thermophysical properties, (iv) product initial and heating medium temperatures, and (v) container type, shape and size. Using information gathered from heat penetration studies, heating rate data (Fig. 2) are determined and used in designing a thermal process schedule.

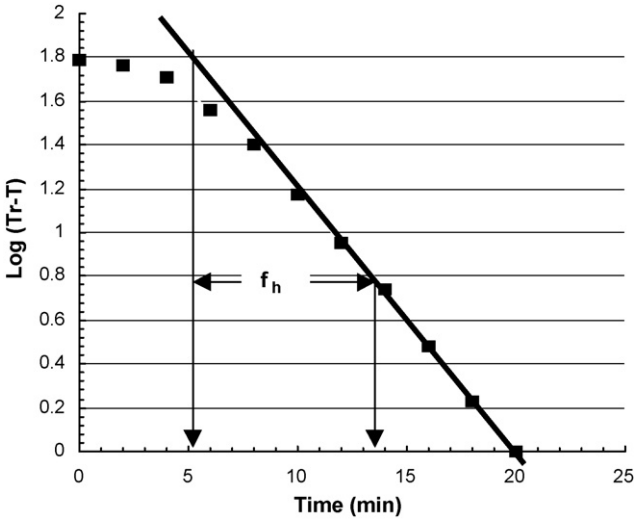

Fig. 2. Typical heat penetration curve.

2.5. Thermal process schedule

A thermal process schedule is established from the product time–temperature history (heat penetration data) and kinetic data (z and F_{req} values) by the general or improved general methods (Eq. (11)). For flexibility in terms of establishing times required to achieve expected cumulative lethality (or vice versa), several formula methods [42–46] have been developed, with the Ball formula method persisting as the most widely used in the food processing industry. The Ball formula method which is derived from the heat penetration curve, is defined as follows:

$$B_B = f_h \log\left[\frac{j_{ch}(T_r - T_i)}{g}\right] \tag{13}$$

where B_B is the process time (min), f_h the heating rate index (min), j_{ch} the lag factor, T_r the retort temperature, T_i the product initial temperature, and g is the number of degrees below retort temperature at the slowest heating point in the container at the end of the heating process. Although the Ball formula method is still being used, the method developed by Stumbo [4] eliminated most of the assumptions made in Ball's method and performs better for estimated lethalities for conduction-heating foods under various conditions [47]. The formula methods have played a useful role in determining the process time or cumulative lethality and vice-versa. However, there are some difficulties for them to be used in optimizing system parameters and automatic control systems since they cannot describe dynamic functions during the whole processing [48]. For a detailed description of the formula methods, the reader is referred to additional information in [6,39,49].

The Ball formula method allows the process time to be estimated for target F_o values (that embodies the D–z concept) and vice versa. For non-linear semi-logarithmic curves that dispute the validity of the D–z concept, new models are necessary to verify the efficacy of the heating cycle during sterilization. An approach using the Weibull model was illustrated by [25] using the relationship:

$$\log_{10} S(t) = -b(T(t))t_{req}^{n(T(t))} \tag{14}$$

First, the temperature dependence of both $n(T)$ and $b(T)$ of the Weibull model (e.g., Eqs. (8) and (9)) have to be established experimentally. Second, the time–temperature history ($T(t)$) at the coldest spot need to be determined experimentally or modeled to describe the heating profile. Knowing the temperature profile $T(t)$, $n(T)$ and $b(T)$, the degree of survival can be calculated using Eq. (14). The time (t_{req}) required to achieve a target lethality (e.g., Φ decimal reductions in microbial population) is obtained by replacing ($\log_{10} S$) in Eq. (14) with the negative of Φ and solving iteratively for t_{req}. Depending on the model defining the $n(T)$, $b(T)$ relationship, Eq. (14) could yield complicated expressions. According to [55] the above approach could be used to estimate the efficacy of a process, provided the condition of path independence is fulfilled or the simulation is treated as a limiting case. The time needed to achieve a target log cycle can also be determined using Eq. (15) that was derived from the Weibull model [16]:

$$t_{ref} = b(-\ln(10^{-\Phi})^{1/n}) \tag{15}$$

Artificial intelligent techniques such as artificial neural networks (ANN) have recently been used as a tool to computerize mathematical procedures for thermal process calculations. ANN models that correlate heat penetration and kinetic data in Stumbo's tables for thermal process evaluations [50] have been studied. The models eliminate the need for a large storage space while computerizing Stumbo's method [50]. Chen et al. [48] used two modeling approaches (a moving window-ANN and hybrid-ANN models) for modeling both lethality (F) and quality (Q) dynamic functions for constant retort temperature (CRT) processing. They concluded that the moving-windows network (a special hierarchical network used to model dynamic systems and unsteady-state processes) had better performance than the hybrid-ANN model.

Process determination for continuous flow systems such as high-temperature short-time (HTST) involve the determination of the minimum holding tube length (L) required to inactivate a target microorganism in a given time (t) at the process temperature. For a power law fluid under laminar flow conditions for instance, the holding tube length is determined as follows:

$$L = t\left(\frac{3n+1}{n+1}\right)V_{mean} \tag{16}$$

where n is the flow index behavior and V_{mean} is the average velocity. Again, for organisms that disobey the first order reaction equation, the time (t) should be derived from the appropriate non-log-linear relationship since HTST processes are comparatively short.

It is important to emphasize that for direct heat exchangers such as steam infusion or steam injection, the appropriate correction factors need to be determined and applied in sizing the holding tube to account for increase in volume and flow rate of the product. As a rule of thumb, approximately one pound of steam will condense for every 10 pounds of product heated,

giving a product dilution rate of 10% [51]. The product is flash evaporated in a vacuum chamber to remove excess water. In addition, the impact of added steam should be considered during product formulation.

The application of artificial neural networks to thermal processing has gained widespread popularity and poised to become a mainstream tool for process evaluation. However, limited or no information has been presented for situations where the semi-logarithmic survival curve is non-linear and modeled to follow a somewhat complex profile. Aseptic processing of foods including those containing discrete particles is one key area where the concepts of ANN can be applied to model the interactions of both system and product parameters to further optimize quality and cost.

3. Effect of thermal processing on quality attributes

Thermal processing techniques emphasize the achievement of commercial sterility while minimizing changes in nutritional value and eating quality. However, no matter how minimal the heating source is, thermal processing can promote reactions that could affect overall quality of foods. Quality loss involves both subjective factors like taste that cannot be readily quantified, and quantifiable factors such as nutrient degradation. Quantifiable factors need to be evaluated using principles that allow comparison and consistency to be made and established for the entire product. Similar requirements in addition to microbiological capabilities would be required from non-thermal alternatives that promise high-quality products.

3.1. Principles of quality loss determination

D and z-values of some nutrients are given in Table 2. Differences between the D and z-values of microorganisms and nutrients (Tables 1 and 2) are exploited to optimize thermal processes. The z-values for cooking and nutrient degradation (25–45 °C) are generally greater than microbial inactivation (7–12 °C). For every 10 °C rise in temperature, the cooking rate generally doubles while the sterilization rate increases 10-fold [6]. A graphical representation of the effect of different time–temperature combinations on vitamin retention and microbial inactivation for HTST and conventional canning has been shown in Holdsworth [6]. The HTST concept has been very successful for milk and fruit juices, while alternative processing techniques such as microwave or ohmic heating may be explored for thicker (conduction-type heating) materials to overcome the problems of consistency (viscosity) with conventional canning operations [6].

A common relationship for estimating quality losses is the "Cook or C values" which was originally proposed by Mansfield [52] for aseptic processing of low-acid foods:

$$C = \int_0^t 10^{(T-T_{\text{refq}})/z_q}\,\mathrm{d}t \tag{17}$$

where z_q and T_{refq} represent the z-value and reference temperature for the most heat labile component. For convenience the reference cook value is characterized by $z_q = 33.1$ °C and $T_{\text{refq}} = 100$ °C and designated as C_o. In terms of quality evaluation, Eq. (17) is of little interest since it focuses on a single point. Instead, the mass-average cook value (C_{mavg}) is preferred and more appropriate for characterizing the impact of different time–temperature combinations on heat sensitive nutrients. A maximum range in the region of 100–200 min is commonly considered as the range beyond which quality is said to be impaired. The mass-average cook value is defined as:

$$C_{\text{mavg}} = D_{\text{ref}}\log\left(\frac{N}{N_o}\right) \tag{18}$$

where N, N_o and D_{ref} refer to the concentration of the nutrient at time 0, time t, and reference D-value, respectively. The N/N_o ratio is defined as follows:

$$\frac{N}{N_0} = \frac{1}{D_{\text{refq}}}\int_0^t 10^{(T-T_{\text{refq}})/z_q}\,\mathrm{d}t \tag{19}$$

For canned foods, Eq. (17) is integrated over the entire volume to give the volume-average cook value. The concept of volume-average cook value could be implemented indirectly by numerical routines for different container shapes. The volume-average cook value for a container of volume V is:

$$C_{\text{vavg}} = \frac{1}{V}\int_0^t\int_0^V 10^{(T-T_{\text{refq}})/z_q}\,\mathrm{d}t\,\mathrm{d}V \tag{20}$$

The above equation shows that the volume-average cook value (referred to as the objective function) is independent of the reference D-value. However, a better measure of heat on nutrients would be the dependence of the mass-average cook value on the reference D-value [53]. The author categorized commonly used objective function evaluation into two: (i) minimization of

Table 2
Kinetic data on thermal destruction of quality factors

	Temperature range (°C)	T_{ref} (°C)	D (s)	z-Value (°C)
Vitamin A				
Beef liver purée	103–127	122	2.40	23.0
Carrot juice	104–132	104	23.60	25.5
Vitamin B_1, thiamin				
Buffer solution pH 6	109–150	109	9.50	24.0
	109–150	150	0.20	24.0
Vitamin B_6				
Pyridoxine hydrochloride				
Pyridoxie model sol.	105–133	118	54.8	22.0
Pyridoxamine	105–133	118	20.9	26.0
Pyridoxal	105–133	118	15.0	30.0
Vitamin C, ascorbic acid				
Peas	110–132	121.1	50.0	18.2
Grapefruit juice11.2° brix	61–96	96	53.0	130.0
Grapefruit juice 62.5° brix	61–96	96	8.2	57.5
Spinach var. Fruhjahr	70–100	100	25.9	74.4
Spinach var. Herbst	70–100	100	1.07	91.2
Model solution				
Buffer pH 4	30–100	100	4.07	31.9
	110–127	120	31.2	39.4

Adapted from Holdsworth [21].

the cook value (Eq. (20)), and (ii) maximization of quality retention. The quality retention alternative (Q/Q_o), which involves both the reference D and z-value is as follows:

$$\frac{Q}{Q_o} = \frac{1}{V}\int_0^V 10^{-(1/D_{ref}V)\int_0^t 10^{(T-T_{ref})/z_q}dt}dV \quad (21)$$

The two concepts [53] of evaluating product quality are equivalent for high-reference D-values (>150 min). However, the average cook value can significantly underestimate the optimal processing temperature for quality retention for low reference D-values [6,53]. Thus, the average cook value concept becomes inferior to the volume average quality retention approach because processing times will have to be increased for underestimated optimal process temperature. With the wide variations in biological materials (e.g., age, variety, weather conditions during growth, etc.) and potentially different chemical reactions that could take place even for the same commodity, reported kinetic data for quality losses may exists for cooked foods, especially those processed at elevated temperatures.

3.2. Process design and quality optimization

The application of heat to inactivate pathogens and spoilage organisms cause undesirable changes to sensory and nutritional attributes. Since safety is the primary concern, thermally processed foods are constrained by the requirement to achieve the target lethality at the coldest spot. The mass-average cook value or retention concepts coupled with process optimization routines, and recent computer modeling capabilities provide a strong scientific background for maximizing quality retention. Factors typically considered in optimization routines may include the maximum practical operating temperature, the minimum degradation of nutrients and organoleptic attributes that could be tolerated in terms of product marketability, and most important of all, the primary constraint of meeting the required lethality.

Obviously, sound mathematical models involving constraints, objective function(s), and appropriate algorithms are needed to characterize quality retention problems. Several authors [54–57] have presented optimization theories, techniques, their relevance and implementation in the food industry. An Integrated Control Random Search (ICRS) algorithm was developed [58] for evaluating three objective functions: (i) the minimum process time, (ii) the maximum overall nutrient retention and (iii) the maximum retention of a quality factor at the surface of the product. The conclusion drawn was that, the use of a variable temperature profile was advantageous for the maintenance of optimum surface quality. Similar studies on the effect of variable retort temperature on surface quality by Noronha et al. [59] indicated that variable temperature profiles improved surface quality by up to 20% compared to a constant temperature retort profile. A change from constant to time-variable retort temperature could increase canning capacity by 20–50% depending on product specifications [60]. The authors used a transient energy balance model that allowed the identification of feasible time–temperature profiles for reduced energy consumption, total process time or both, retort type, process lethality, and quality retention. An empirical equation for determining optimal temperatures that minimize surface quality and nutrient losses has been presented for retorts [61,62], and extended to accommodate the effect of the cooling phase and infinite heat transfer coefficient for simple geometric shapes (sphere, infinite cylinder and slab). The empirical equation is of the general form:

$$T_{op} = a + b\log\left(\frac{F_t}{f_h}\right) + c\ln z_q + dT_o \quad (22)$$

where T_{op}, F_t, f_h and z_q are is the optimal temperature, the sterilization value (lethality) constraint, the heating rate index and z-value for the heat labile nutrient, respectively. The coefficients a, b, c and d are 86.68, 9.73, 10.46 and 0.025, respectively. For a *finite* surface heat transfer coefficient (h) (which can be expected to be valid for either water immersion or steam/air mixtures), the optimal heating medium temperature that maximizes surface quality retention ($(T_{op\,(surf)})$ will depend on the geometry, heating rate index (f_h), the thermal diffusivity (α) and conductivity (k), the Biot number ($Bi = h/Lk$), the z_q-value for the target quality factor, and the target sterility value (F_t) as follows [63]:

$$T_{op(surf)} = a + b\log\left(\frac{F_t}{f_h}\right) + c\ln z_q + \frac{d}{Bi} + \frac{ez_q}{Bi} \quad (23)$$

where $a = 91.37$, $b = 9.71$, $c = 9.32$, $d = -6.58$ and $e = 1.15$ are constants for an infinite slab. According to the authors, the above equation predicts accurate optimal sterilization temperatures for maximizing surface quality of products in retort pouches, but cautioned that the accuracy will depend to a large extent on the characteristic dimension L (which is the half-dimension perpendicular to the surface where the quality retention is optimized) chosen. It is important to emphasize that the accuracy of the above equation depends on the range of variable tested, which are as follows for pouches: thermal diffusivity ($\alpha = 1.59$ to 1.65×10^{-7} m^2/s); target lethality ($F_t = 3$–15 min); heat transfer coefficient ($h = 200$–600 W/m^2 K); heating rate index ($f_h = 40$–60 min); quality factor ($z_q = 20$–45 °C); reference decimal reduction time for quality factor ($D_{refq} = 65$–500 min); and pouch height ($H/2 = 20$–23 mm).

Quite recently, Noronha et al. [64] presented simple empirical equations that were reported to reduce calculation efforts for determining variable retort temperature profiles. The application of an optimum variable temperature profile provides a unique solution for minimizing the impact of heat on nutrients. Non-uniformity in quality retention from container to container in an industrial retort can be large such that, it might be impossible to design an optimum process [65]. The authors compared mathematical simulation and experimental data and concluded that non-uniformity in retort temperature will to a large extent, overshadow process optimization. In addition to fluctuation in environmental processing parameters, variability in product thermophysical properties, and a distribution in product initial temperature will contribute to dispersion in product temperature for containers in the same batch [66]. This becomes an issue from a quality standpoint when temperature dispersion combines with irreversible quality changes to produce a permanent variability in product quality. An optimization software was used to exam-

ine the dispersion in product quality caused by variability in product thermal behavior [66]. Strategies necessary to diminish variability in the quality of discrete packaged food during thermal processing were also suggested [66]. According to the authors, thermal processes may be more profitably optimized by considering the effects of temperature on both the mean and dispersion in quality than considering the mean quality value only.

Variable retort temperature (VRT) processes whereby the temperature within the retort is modulated to follow a predefined sequence have been investigated [67] to optimize product quality and energy efficiency. This approach was first considered by Teixeira et al. [68] and later investigated by [69,70] for alternative ways of identifying optimal VRTs. Apparently, the VRT approach requires robust and accurate optimization routines in selecting an "optimized VRT" sequence. The promising results presented by Banga et al. [58] who used different objective functions and control vector parameterization (that translated the optimal control problem into non-linear programming) somewhat inspired further investigation into the potential benefits of VRT applications.

Durance et al. [71] used the random centroid optimization routine to study VRT processes for pacific salmon in 307 × 115 container. The VRT process was consistently better than the best constant retort temperature (CRT) process and reduced operator's process time and thiamine losses by 10 min and 2.8%, respectively [71]. Chen and Ramaswamy [72] coupled artificial neural network (ANN) models to genetic algorithms (GA) for optimizing process time and quality retention for VRT functions (sine and exponential) and CRT. The ANN-GA models can describe the relationship between operating variables and VRT function parameters as well reduce process time (more than 20%) and surface cook value between 7 and 10% [72]. Similar benefits of using VRT for cylindrical and spherical geometries have recently been reported [73].

Process optimization using VRT is a valuable approach when multiple quality attributes are of interest. In such situations, the objective function should be formulated in terms of maximizing final retention and not minimizing the cook values as used in single factor optimization [74]. When maximizing quality retention for multiple components the objective function to use could be [74]:

$$\text{Objective function} = \sum_{i}^{n} w_i \frac{Q^i}{Q^i_o} \tag{24}$$

where Q^i/Q^i_o and w_i represent the retention for the ith quality factor and weighted factors, respectively. Undoubtedly, a system meant to deliver VRT will require computerized temperature control modules that can monitor, control and prevent potential deviations.

Designing and optimizing thermal processes that depend on a set of complex non-linear partial differential equations (PDE's) is a daunting task and cost ineffective in terms of computation time. More importantly, real-time tasks including simulation/optimization or model-predictive control where predictions have to be completed quickly will be limited when complex equations are involved. Balsa-Canto et al. [75] used a model reduction technique based on proper orthogonal decomposition (POD) in translating a set of non-linear PDE's into a small set of differential and algebraic equations (DAEs). Translating complex optimization/control routines into simple DAEs and solving with the POD strategy can produce faster (than the numerical method of lines (NMOL), finite difference, finite elements and volume approaches) and accurate solutions, thus minimizing "time-critical" computing requirements [76] necessary for real-time industrial optimization and control applications.

Open loop control strategies were applied to determine optimal retort temperature profiles that assured required lethality while minimizing costs [77]. The costs were defined in terms retort batch time and nutrient retention. The optimal control strategy used also took into consideration the distributed nature of the system and mathematical model (for temperature distribution in the container) uncertainty due product thermal diffusivity [77]. Based on the analysis of the open optimal loop control strategy, the authors designed a full-state feedback receding horizon control (RHC) with the potential to correct for deviations between desired and measured retort temperature profiles.

Optimization methods that have been used for food-related research include (i) the Pontryagin's maximum principle theory [69], (ii) optimization algorithm based on non-linear programming [58], (iii) the Davis–Swann–Campey method [53], (iv) quadratic interpolation search of Davis–Swann–Campey method [63], (v) the quasi-Newton routine multivariable routine [64], (vi) the optimal control theory [78], and (vii) the Complex Method [74,79]. A reviewed on barriers to the use of simulation and optimization methods, and dynamic optimization applications in food process engineering has been published [80].

For optimum processing conditions, it is often desirable to assume an acceptable sterility (F_p) and a maximum cook value (C_{max}), both of which give the desired product. A safe product will then require that the actual lethality (F) will exceed F_p, while the cook value will be less than C_{max}. The sterility and quality ratios defined as $\xi_F = F/F_p$ and $\Psi_q = C/C_{max}$, respectively, could then be used concurrently to determine process adequacy. There is lack of research that validates most of the optimization models presented in the literature, especially those related to VRTs. This obviously hinders the relevance of developed models and their implementation for on-line control as well as situations where microbial survival disobeys the classical first order equation.

4. Process verification/validation

Process verification and validation is key to assure the safety of thermally processed foods. It is often desirable to confirm calculated processes using inoculated pack or count reduction procedures. Typically, the product is inoculated with an appropriate test microorganism of know resistance and subjected to various heating times at one or a number of different processing temperatures. The product is then incubated at the appropriate growth temperature for survivors. A satisfactory process would be one with no evidence of spoilage. Although microbiological validation (using surrogates) gives direct proof of product sterility, monitoring chemical changes in foods offers an excellent alternative for assessing the integrated time–temperature

exposition of foods to lethal temperatures. Several chemical indicators including thiamine hydrochloride, methylmethionine sulfonium (MMS), 2,3-dihydro-3,5-dihydroxy-6-methyl-(4H)-pyran-4-one, ascorbic acid, acid hydrolysis of sucrose and peroxidase [81–86] have been used to evaluate heat penetration, process efficacy, and quality degradation. Proposed chemical indicators for thermal process applications have been listed in [86]. The formation of chemical markers at sterilization temperatures from precursors such and D-fructose, glucose and ribose have been developed [87,88] and evaluated at 110 °C for fluid flow in a holding tube simulator [89].

Traditionally, one would typically investigate a known compound with proven consistency for evaluating changes relative to microbial inactivation. Such indicators and their mode of use must be simple, reproducible, and sensitive to experimental conditions.

5. Effect of heat on quality and nutritional attributes

Although the concern with pasteurized products is the fact that they are limited in terms of shelf-stability to a few days or weeks, minor changes to the nutritional and sensory characteristics do occur for most pasteurized foods from the mild heat treatment. For fruit juices, enzymes such as pectin methyl esterase (PME), polyphenol oxidase and peroxidase are generally present. These enzymes are capable of causing undesirable changes. Among them, pectin methylesterase is dominant and the most heat resistant in several fruits. The enzymatic browning effect has been linked to the presence of oxygen. Therefore, fruit juices are routinely deaerated prior to pasteurization. Typical pasteurization conditions for fruit juices geared towards inactivating PME and polygalacturonase are 65 °C for 30 min, 77 °C for 1 min and 88 °C for 15 s [90]. Losses in volatile aroma compounds during pasteurization of juices causes a reduction in quality and may unmask other cooked flavors [1], while other pigments from plant and animal origins are unaffected by pasteurization.

Processed food products that are stored un-refrigerated require severe heat treatment to eliminate spoilage and pathogenic microorganisms. Although some changes may be desirable, the rather harsh temperature for an extended period of time would trigger chemical reactions, and loss of nutrients and sensory characteristics such as appearance, color, flavor and texture.

5.1. Vitamins

Vitamins are among the most sensitive food component to be affected by heat sterilization. Vitamin degradation during heat treatment is not simple and dependent on other agents such as oxygen, light and water solubility. In addition, vitamin degradation depends on pH and may be catalyzed by chemicals present, metals, other vitamins and enzymes [91]. Heat sensitive vitamins are the fat-soluble Vitamins A (in the presence of oxygen), D, E and β-carotene, and water-soluble Vitamin C (ascorbic acid), Vitamins B_1 (thiamine), B_2 (riboflavin) in acid environment, nicotinic acid, pantothenic acid and biotin C [92]. In general, the largest loss of Vitamin C in non-citrus foods occurs during heating [93]. In canned juices, the loss of Vitamin C tends to follow consecutive first-order reactions; i.e., a rapid oxygen-dependent reaction that proceeds until oxygen is depleted, followed by anaerobic degradation [93]. Of the heat-sensitive vitamins, thiamine appears to have the most stable denaturation kinetics [92]. Negligible losses are associated with vitamin losses in aseptically processed milk while lipids, carbohydrates and mineral are virtually unaffected [1].

5.2. Browning

Even mild heat treatment can trigger Maillard reactions, which are a complex series of reactions between proteins and reducing sugars via Amadori re-arrangements. The initial Maillard reaction is characterized by colorless solution, but after several reactions, a brown or black insoluble compound called melanoidins are formed [94]. Although such reactions may be desirable in generating characteristic flavors identified with some cooked products, the nutritional value of the product will be compromised by protein damage and loss of amino acids, including lysine, L-arginine, and L-histidine. The loss of lysine is important due to its essentiality in diet. Maillard browning can be inhibited by decreasing moisture to very low levels or, by increasing dilution, lowering pH and temperature if the product is in the form of a liquid. Browning can also be reduced by removing one of the substrates responsible for it, which is usually, the sugar component [94]. Yamaguchi and Kishimoto [95] studied a browning reaction in retortable pouches to investigate the relationship between temperature and browning for different pouch thickness. Minimum browning was achieved at 130 °C for 20 mm, 135 °C for 15 mm and 140 °C for 8 mm thick pouch.

5.3. Proteins

The effect of thermal processing on proteins can be divided into two: those responsible for altering the secondary, tertiary and quaternary structure of proteins and those that alter the primary structure. Breaking the secondary, tertiary and quaternary structures unfolds the proteins and improves their bioavailability since peptide bonds become readily accessible to digestive enzymes. Modifications of primary protein structures [96] on the other hand may lower digestibility and produce proteins that are not biologically available.

5.4. Color

The color of processed foods plays a role by influencing consumer acceptability. Natural occurring pigments in foods are susceptible to changes or degradation from heat. chlorophylls (in photosynthetic tissues), anthocyanins (the red and blue hues associated with many fruits and vegetables), carotenoids (found in fruits, dairy products, egg, fish and vegetables) and betanins (present in red beet roots and meat) form the major classes of pigments. Chlorophylls are converted to pyropheophytin via pheophytin in fruits and vegetables, while carotenoids are isomerized from 5,6-epoxides to 5,8-epoxides which have less color

intensity. Anthocyanins are changed by heat to brown pigments. While traditional retorting can change some of these pigments due to prolonged heat exposure, high-temperature short-time operations can be expected to minimize these changes considerably. One major pigment that has been researched enormously is the chlorophyll content of green vegetables. These products would benefit from aseptic processing for better retention of green color [97].

All indications point to vitamins as the most sensitive food component that would probably continue to be used as yardstick for quality evaluation of processed foods. Notwithstanding the above observation, product-specific quality attributes will play a vital role in dictating consumer acceptance of sterilized foods.

6. Process methods for minimizing nutrient degradation

Over the years, several processing and packaging techniques have been developed to minimize the impact of heat on nutrients. These techniques somewhat deviate from the traditional batch-type still retorts were containers are stacked on racks, trays or bussee loaded prior to sterilization with either steam, water or steam/air mixtures. Variable retort temperatures, container agitation, and thin profile packages (pouches) have been considered for some of these systems to enhance the quality of conduction heating products. Novel heating alternatives that offer faster heating rates could replace convention heat exchangers for conduction heating products that heat rather slowly and have the potential to foul heat exchangers. However, the adoption of novel alternatives would require prior justification in terms of significant quality improvements and economic viability to the food processor. The following section is not intended to give a detailed overview of all available methods, but to highlight some of the techniques that could be used to enhance the quality of thermally processed foods.

6.1. Agitating retorts

These systems can be categorized into two: (i) continuous container handling systems that provide intermittent agitation and (ii) discontinuous (batch-type) container handling systems that provide both end-over-end or side-over-side container agitation. The continuous container handling systems consist of at least two cylindrical shells in which processing and cooling takes place in a continuous fashion. Special transfer valves allow containers to move from the cooker to the cooler shell without compromising temperature/pressure losses. As containers roll on the bottom of the retort shell, the product and headspace bubble moves in the container. This form of mechanical agitation enhances heat transfer by increasing the rate of heat transfer to the food product. By agitating containers, the product is uniformly distributed and quality is enhanced. Although product agitation allows higher temperatures (up to 280 °F) and reduced process times to be used, solid packed product will not benefit from this form of enhanced heating. Critical factors that need to be controlled to prevent under-processing include product consistency, headspace, fill-in weight and speed of the rotating reel that augers containers through the retort. Discontinuous container (batch-type) handling retorts allow faster rotational speeds to be implemented since containers are positively held in baskets or racks in the retort. Due to the faster speeds and increased rate of agitation, processing times are relatively shorter. For instance, a 603 × 700 can of cream style corn may receive a 20 min process at 260 °F (126.7 °C) in these retorts compared to 200 min in a still retort [3]. In general rotational retorts have been used commercially in the production of high-quality peas, corn, asparagus, mushrooms and a variety of semi-solids such as soups with particulates. Unfortunately, some products including canned pumpkin, tuna, salmon, ham and corned beef, cannot benefit from enhanced heating through container agitation. Variable retort temperatures have been proposed as a promising heating alternative for such products [67].

6.2. Thin profile processing: flexible pouches

The retortable pouch was developed during the 1960s in the USA, by a consortium of food packaging/processing companies working in conjunction with the US Army Natick Laboratories [98]. The retort pouch is a 3-ply multi-layer flexible packaging consisting mainly of polypropylene, aluminum foil and polyester. To enhance its strength, nylon has also been added as an additional layer. Pouches can withstand sterilization temperatures up to 130 °C, making it amenable to HTST operations. Coupled with its thin profile, retortable pouches allow more rapid heat transfer than cylindrical metals and glass containers of equivalent volume. Commodities that have been packed in thin profile pouches include meat curries, stews, high-quality meat products, frankfurters, ready meals, gourmet sauces, corn, green beans, slice or diced carrots. Theoretical analysis and experimental measurements of Vitamin C concentration in a three dimensional pouch filled with carrot–orange soup during thermal processing at 121 °C has been reported [99]. Simulated results indicated that natural convection plays an important role in the transfer of heat within the liquid product, while the slowest heating zone migrated towards the bottom of the pouch (within 30–40%) of the pouch height. The Vitamin C profile within the pouch depended on the temperature and velocity profiles within the pouch. Simpson et al. [100] developed a mathematical model for a cone-shaped and validated the model using vacuum-packed mackerel in a retortable pouch with steam/air mixture at 116.8 °C. The overall heat transfer coefficient (U) expression used in validating the model for a constant temperature was:

$$U = \frac{1}{h} + \frac{e_p}{k_p} \tag{25}$$

where e_p and k_p represent the width and thermal conductivity of the pouch. The localized heat transfer coefficient (h) was estimated using the expression [$h = 1182 \exp^{(2.06 \times \text{steam fraction})}$] developed by [101]. The researchers developed a relationship involving the major and minor radius of the pouch to locate the cold spot. Simulated data using a time-variable retort temperatures resulted in 20–30% reduction in process time [100]. However, the authors failed to demonstrate saved time experimentally for time-dependent retort temperature profiles.

Traditionally, retortable pouches are sterilized in batch-type retorts with custom designed racking systems. A method that allows continuous sterilization of flexible (soft) packaging materials (including retortable pouches) in a hydrostat has recently been patented [102]. First, a package slip is attached to the package, which is then attached to a cable-driven conveying system that moves through the hydrostat. The proposed hydrostat makes use of multiple water legs to increase the cooking pressure without increasing the overall height of the system. In order to develop the over-pressure needed for flexible (soft) packages, the water legs must be either twice as tall or several legs must be run in series [102].

Assuming a parallelepiped configuration for a pouch during modeling can lead to over-estimation of the thermal process, resulting in unnecessary degradation of quality attributes [103]. Irregular-shaped pouches can readily be accommodated by finite element modeling techniques. Cristianini and Massaguer [103] compared three mathematical models (analytical, two-dimensional and three-dimensional finite element) for predicting the temperature profiles for tuna [425 g and 2%, w/v NaCl] in institutional size retortable pouches (190 mm × 180 mm × 19 mm) during processing by water immersion (121 °C; 20 psi over-pressure for a target heating F_o of 7 min). The authors concluded that the finite element models provided more accurate results than the analytical approach, especially for the cooling phase where both cold and hot water mixes at the beginning. A sterilizing value of 7.9 min was calculated by the general method at the coldest point at the end of heating while the analytical, 2D and 3D models predicted 7.2, 8.1 and 8.7 min, respectively.

Quite recently the retortable pouch has re-emerged as a packaging alternative for several foodstuffs. Key bottlenecks identified with pouches include product entrapment at the seal interface and micro-leak channels that could allow microbial invasion. Non-destructive detectors with on-line capabilities for high volume operations will inspire further, the use of the pouch.

6.3. Aseptic processing

The concept of high-temperature short-time (HTST) and ultra-high-temperature (UHT) processing involves the sterilization of the food product (in a direct or indirect heat exchanger), followed by holding to achieve required lethality, and rapid cooling to minimize the impact of heat on nutrients. Packaging of the product is done in a sterile environment where a sterilized product is introduced into sterilized packaging materials (using hydrogen peroxide either alone or in combination with other sterilants) of different shapes, sizes and colors. In contrast to in-container sterilization where most lethal effect occurs at the end of the heating stage and beginning of the cooling phase, commercial sterility in HTST operations occurs in the holding tube at a constant temperature within seconds. Due to complications associated with the effect of temperature on product viscosity and residence time distribution, the Food and Drug Administration (FDA) in the past, considered lethality from the holding tube as the basis for thermal processes, while lethality contributions from heating and cooling were considered as safety factors. More recently, the FDA will accept lethality contributions from heating and cooling provided appropriate data are presented to support any claims [51].

The aseptic concept has been a success story mostly for liquid foods or liquid foods with small particulates. The primary motivation for aseptic processing is that the use of high-temperature promotes better quality retention while ensuring commercial sterility. In addition, aseptic systems have higher energy efficiency due to the rapid heat transfer rates. Notwithstanding the advantages associated with it, HTST adoption is challenged by the apparent difficulty in destroying heat-resistant enzymes, and its limitation to pumpable fluid with low viscosity. Today, aseptic processing is used to produce a wide range of high-quality products including milk, fruit juices, yoghurt, salad dressing, egg and ice cream mix, cheese, and baby foods,

Over the last decade, considerable research efforts and capital investment have focused on extending the aseptic concept to products containing large particles. These efforts somewhat paid off when the Food and Drug Administration approved a low acid soup containing large potato particles [104]. However, commercialization of large particle/liquid mixtures lags behind due to stringent regulatory demands for clear demonstration of achievable lethality. The major concerns with large particle products include the complexity of residence time distribution and heat transfer to particles in motion. Factors that have been studied to affect residence time distribution (RTD) include the size, shape, density, and concentration of particles; the density, flow rate, viscosity, and non-Newtonian behavior of the liquid portion. The characteristics of the pipe such as diameter and the number and position of bends also contribute to the behavior of residence time distribution. Recently, methodology such as embedded magnets/magnetic thermometry has been used to study and understand RTDs. Such techniques would require extensive verification and validation of data to assure consistency. The Stork Rota-Hold system that provides different residence times to the liquid and solid portions offer an excellent alternative whereby residence times can be set and accurately controlled.

Researchers have modeled experimental RTD data to follow either the normal, log-normal or gamma distribution. Other researchers have correlated the average and minimum particle residence times in simplistic terms such as the relationship developed for multiple particles in a circular holding tube by [105]:

$$\frac{t_{\min}}{t_{\text{avg}}} = 1.35\text{Re}'^{((0.3-0.31)/n)}\varphi^{0.076}n^{0.29} \tag{26}$$

where $t_{\min}$, t_{avg}, Re', φ and n represent the minimum time, average time, Reynolds number, volume fraction, and power law index, respectively. Biological products such as food particles have complex structures and potential variations in thermophysical properties that must be accounted for. Therefore, to prevent particles from settling at the bottom of the holding tube (due to property variations), the incipient velocity (i.e., the critical velocity needed to initiate particle flow) can provide useful information as to the relationship between the particle and fluid dynamics. A dimensionless relationship for estimating the incipient Reynolds number for carrots, potato, and parsnip cubes in

water and starch solutions have been developed as follows [106]:

$$Re_o = 0.0056 Ar^{0.615} \left[\frac{d_c}{D}\right]^{-0.07} \psi^{-8.5} \quad (27)$$

where Re_o, Ar, d_c, D and ψ represent the generalized Reynolds number, the Archimedes number, particle dimension, tube diameter, and sphericity factor, respectively. Additional information on RTD is provided in [91,107].

The other major issue with large particles is heat transfer to the coldest spot of the moving particles. Mathematical models and different experimental techniques have been proposed for establishing heat transfer to particulates that include: (i) stationary particle method, (ii) transmitter method, (iii) liquid/temperature calorimetry method, (iv) relative velocity method, (v) liquid crystal, (vi) relative velocity, (vii) moving thermocouple, and (viii) microbiological method [91,108]. Methods to enhance and/or measure heat transfer to particulates will continue to evolve. The bottom-line for acceptability would certainly include method sensitivity, flexibility of use and accuracy in terms of predicting time–temperature data for evaluating cold spot lethality.

Using a mathematical model designed for heterogeneous foods under continuous flow conditions, three approaches for scheduling liquid/particle mixtures were compared [109]. The authors indicated that ignoring the thermal contribution from the heat exchanger, while scheduling a thermal process for a particle center F_o of 6.0 min could result in an effective F_o of 78 min using the "hold only" approach. Although the "hold only" approach of process determination may not reflect a typical and/or practical routine for "liquid only" products, it clearly demonstrates that significant over-processing could result if come-up contributions are neglected.

Novel technologies have been recognized as options to solving some of the problems associated with large particulate products. Overall process validation using microbiological markers, enzymes/chemical marker or other properly calibrated time–temperature indicators will justify the appropriate methodology or technology to use.

6.4. Microwave (MW), radio frequency (RF) and ohmic heating

Successful application of electromagnetic heating alternatives that offer large volumetric heating under continuous flow situations could motivate industry to replace heat exchangers that transfer heat rather slowly, and are prone to fouling. Electromagnetic heating methods transfer energy from its source directly into the food without heating up the heat transfer surface of the processing equipment. The frequency range within which these heating methods operate are: 50/60 Hz for electric resistance (ohmic) heating; 10–60 MHz for radio frequency heating; 1–3 GHz for microwave applications. The frequency range within which electromagnetic heating equipment operate are regulated. Radio frequency applications are restricted to 13.56, 27.12 and 40.68 MHz for domestic, industrial, scientific and medical purposes. Industrial microwave food processing applications use the two frequencies of 915 and 2450 MHz, while domestic ovens use 2450 MHz.

Two mechanisms (dielectric and ionic) are involved in microwave and radio frequency heating, with water in food serving as the primary component for heating. The water molecules respond readily to the oscillating electromagnetic field, resulting in frictional interactions that generate heat. The other mechanism of heating is the oscillatory migration of ions present in the food. A comparison of the characteristics between microwave and radio frequency applications have been detailed by several authors [110–112]. Radio frequency heating is more appropriate for materials of regular shape, of large dimensions and offering high loss factor [110]. Microwave heating on the other hand is better adapted to compact materials with complex shapes and low loss factor. Radio frequency and microwave energy would more likely provide better quality compared to conventional heating, however, their effects at sublethal temperatures have been a controversial subject in both industry and academia. While some researchers found lethal contributions from microwaves, others have reported otherwise [113–116]. Investigations with *Saccharomyces cerevisiae* and *Lactobacillus plantarum* in apple juice [116] indicated that microwave energy had no non-thermal effects at sublethal temperatures. The authors determined that at equivalent heat treatments, microwaves enhanced microbial inactivation. Comparatively, several studies on electromagnetic heating have focused on microwave pasteurization and sterilization applications for a variety of fruit juices, milk, and milk-based products have been reported [117–120]. Radio frequency heating applications in the food industry was reviewed [121] and other studies relevant to continuous flow applications have been investigated [122,123]. Quite recently, radio frequency sterilization on a pilot scale has been demonstrated for its effectiveness in reducing processing time, and quality retention [124]. Using a chemical marker as quality index, the authors determined that the cook value of RF sterilized samples was half that of a conventionally sterilized sample for an identical F_o value. Demeczky [125] demonstrated that bottled juices including peach, quince and orange moving through an RF applicator offered better bacteriological and organoleptic qualities than juices treated by conventional thermal processing methods.

In resistance or ohmic heating, the food product acts as a conductor of electricity, with the electrodes of the heater coming in direct contact with the food. The electrodes are constructed of coated titanium to prevent electrochemical reactions that could potentially contaminate the food. Heating of the food product follows Ohm's law where the conductivity of the food (i.e., the inverse of resistance) dictates the current the passes through the food. Since the electrical conductivity of most foods increases with temperature [126] ohmic heating becomes very effective. However, thermal runaway and arching resulting from the deposition of proteins on electrodes could take place. One primary advantage claimed by ohmic heating is its ability to heat materials rapidly and uniformly, including those containing particulates. By manipulating the ionic contents in formulated products, particulates can be made to heat faster than the liquid. At least 18 ohmic heaters have been installed in Europe, Japan

and the United States, with systems used for whole strawberry and yogurt in Japan, and low acid ready-to-eat meals in the USA being the most successful [112]. The authors also indicated that the APV ohmic heating system for pasteurization and sterilization provide excellent quality. Ohmic heating has the promise to be one of the thermal processing alternatives that could provide value-added, shelf-stable foods as well as other applications that include blanching, evaporation, fermentation, dehydration and extraction [127].

7. On-line control during thermal processing

On-line retort control (automation) capabilities probably stems from the need to: (i) operate the retort in accordance with a scheduled process, (ii) minimize the occurrence of deviant processes, (iii) quickly implement corrective action for deviant processes, (iv) optimize product quality using optimal processing conditions, (v) improve system accuracy and consistency between batch processes and (vi) operate cost effectively.

Intelligent on-line control capabilities can meet strict regulatory requirements for documentation and record keeping. Resistance temperature detectors (RTDs) and other remote sensing devices would certainly have to replace measuring devices such as the mercury-in-glass thermometer (MIG). Powerful computer-based control systems with multi-tasking capabilities will replace obsolete automatic controllers and relay-logic systems for the full potential of intelligent automation systems to be realized.

Teixeira and Tucker [128] reviewed three approaches for intelligent on-line control of thermally processed foods. The first approach (known as the real-time data acquisition system for on-line retort control), which is impractical and cost-prohibitive from a large-scale/high-volume production standpoint [128], is to thermocouple multiple containers that relay data for real-time calculation of cumulative lethality. Using this information, the retort is operated to meet pre-defined lethality. This approach has been used quite recently in a micro-controller-based retort control system where on-line time–temperature data are captured and further processed by a software for cumulative lethality. The sterilization process is then controlled until the required lethality is attained [129].

The second approach is the application of a correction factor that primarily extends the process time to compensate for deviations. The work of Giannoni-Succor and Hayakawa [130] shows how the correction factor is determined and used to minimize over-processing. The correction factor approach has been criticized to lack flexibility.

The third approach (referred to as intelligent control with heat transfer models) is the idle one for on-line computer-based control [128]. With this approach, real-time (dynamic) time–temperature data from the retort is used in conjunction with appropriate heat transfer model that describes heat flow to the container for continuous cold-spot lethality calculations. On-line correction can be made and simultaneously documented while processing is under way in real-time [128]. This approach can accommodate simple, yet robust optimization routines that minimize computation time. Noronha et al. [131] developed semi-empirical procedures that allowed container cold-spot time–temperature data to be calculated (using heat penetration data: j and f_h) for time-dependent retort temperature. According to the authors, developed procedures could permit deviant processes to be evaluated and corrected on-line for the target lethality, but cautioned its use due to their empirical nature.

The unsteady state heat transfer to the product and dynamic variability of the food processing plant have been demonstrated to cause significant performance degradation when simple PID-type controllers are used for system control [132]. This is relevant with high-temperature and low energy consumption type of operation. To overcome performance degradation issues, a priori information derived from mass and energy principles must be complemented and incorporated into control structures that combine with recursive identification techniques [132]. Modeling and a hybrid adaptive controller have proven to perform efficiently in tracking constant and variable time–temperature profiles [132]. Teixeira et al. [133] tested the performance of the CAN-CALC© thermal process simulation software for process deviations associated with different heating characteristics and dynamic retort temperatures. The idea of testing the performance of the CAN-CALC© software was to further integrate it into a computer-based on-line control system. The CAN-CALC© software incorporated a proposition made by [131] that included the use of a sphere as a solid body shape to reduce computation time. Studies by Kim and Teixeira [134] supported Noronha's proposal that the food container need not be shaped as the solid object used for modeling heat transfer, provided the performance/temperature predictions are based on cold spot location within the container. The other proposition by Noronha et al. [131] was that a shift in radial location within the container could be used to incorporate the heating lag factor for convective heating products to allow for unexpected onset of cooling.

8. Conclusions

Traditional technologies used in thermal processing of shelf-stable foods have proven to be effective in terms of product safety. In the canning industry for low-acid foods, the 12D concept (based on *C. botulinum*) has been as reference for safety assurance from a public health standpoint. However, the first order reaction from which the D-value is determined has been scrutinized to misrepresent the behavior of microorganisms to lethal agents like heat. In addition, the 12D-reduction assumption has been challenged to be excessive. It sounds illogical for the food industry to re-invent products (already established with TDT data) from a safety standpoint, given recent advances (and probably the controversies) surrounding the response of microorganisms to heat. The need to optimize processes in terms of quality and operating costs while meeting all safety requirements, demand more research to streamline our understanding of microbial inactivation. Microbial inactivation studies should include validation of adopted or developed models including statistical analysis of data variability. The sensitivity of the method used in enumerating survivors should be verified. For inactivation curves that disobey the first order reaction (or the D–z concept), there will be the need for simple,

robust and yet, a user-friendly expression for calculating equivalent processes for legacy systems that may not be retrofitted with computer controls.

Process optimization of thermally processed food has been the focus of research studies in recent years. Several optimization methods and techniques for solving them have been reported for simulated conditions that reveal gains to be made such as enhance quality and reduced costs. For instance, the use of variable retort temperatures (VRTs) have been cited in several studies to provide considerable improvement in quality and reduced operator's time. However, very limited experimental studies using industrial conditions have been reported to support or justify the practicality of VRT applications. Obviously, there is the need for computer controlled systems that allow VRT/optimization routines to be implemented in real-time. Most of the models presented for quality optimization have considered the D–z model for both quality and microbial inactivation with temperature only as the lethal agent. However, flexible packages such as pouches need over-pressure to maintain package integrity (including size and shape), since heat transfer models for a predefined shape will no longer hold valid (e.g., for instance when the pouch is bloated).

The food industry is poised to adopted new concepts and technologies that offer competitive advantages over conventional systems. Extensive validation and verification, robustness, accuracy and cost effectiveness, controls and monitoring capabilities, are some of the key elements that will justify the adoption of developed systems/optimization routines.

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