Thermal Food Processing

New Technologies and Quality Issues

Edited by
Da-Wen Sun

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Thermal Food Processing

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Preface

Thermal processing is one of the most important processes in the food industry. The concept of thermal processing is based on heating foods for a certain length of time at a certain temperature. The challenge of developing advanced thermal processing for the food industry is continuing in line with the demand for enhanced food safety and quality, because associated with thermal processing is always some undesirable degradation of heat-sensitive quality attributes. Therefore, this book covers a comprehensive review of the latest developments in thermal food processing technologies, stresses topics vital to the food industry today, and pinpoints the trends in future research and development. This book is written for food engineers and technologists in the food industry. It will also serve as an essential and complete reference source to undergraduate and postgraduate students and researchers in universities and research institutions.

The contents of the book are divided into three parts: modeling of thermal food processes, quality and safety of thermally processed foods, and innovations in thermal food processes.

Part I deals with topics relating to modeling, which is needed for the design and optimization of thermal processing of foods. This part begins with Chapter 1 on thermal physical properties of foods, which contains fundamental data and equations used in modeling. The recent developments in heat and mass transfer during thermal processing are reviewed in Chapter 2. The remaining three chapters discuss innovative modeling techniques, including simulation using deterministic models (Chapter 3), modeling using an artificial neural network (Chapter 4), and computational fluid dynamics (Chapter 5), which have been increasingly applied in the food industry.

Maintenance of high quality and safety of thermally processed foods has been a major challenge in food processing. Part II presents recent R&D in this area. This part consists of nine chapters, each of which describes one type of food product. The first three chapters address respectively the quality and safety of thermally processed meat (Chapter 6), poultry (Chapter 7), and fishery products (Chapter 8). Dairy products are dealt with in Chapter 9, with ultra-high-temperature (UHT) milk being a separate chapter, as UHT is the most common thermal treatment technique for milk (Chapter 10). Chapter 11 gives the recent and potential future development in thermal processing of canned foods, which remains the most universal and economic method for preserving foods with a long shelf life. In recent years, ready meals have shown high rates of growth, indicating the importance of innovation in thermal processing technology to cater for development of new food products, which is discussed in Chapter 12. Finally, this part is concluded with a chapter on quality and safety of thermally processed vegetables (Chapter 13).

Various alternative thermal processing technologies have been developed in the past. These innovations demonstrate the potentials for their applications in the food industry to increase processing efficiency, enhance product quality, and improve food safety. Part III addresses in detail these innovations. Chapter 14 covers the ohmic heating technique, which has been subjected to intensive research work in the past two decades as a promising technology for new high-quality products. Using radio frequency (RF) energies or infrared rays to heat foods is a fast and effective thermal processing technique that results in short treatment times preferred for maintaining high quality. These techniques are respectively presented in Chapters 15 and 16. Furthermore, innovations by combining pressure and pH with thermal processing are described in Chapters 17 and 18. Last but not least, the use of time–temperature integrators (TTIs) to evaluate and control thermal processes is discussed in the final chapter of this book (Chapter 19).

In this book, each chapter is written by an international expert (or experts), presenting thorough research results and critical reviews of one aspect of the relevant issue and including a comprehensive list of recently published literature. It should therefore provide valuable sources of information for further research and developments for the food processing industry.

The Editor

Born in Southern China, **Professor Da-Wen Sun** is an internationally recognized figure for his leadership in food engineering research and education. His main research activities include cooling, drying, and refrigeration processes and systems, quality and safety of food products, bioprocess simulation and optimization, and computer vision technology. Especially, his innovative work on vacuum cooling of cooked meats, pizza quality inspection by computer vision, and edible films for shelf-life extension of fruit and vegetables has been widely reported in national and international media. Results of his work have been published in over 150 peer reviewed journal papers and more than 200 conference papers.

Dr. Sun received first-class honors B.Sc. and M.Sc. degrees in mechanical engineering and a Ph.D. degree in chemical engineering in China before working in various universities in Europe. Dr. Sun became the first Chinese to be permanently employed in an Irish University when he was appointed college lecturer at National University of Ireland, Dublin (University College Dublin) in 1995, and was then promoted to senior lecturer. Dr. Sun is now a professor and director of the Food Refrigeration and Computerised Food Technology Research Group at the Department of Biosystems Engineering, University College Dublin.

As a leading educator in food engineering, Professor Sun has significantly contributed to the field of food engineering. He has trained many Ph.D. students, who have made their own contributions to the industry and academia. Professor Sun has also given lectures on advances in food engineering on a regular basis to academic institutions internationally and delivered keynote speeches at international conferences. As a recognized authority in food engineering, he has been conferred adjunct/visiting/consulting professorships from ten top universities in China, including Zhejiang University, Shanghai Jiao Tong University, Harbin Institute of Technology, China Agricultural University, South China University of Technology, and Southern Yangtze University. In recognition of his significant contribution to food engineering worldwide, the International Commission of Agricultural Engineering (CIGR) awarded him the CIGR Merit Award in 2000, and the Institution of Mechanical Engineers (IMechE) based in the U.K. awarded him Food Engineer of the Year 2004.

Professor Sun is a fellow of the Institution of Agricultural Engineers. He has also received numerous awards for teaching and research excellence, including twice receiving the President Research Award of University College Dublin. He is chair of CIGR Section VI on Postharvest Technology and Process Engineering, guest editor of *Journal of Food Engineering* and *Computers and Electronics in Agriculture*, and editorial board member for the *Journal of Food Engineering*, the *Journal of Food Process Engineering*, and the *Czech Journal of Food Sciences*. He is also a chartered engineer registered in the U.K. Engineering Council.

Contributors

José Manuel Gallardo Abuín
Instituto de Investigaciones Marinas (CSIC)
Vigo, Spain

Jasim Ahmed
Department of Food Science
McGill University
Ste-Anne-de-Bellevue, Canada

Inês de Castro
Department of Biological Engineering
University of Minho
Braga, Portugal

C.R. Chen
Agriculture and Agri-Food Canada
Quebec, Canada

Xiao Dong Chen
Department of Chemistry and Materials Engineering
University of Auckland
Auckland, New Zealand

N. Datta
School of Land and Food Sciences
University of Queensland
Queensland, Australia

Paul L. Dawson
Food Science and Human Nutrition Department
Clemson University
Clemson, South Carolina

H.C. Deeth
School of Land and Food Sciences
University of Queensland
Queensland, Australia

A.E. Delgado
Food Refrigeration and Computerised Food Technology Research Group
University College Dublin
Earlsfort Terrace
Dublin, Ireland

P.S. Fernández
Universidad Politécnica de Cartagena
Cartagena, Murcia, Spain

A.L. Kelly
Department of Food and Nutritional Sciences
University College Cork
Cork, Ireland

Sunil Mangalassary
Food Science and Human Nutrition Department
Clemson University
Clemson, South Carolina

Pamela Manzi
Istituto Nazionale di Ricerca per gli Alimenti e la Nutrizione
Roma, Italy

Weijie Mao
Tokyo University of Marine Science and Technology
Tokyo, Japan

Antonio Martínez
Instituto de Agroquímica y Tecnología de Alimentos
Valencia, Spain

Isabel Medina Méndez
Instituto de Investigaciones Marinas (CSIC)
Vigo, Spain

M.J. Ocio
Universidad de Valencia
Valencia, Spain

Takashi Okazaki
Hiroshima Prefectural Food Technology Research Center
Hiroshima, Japan

Alfredo Palop
Departamento de Ingeniería de Alimentos y del Equipamiento Agrícola
Universidad Politécnica de Cartagena
Cartagena, Spain

Laura Pizzoferrato
Istituto Nazionale di Ricerca per gli Alimenti e la Nutrizione
Roma, Italy

H.S. Ramaswamy
Department of Food Science and Agricultural Chemistry
McGill University
Quebec, Canada

D. Rodrigo
Instituto de Agroquímica y Tecnología de Alimentos
Valencia, Spain

A.C. Rubiolo
Instituto de Desarrollo Tecnológico para la Industria Química (INTEC)
Universidad Nacional del Litoral (UNL)
Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET)
Santa Fe, Argentina

Noboru Sakai
Department of Food Science and Technology
Tokyo University of Marine Science and Technology
Tokyo, Japan

Marcos Sanchez
Department of Food Science and Technology
University of Nebraska–Lincoln
Lincoln, Nebraska

Brian W. Sheldon
North Carolina State University
Raleigh, North Carolina

U.S. Shivhare
Department of Chemical Engineering and Technology
Panjab University
Chandigarh, India

Da-Wen Sun
University College Dublin
Earlsfort Terrace
Dublin, Ireland

Kanichi Suzuki
Department of Applied Biological Science
Hiroshima University
Kagamiyama Higashi-Hiroshima, Japan

Arthur A. Teixeira
Agricultural and Biological Engineering Department
University of Florida
Gainesville, Florida

José António Teixeira
Department of Biological Engineering
University of Minho
Braga, Portugal

Harshavardhan Thippareddi
Department of Food Science and Technology
University of Nebraska–Lincoln
Lincoln, Nebraska

Gary Tucker
Department of Food Manufacturing Technologies
Campden & Chorleywood Food Research Association
Chipping Campden, Gloucestershire, United Kingdom

António Augusto Vicente
Department of Biological Engineering
University of Minho
Braga, Portugal

Lijun Wang
Department of Biological Systems Engineering
University of Nebraska–Lincoln
Lincoln, Nebraska

Z. Jun Weng
FMC Technologies, Inc.
Madera, California

Yanyun Zhao
Department of Food Science and Technology
Oregon State University
Corvallis, Oregon

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Part I

Modeling of Thermal Food Processes

1 Thermal Physical Properties of Foods

A.E. Delgado, Da-Wen Sun, and A.C. Rubiolo

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1.1 INTRODUCTION

Thermal food processes, whether electrical or conventional, may be broadly classified as unit operations in blanching, cooking, drying, pasteurization, sterilization, and thawing, and involve raising the product to some final temperature that depends on the particular objective of the process.[1] The design, simulation,

optimization, and control of any of these processes require the knowledge of basic engineering properties of foods.

Thermophysical properties in particular are within the more general group of engineering properties and primarily comprise specific heat and enthalpy, thermal conductivity and diffusivity, and heat penetration coefficient. Other properties of interest are initial freezing point, freezing range, unfreezable water content, heat generation (and evaporation), and the more basic physical property of density.[2]

The thermal properties depend on the chemical composition, structure of the product, and temperature; however, the processing of the food and the method of measurement are important as well. The temperature range of interest to food engineers, –50 to 150°C, covers two areas of food engineering, the applications of heat and cold. At low temperatures, where the conversion of water into ice takes place, the change in thermophysical properties is dramatic for all water-rich foods. However, the upper end, which is the temperature range considered here, is less dramatic. Despite that, products rich in fat will also show phase change effects.[2]

In general, for each property, the following information is normally sought: (1) reliable method(s) of measurement, (2) key food component(s), and (3) widely applicable predictive relationships.[3] Sensitivity tests have demonstrated the significance of the thermophysical properties.[4] For example, two thermal properties, thermal conductivity and specific heat, and two mechanical properties, density and viscosity, determine how a food product heats after microwave energy has been deposited in it.[5]

The thermal properties treated in this chapter are specific heat, thermal conductivity, thermal diffusivity, and density. Since alternative methods to supply heat are considered in this book (e.g., radio frequency and microwave heating), the dielectric constant and dielectric loss factor are also taken into account.

1.2 DEFINITION AND MEASUREMENT OF THERMOPHYSICAL PROPERTIES

The measurement of the thermal properties has been notably described previously by many authors in the literature[6–11] and will not be detailed here. Thermal properties of food and their measurement, data availability, calculation, and prediction have also been well described as one of the subjects undertaken within COST90, the first food technology project of COST.[2,12–14] Dielectric properties have also been discussed within electrical properties in the other EU concerted project, COST90bis.[15] Therefore, a brief comment on the recommended methods used to measure thermal properties is given below.

For most engineering heat transfer calculations performed in commercial heating or cooling applications, accuracies greater than 2 to 5% are seldom needed, because errors due to variable or inaccurate operating conditions (e.g., air velocity, temperature) would overshadow errors caused by inaccurate thermal properties.[9] Thus, precision and accuracy of measurement with regard to the application of the data are important factors to consider when selecting a measurement method.

1.2.1 Specific Heat Capacity

The heat capacity (c) of a substance is defined as the amount of heat necessary to increase the temperature of 1 kg of material by 1°C at a given temperature. It is expressed as Joules per kilogram Kelvin in SI units, and it is a measure of the amount of heat to be removed or introduced in order to change the temperature of a material. If ΔT is the increase in temperature of a given mass, m, as a consequence of the application of heat, Q, the calculated specific heat is the average, that is:

$$c_{aveg} = \frac{Q}{m\Delta T}. \tag{1.1}$$

If ΔT is small, and $q = Q/m$, Equation 1.1 gives the instantaneous value of c:[11]

$$c = \lim_{\Delta T \to 0} \left(\frac{q}{\Delta T} \right)_T = \left(\frac{dq}{dT} \right)_T . \tag{1.2}$$

If both a temperature change and a thermal transition are included, this specific heat is then called the apparent specific heat.

There exist two specific heats, c_p and c_v; the former is for constant pressure process and the latter for constant volume process. The specific heat for solids and liquids is temperature dependent, but does not depend on pressure, unless very high pressures are applied. For the food industry, c_p is commonly used, as most of the food operations are at atmospheric pressure. Only with gases it is necessary to distinguish between c_p and c_v.

The methods often used to measure the specific heat and also the enthalpy are the method of mixing, the adiabatic calorimeter, and the differential scanning calorimeter (DSC). Over the years, Riedel[16–19] has published extensively on both the specific heat and enthalpy of a wide range of food products.[20] He used the adiabatic calorimeter, which is a method that can provide high precision but involves long measuring times and difficulties for preparing the sample. Although DSC has disadvantages, such as necessity of calibration and requirement of small samples and good thermal contact, it is the method generally recommended for measuring specific heat.

1.2.2 Enthalpy

Enthalpy is the heat content or energy level in a system per unit mass, and the unit is Joules per kilogram (J/kg). It can be written in terms of specific heat as:[10]

$$H = \int c dT. \tag{1.3}$$

The specific heat and enthalpy are properties of state. Enthalpy has been used more for quantifying energy in steam than in foods. It is also convenient for frozen foods because it is difficult to separate latent and sensible heats in frozen foods, which often contain some unfrozen water even at very low temperatures.[9]

1.2.3 Thermal Conductivity

Thermal conductivity (k) represents the basic thermal transport property, and it is a measure of the ability of a material to conduct heat. It is defined by the basic transport equation written as *Fourier's law* for heat conduction in fluids or solids, which is integrated to give:

$$\frac{q}{A} = \frac{k(T_1 - T_2)}{z}, \tag{1.4}$$

where q is the heat transfer rate in Watts (W), A is the cross-sectional area normal to the direction of the heat flow in square meters (m^2), z is the thickness of the material (in meters [m]), T_1 and T_2 are the two surface temperatures of the material, and k is the thermal conductivity in Watts per meter Kelvin (W/m K). Thermal conductivity is an intrinsic property of the material. For hygroscopic moist porous materials, k is a strong function of the porosity of the material.[21] Heat transfer in porous moist materials may occur by heat conduction and mass transfer simultaneously, so the effective thermal conductivity is used to precisely evaluate the coupled heat and moisture transfer through porous materials.

For measuring the thermal conductivity of foods, the line heat source probe has frequently been used and is the method recommended for most food applications. This technique is implemented in two designs: the hot-wire k apparatus and the k probe. The hot-wire apparatus is widely accepted as the most accurate method for measuring the k of liquids and gases, but it is more complicated to adapt to instrumentation and more difficult to use in solid materials.[22] The *k probe* method is fast, uses small samples, and requires known and available instrumentation.[23] However, it is not well suited for nonviscous fluids due to convection currents that arise during probe heating.[9] The technique has also been used to measure k of moist porous foods materials at elevated temperatures.[24] Although the thermal conductivity probe is derived from an idealized heat transfer model, there are unavoidable differences between the real probe and the theoretical model, which cause errors in the application of the k probe and lead researchers to corrective measures to either compensate or minimize these errors.[22] Various design parameters of the k probe have been analyzed and recommendations given for applications to nonfrozen food materials.[22] As a result, it is recommended that users should design their thermal conductivity probes using the highest acceptable error for their intended application.

1.2.4 Thermal Diffusivity

Thermal diffusivity (α) determines how rapidly a heat front moves or diffuses through a material and can be defined as

$$\alpha = \frac{k}{\rho c_p}, \tag{1.5}$$

where ρ is the density (kg/m^3), c_p is the specific heat at constant pressure (J/kg K), and k is the thermal conductivity (W/m K) of the material. The SI unit of α is square meters per second (m^2/sec). Thermal diffusivity measures the ability of a material to conduct thermal energy relative to its ability to store thermal energy; products of large α values will respond quickly to changes in their thermal environment, while materials of small α values will respond more slowly.

The thermal diffusivity of unfrozen foods ranges from about 1.0×10^{-7} to 1.5×10^{-7} m^2/sec and does not change substantially with moisture and temperature because any changes of k are compensated by changes of the density of the material.[21] In microwave heating, for example, the fact that thermal diffusivities of unfrozen foods are similar means that foods heat similarly for equivalent energy deposition.[5]

The measurement of thermal diffusivity can be divided into two groups: *direct measurement* and *indirect prediction*.[10] Indirect prediction, that is, the estimation from experimentally measured values of thermal conductivity, specific heat, and density, is the recommended method to determine α.[9] Since specific heat can be estimated with sufficient accuracy from the product composition, the experimental determinations are the thermal conductivity and the mass density.[9]

1.2.5 Density

Density (ρ) is a physical property widely used in process calculations. Density of food materials depends on temperature and composition, and it is the unit mass per unit volume:

$$\rho = \frac{m}{V_s}. \tag{1.6}$$

The SI unit of density is kilograms per cubic meter (kg/m^3). Different ways of density definition, measurement, and usage in process calculations are well discussed in the literature.[10] In some cases, the *apparent density* is used as *bulk density.* The apparent density is the density of a substance, including all pores remaining in the material, while bulk density is the density of a material when packed or stacked in bulk.[10] Hence, it is necessary to mention the definition of density when presenting or using data in process calculations.[10]

The density of a food product is measured by weighing a known volume of the product. Since food products are different in shape and size, the accurate measurement of volume can be challenging.[25] An easy procedure recommended for measuring ρ in meats is to add a known mass (approximately 5 g) of sample to a calibrated 60-ml flask, and complete the volume with distilled water at 22°C.[11] Density is evaluated from the following equation:

$$\rho = \frac{m}{V_s} = \frac{m}{60 - V_w}, \tag{1.7}$$

where m and V_s are the mass and volume of the sample, respectively, calculated from the added water volume V_w.

The bulk and solids densities can be measured experimentally, and they can be used to estimate the bulk porosity. Porosity is an important physical property, since its changes during processing may have significant effects on the heat and mass transport properties (e.g., thermal conductivity), and thus the quality (nutritive and sensory) of the food product.[4]

1.2.6 Dielectric Constant and Dielectric Loss Factor

Electrical properties of foods are of general interest as they correlate the physical attributes of foods with their chemical ones, and they are of practical interest in optimization and control of dielectric heating processes.[26] The most intensively investigated electrical properties of foods have been the *relative dielectric constant* (ε') and *loss factor* (ε''). These dielectric properties determine the energy coupling and distribution in a material subjected to dielectric heating.[27] The dielectric constant or "capacitivity" is related to the material's capacitance and its ability to store electrical energy from an electromagnetic field, and it is a constant for a material at a given frequency. The dielectric loss is related to a material's resistance and its ability to dissipate electrical energy from an electromagnetic field.[1] A material with high values of the dielectric loss factor absorbs energy at a faster rate than materials with lower loss factors.[28] It should always be remembered that dielectric properties in a time-varying electric field are complex; that is to say, they have two components: real, ε', and imaginary, ε''.[29] The dielectric loss factor in turn is the sum of two components: *ionic*, ε''_σ, and *dipole*, ε''_d, *loss*. The ratio of the dielectric loss and dielectric constant is called the loss tangent or the dissipation (power) factor of the material (tan δ). The *permitivity*, which determines the dielectric constant, the dielectric loss factor, and dielectric loss angle, influences the dielectric heating.[28]

The relative ionic loss, ε''_σ, is related to the electrical conductivity of a food material (σ) with the following relationship:[30]

$$\varepsilon''_\sigma = \frac{\sigma}{2\pi f \varepsilon_0}, \tag{1.8}$$

where ε_0 is the permitivity of free space (8.854×10^{-12} F/m), and f is the frequency of the electromagnetic waves (Hz).

Power *penetration depth* (d), one of the essential dielectric processing parameters, is defined as the distance that the incident power decreases to $1/e$ ($e = 2.718$) of its value at the surface.[30] The penetration depth is calculated from the dielectric constant and dielectric loss data by using the following expression:[31]

$$d = \frac{c_0}{f} \frac{0.1125394}{\left\{ \varepsilon' \left[\left(1 + \tan^2 \frac{\varepsilon''}{\varepsilon'} \right)^{1/2} - 1 \right] \right\}^{1/2}}, \tag{1.9}$$

where c_0 is the speed of light in vacuum (3×10^8 m/sec). An approximation for determining the penetration depth that holds for virtually all foods is given by[5]

$$d = \frac{\lambda_0 \sqrt{\varepsilon'}}{2\pi\varepsilon''}, \tag{1.10}$$

where λ_0 is the free space microwave wavelength, which can be in any units of length. For 2450 MHz, λ_0 is equal to 122 mm. Knowledge of the penetration depth helps in selecting a correct sample thickness to guide the microwave or *radio frequency* (RF) *heating* processes.[30] It has been reported that for mashed potatoes, for example, after calculating the penetration depth, *microwave heating* is advisable for packages with relatively smaller thickness (for example, 10 to 20 mm for two-sided heating), and RF heating should be applied for packages and trays with large institutional sizes (for example, 40 to 80 mm depth).[30]

The food map plot for ε'' vs. ε' with constant penetration depth lines (d) is a recommended way to illustrate the dielectric properties.[5]

The dielectric properties of liquid and semisolid food products depend primarily on their moisture, salts, and solids contents. However, the extent to which each of these constituents affects food dielectric behavior depends very much on the processing frequency and the temperature history of the product.[1] In an experiment about the effect of sample heating procedures (temperature being raised in 10°C intervals or being raised directly to a set point, 121°C) on the results of measurements for whey protein gel, cooked macaroni noodles, cheese sauce, and macaroni and cheese, it was found that the heating procedures did not affect the results of the dielectric property measurements for the materials tested.[32]

Dielectric properties can be measured by the methods reviewed within the collaborative research project COST90bis.[29] The measuring methods can vary even in a given frequency range. Four groups of measurement methods can be considered: lumped circuit, resonator, transmission line, and free space methods.[33] One of the most commonly used measuring methods employs resonant cavities, since they are very accurate but can also be sensitive to low-loss tangents.[28]

The method can be easily adapted to high (up to 140°C) or low (–20°C) temperatures. Another popular technique is the open-ended coaxial probe method,[28] because it requires no particular sample shapes and offers broad-band measurement.[30]

1.3 DATA SOURCES ON THERMOPHYSICAL PROPERTIES

Thermal property data have been measured since the late 1800s, with almost two thirds of that being published in the 1950s and 1960s.[9] A problem that industrial users normally face is that the data available are often of limited value because information about composition, temperature, error in measurement, etc., is not reported. Furthermore, moisture and air content ranges tend to cover a narrow band and thermophysical data at both elevated and low temperatures are sparse.[34] Though information available is only partial, such data are very useful for preliminary design, heat transfer calculations, and food quality assessment.

Different ways can be recognized to obtain information on thermal properties, namely: (1) original publications, (2) summarizing publications such as articles, monographs, and books, (3) bibliographies and compilations of literature references, (4) handbooks and data books, and finally (5) computerized data banks.[2] The recommendation of the COST90 project in 1983 was to replace the first four choices mentioned above with one compilation of basic data and thermophysical properties by product, containing calculated values and experimental data as references, accompanied also by a reference to their sources in case more information was needed. Computer programs such as COSTHERM and FoodProp were developed for the thermal properties of foods, but the diverse and variable data of other properties prevented the development of other computer programs.[4] *Food Properties Database*, Version 2.0 for Windows,[35] was the first such database assembled in the U.S.[34] This database includes over 2400 food–property combinations and over 2450 food materials; it also features a collection of mathematical models that have been proposed for predicting food property values. In the EU there is an online database available for physical properties of agro-food materials (www.nelfood.com).[34] The database contains five main categories of data: thermal, mechanical (rheological and textural), electrical, diffusional, and optical (spectral and color) properties. The future work of NELFOOD database will improve the predictive features of the database. The novelty of the database is that it specifies both the experimental method and the descriptions of the food, and also provides a score (four-point scale) indicating the quality of the method specification and food definition. This characteristic in particular is very helpful when selecting appropriate values or models from many sources available, since it is not only the data but also the interpretation and application that are equally important.

References to important sources of information on thermophysical properties have been published in the literature[2]; Table 1.1 presents additional information on data recently available. The database of the Food Research Institute of Prague

TABLE 1.1
Literature on Thermal Physical Properties of Foods

Source	Information
Nesvadba et al. (2004)[34] http://www.nelfood.com Database	Thermal, mechanical, electrical, diffusional, and optical properties; data available in tables and equations as function of temperature, pressure, composition, etc.
Nesvadba et al. http://www.vupp.cz/envupp/research.htm Database	Physical properties data at the Institute of Food Research, Prague
Krokida et al. (2001)[36] Article	Compilation of thermal conductivity data with range of material moisture content and temperature
Singh (1995)[35] Database	Experimental values and mathematical models of food properties, along with literature citations
Rahman (1995)[10] *Food Properties Handbook* Chapters 3 to 6 Textbook	Density, specific heat, enthalpy, latent heat, thermal conductivity, and thermal diffusivity Measurement, experimental values, and prediction models
Datta et al. (1995)[31] Engineering properties of foods Chapter 9	Dielectric property data of fruits, vegetables, meats, and fish
ASHRAE (1993)[39] *Fundamentals Handbook* Chapter 30	Specific heat, thermal diffusivity, and thermal conductivity

contains more than 16,000 manuscripts, which can be accessed in part through the NELFOOD database. Average values and variation ranges of thermal conductivity of more than 100 food materials, classified into 11 food categories, were also compiled.[36] More than 95% of these data are in the ranges of 0.03 to 2 W/mK for thermal conductivity, 0.01 to 65 kg/kg db for moisture content, and –43 to 160°C for temperature range.

Very few thermal diffusivity data are available; however, thermal diffusivity can be calculated from specific heat, thermal conductivity, and mass density[9] if they are available, as shown in Equation 1.5.

A compilation of dielectric property data has been presented (dielectric constant ε', dielectric loss ε'', and penetration depth d) for a wide range of fruits, vegetables, meats, and fish for the frequency range of 2000 to 3000 MHz.[31] The references for each set of data and the type of measurement used are provided as well. In some cases, the composition data are from sources other than those from which the data were taken. The amount of information available on the dielectric properties of foods in the RF range is limited in comparison with data at microwave frequencies. Dielectric properties of selected foods in the RF range 1 to 200 MHz have been reported recently, along with information related to data sources.[28] Except for one

work,[37] very few studies provide the dielectric properties above 65°C.[38] Dielectric properties of whey protein gel, cooked macaroni noodles, cheese sauce, and macaroni and cheese, at both microwave and radio frequencies (27, 40, 915, and 1800 MHz) over a temperature range of 20 to 121.1°C, were recently reported.[32]

It is important to note that the data files for specific heat capacity published in ASHRAE's *Fundamentals Handbook*[39] are not experimentally measured values; instead, they are calculated from equations based on water content, which can result in considerable error for calculations.

In summary, considerable data on thermal properties have been published to the present, though in many cases the information available is only partial. Therefore, when reporting thermal property data, researchers should provide a detailed and informative description of the product tested (variety, chemical composition, pretreatment, etc.), the experimental procedures (process variables), and the data obtained.[9]

1.4 PREDICTIVE EQUATIONS

Thermal processing was the first food process to which mathematical modeling was applied, because of its great importance to the public's health and safety and the economics of food processing.[4] Modeling requires the information of the mean or effective values of the components, together with the representation of the physical structure.[11] Because of the large variety of foods and formulations, it is almost impossible to experimentally measure the thermal properties for all possible conditions and compositions. Therefore, the most viable option is to predict the thermophysical properties of foods using mathematical models. However, if more accuracy is required, a good solution is the experimental determination.

Water as a major component in foods affects safety, stability, quality, and physical properties of food. Analysis of published data shows that the less water there is in the material, the more discrepancies between predicted and measured values that exist.[27] It seems that discrepancies arise from the treatment of whole water in food as bulk water, without taking into account the interactions between water and food components, which must affect thermal properties.

Most of the thermal property models are empirical rather than theoretical; that is, they are based on statistical curve fitting rather than a theoretical derivation involving heat transfer analyses.[9] A comprehensive compilation of predictive equations of thermal physical properties of foods is provided in the literature.[10–12,40] From the many published equations, some examples of commonly used correlations are given below.

1.4.1 Specific Heat

Water has a high specific heat in comparison to other food components; hence, even small amounts of water in foods affect its specific heat substantially.[27] The simplest specific heat model for low-fat foods has the following form:[27]

$$c_p = a + bx_w, \tag{1.11}$$

TABLE 1.2
Linear Models for Specific Heat of Foods

Material	*a*	*b*	x_w Range	T Range (°C)
Foods	837	3349		
Fish and meats	1670	2500	Less than 0.25	
Fruits and vegetables	1670	2500	Higher than 0.25	
Orange (navel)	1452	2515	0.00–0.89	
Lentil	1030	4080	0.02–0.26	10–80
Potato	904	3266	Higher than 0.5	
Potato	1645	1830	0.20–0.50	
Milk products				
Cheese (processed)	1918	2258	0.425–0.684	40
Dulce de leche	1790	2640	0.28–0.60	30–50
Sorghum and cereals	1400	3200	Low water	
Sorghum	1396	3222	0.00–0.30	
Wheat (hard red spring)	1090	4046	0.00–0.40	0.6–21.1
Soybeans	1637	1927		
Soy flour (defatted)	1748	3363	0.092–0.391	130

Source: Adapted from Rahman, S., *Food Properties Handbook*, CRC Press, Boca Raton, FL, 1995, pp. 179–390.

where a and b are constants that depend on the product and temperature, x_w is the water content in decimals, and c_p is in Joules per kilogram degrees Centigrade (J/kg °C). Table 1.2 lists the constants a and b, the moisture content, and temperature range for a great variety of foods.[10]

It is generally accepted that specific heat obeys the rules of additivity. This means that the specific heat of a product is equal to the sum of the fractional specific heats of the main constituents.[27] Using the additivity principle, specific heat can be calculated as follows:

$$c_p = \sum c_{pi} x_i, \tag{1.12}$$

where c_{pi} is the specific heat at a constant pressure of the food component i, and x_i is the mass fraction of the ith food component (water, x_w; protein, x_p; fat, x_f; carbohydrate, x_c, and ash, x_{as}). The thermal properties of the major food components as a function of temperature can be found in the literature.[41] When the food contains a large amount of fat, the specific heat is made up from the contribution of the fat fraction and also from the phase transition of the fat.

The specific heat above the initial freezing point can be calculated if the c_p of the fat is assumed to be half of the c_p of water, and the c_p of the solids, which have similar specific heats, is assumed to be 0.3 times that of water's c_p:[20,42]

$$c_p = 4180\ (0.5x_f + 0.3x_s + x_w). \tag{1.13}$$

Equation 1.13 gives a rough estimate of the specific heat above the freezing point of the product.

An empirical equation for the calculation of c_p of some different foods is given as[43]

$$c_p = 4187\ [x_w + (\gamma + 0.001\mathrm{T})(1 - x_w) - \beta \exp(-43x_w^{2.3})], \qquad (1.14)$$

where the temperature T is in degrees Centigrade (°C) and the numerical values of the coefficients in Equation 1.14 for some foods are

$$\gamma_{\text{beef}} = 0.385, \qquad \beta_{\text{beef}} = 0.08$$

$$\gamma_{\text{white bread}} = 0.350, \qquad \beta_{\text{white bread}} = 0.09$$

$$\gamma_{\text{sea fish}} = 0.410, \qquad \beta_{\text{sea fish}} = 0.12$$

$$\gamma_{\text{low-fat cheese}} = 0.390, \qquad \beta_{\text{low-fat cheese}} = 0.10.$$

If detailed composition data are not available, the following simpler model can be used:[44]

$$c_p = 4190 - 2300x_s - 628x_s^3\,, \qquad (1.15)$$

where x_s is the mass fraction of solids, and c_p is in Joules per kilogram degrees Centigrade (J/kg °C).

Gupta[45] developed the following correlation to predict the specific heat of foods as a function of moisture content and temperature considering 15 types of foods:[10]

$$c_p = 2476.56 + 2356x_w - 3.79T, \qquad (1.16)$$

where T is in Kelvin (K), and c_p is in Joules per kilogram Kelvin (J/kg K), and x_w ranges from 0.001 to 0.80 and T from 303 to 336 K. Equation 1.16 gives fairly good values for substances like sugar, wheat flour, starch, dry milk, rice, etc. For substances containing higher moisture (more than 80%), Equation 1.16 shows higher deviations from reported values.

The specific heat is related to the dielectric properties and the temperature increase (ΔT) through the following equation:[28]

$$\Delta T = \frac{2\pi tf\varepsilon_0\varepsilon' \tan\delta V^2}{c_p\rho}, \qquad (1.17)$$

where t is the temperature rise time (sec), ε_0 is the dielectric constant of free space, and V, the electric field strength, is equal to voltage/distance between plates (V/cm). Equation 1.17 shows that the specific heat affects the resulting ΔT.

A material with greater specific heat will undergo a smaller temperature change since more energy is required to increase the temperature of 1 g of the material by 1°C.[28] In a multicomponent product, where the components have wide differences in dielectric and thermal properties, it is often necessary to balance both sets of properties in order to approach equal heating for each component. It is usually more fruitful to adjust specific heat rather than dielectric properties to obtain such a balance.[5]

1.4.1.1 Specific Heat of Juices

The specific heat for fruit juices with water content greater than 50% can be calculated as follows:[46]

$$c_p = 1674.7 + 25.12x_w. \tag{1.18}$$

The specific heat (J/kg °C) of clarified apple juice as a function of concentration (6 to 75°Brix) and temperature (30 to 90°C) can be estimated from[11,47]

$$c_p = 3384.57 - 18.1774\text{Bx} + 2.3472T. \tag{1.19}$$

Equation 1.19 gives a good fit (correlation coefficient $R^2 = 0.99$) of the experimental data in the entire range of concentrations and temperatures under consideration.

Alvarado[48] developed a general correlation using 140 data for fruit pulps, with moisture content ranging from 0.012 to 0.945 and temperatures from 20 to 40°C, which is given below:[10]

$$c_p = 1560\ [\exp(0.9446x_w)]. \tag{1.20}$$

1.4.1.2 Specific Heat of Meats

Sanz et al.[40,49] presented a list with experimental values and the most appropriate equations to calculate the specific heat, thermal conductivity, thermal diffusivity, and density of meats and meat products. The following general correlation for meat products for temperatures above the initial freezing point is proposed:

$$c_p = 1448(1 - x_w) + 4187x_w. \tag{1.21}$$

c_p in lamb meat can be estimated with the following expression:[50]

$$c_p = 979 + 3175.4x_w, \tag{1.22}$$

where x_w is the moisture content in percent wet basis, and c_p is in J/kg °C.

AbuDagga and Kolbe[51] measured and modeled the apparent specific heat of salt-solubilized surimi paste with 74, 78, 80, and 84% moisture content in the

temperature range 25 to 90°C. The following linear model was fitted to the experimental data as function of the temperature and moisture content:

$$c_p = 2330 + 6T + 14.9x_w, \tag{1.23}$$

where c_p is in Joules per kilogram degrees Centigrade (J/kg °C), and the moisture content, x_w, is in percent wet basis. Equation 1.23 can be considered a workable engineering model in most design circumstances.

1.4.1.3 Specific Heat of Fruits and Vegetables

The specific heat (J/kg °C) of Golden Delicious apples for the temperature range from –1 to 60°C can be estimated with the following correlation:[52]

$$c_p = 3360 + 7.5T, \tag{1.24}$$

and for Granny Smith:

$$c_p = 3400 + 4.9T. \tag{1.25}$$

Hsu et al.[53] proposed the following equation to predict c_p (J/kg °C) for pistachio with water contents ranging from 5 to 40% on wet basis:[11]

$$c_p = 1074 + 27.79x_w. \tag{1.26}$$

c_p for potatoes (Desiree variety) can be estimated with the following correlation, which was generated from data obtained with DSC measurements, for a temperature range from 40 to 70°C and moisture content from 0 to 80% on wet basis:[54]

$$c_p = 4180(0.406 + 1.46 \times 10^{-3}\mathrm{T} + 0.203x_w - 2.49 \times 10^{-2}x_w^2). \tag{1.27}$$

The main relative percentage deviation of Equation 1.27 is equal to 3.36%, which indicates a reasonably good fit for practical purposes.

1.4.1.4 Specific Heat of Miscellaneous Products

For milk, the following expression is proposed[55] at temperatures above freezing:[9]

$$c_p = 4190x_w + [(1370 + 11.3\mathrm{T})(1 - x_w)], \tag{1.28}$$

where T is in degrees Celsius, and c_p is in Joules per kilogram degrees Centigrade (J/kg °C).

c_p (J/kg °C) for processed cheese can be estimated from the general correlation[56]

$$c_p = 4101 + 1.2T - (1673 + 0.27\mathrm{T})x_f - (2716 - 1.1\mathrm{T})x_{ns}. \tag{1.29}$$

Equation 1.29 is applicable to a temperature range from 40 to 100°C, from 0.316 to 0.575 mass fraction of solutes, and from 0.135 to 0.405 mass fraction of nonfat solids, x_{ns}.[10]

Christenson et al.[57] assumed that the dependence of the specific heat of bread with moisture follows a mass fraction model:[11]

$$c_p = c_{pw}x_w + c_{pdry\ solid}(1 - x_w), \tag{1.30}$$

where c_p of a dry solid is given by

$$c_{pdry\ solid} = 98 + 4.9T. \tag{1.31}$$

T is in Kelvin (K) for 298 to 358 K temperature range, and c_p is in J/kg K.

1.4.2 Enthalpy

The *enthalpy* content is a relative property. For temperatures above the initial freezing point, it can be evaluated with the following general expression:[12]

$$H = \sum x_i \int_0^T c_{pi}dT, \tag{1.32}$$

which is valid at atmospheric pressure. If the specific heats, c_{pi}, are independent of temperature, then the following equation should be used:

$$H = T\sum x_i c_{pi}. \tag{1.33}$$

1.4.3 Thermal Conductivity and Thermal Diffusivity

Thermal conductivity and thermal diffusivity strongly depend on moisture content, temperature, composition, and structure or physical arrangement of the material (e.g., voids, nonhomogeneities). The thermal conductivity of fluid foods is a weak function of their composition, and simple empirical models can be used for its estimation. However, to model the thermal conductivity of solid foods, structural models are needed, due to differences in micro- and macrostructure of the heterogeneous materials.[21,58]

Porous foods are difficult to model because of the added complexity of the void spaces. The effective thermal conductivity depends on the heat flow path through solids and voids; it may be affected by pore size, pore shape, percent porosity, particle-to-particle resistance, convection within pores, and radiation across pores.[9] At low moistures, the thermal conductivity and thermal diffusivity of porous foods

are nonlinear functions of the moisture content, due to significant changes of bulk porosity; at moistures higher than 30%, k increases linearly with the moisture content.[4] Despite the attempts in developing structural models to predict the thermal conductivity of foods, a generic model does not exist at the moment.[36]

Since theoretical models have a number of limitations for application in food material, empirical models are popular and widely used for food process design and control, even though they are valid only for a specific product and experimental conditions.[59]

Similar to specific heat, most of the models used to calculate the thermal conductivity of foods with high moisture content have the following form:[27]

$$k = c_1 + c_2 x_w, \tag{1.34}$$

where c_1 and c_2 are constants. At $x_w = 1$, most of the equations converge on the thermal conductivity of water. Predictions agree at high water contents, and discrepancies between experimental and predicted values are marked at low water contents. Table 1.3 lists some simple equations, which only take into account the water content of the food (x_w is in decimal form). Linear models similar to

TABLE 1.3
Simple Thermal Conductivity Equations for Foods

Material	Model	Reference
Fruits and vegetables	$k = 0.148 + 0.493x_w$ $0 < x_w < 0.60$	9
Tomato paste	$k = 0.029 + 0.793x_w$ $0.538 < x_w < 0.708$, $T = 30°C$	10
Tomato paste	$k = -0.066 + 0.978x_w$ $0.538 < x_w < 0.708$, $T = 40°C$	10
Tomato paste	$k = -0.079 + 1.035x_w$ $0.538 < x_w < 0.708$, $T = 50°C$	10
Spring wheat (hard red)	$k = 0.129 + 0.274x_w$ $0.014 < x_w < 0.148$, $32°C < T < 60°C$	10
Dairy products and margarine	$k = 0.141 + 0.412x_w$	11
Meats and fish	$k = 0.080 + 0.52x_w$ $0.60 < x_w < 0.80$, $0°C < T < 60°C$	12
Fish	$k = 0.0324 + 0.3294x_w$	12
Minced meat	$k = 0.096 + 0.34x_w$	12
Fruit juice	$k = 0.140 + 0.42x_w$	12
Sorghum	$k = 0.564 + 0.0858x_w$	12
Pistachio	$k = 0.0866 - 0.2817x10^{-3}x_w$ $5\% < x_w < 40\%$	53

Equation 1.34 are also commonly used to estimate the thermal diffusivity, with the moisture content or the temperature as variables.[10] Riedel[60] proposed the following equation for estimating α:[12]

$$\alpha = 0.088 \times 10^{-6} + (\alpha_w - 0.088 \times 10^{-6}) x_w, \tag{1.35}$$

where α_w is the thermal diffusivity of water.

Several composition models have been proposed and discussed in the literature.[9,10,12] Additivity principles can also be used to calculate the thermal conductivity of many liquid and solid foods, by taking into account the water, protein, carbohydrate, fat, and sometimes also the ash content. The following equations are recommended for estimating k of foods that are not porous:[9]

$$k = 0.61 x_w + 0.20 x_p + 0.205 x_c + 0.175 x_f + 0.135 x_{as} \tag{1.36}$$

and

$$k = 0.58 x_w + 0.155 x_p + 0.25 x_c + 0.16 x_f + 0.135 x_{as}. \tag{1.37}$$

For the thermal diffusivity, Hermans[61] proposed the following equation, which is slightly dependent on temperature (K):[12]

$$\alpha = (0.0572 x_w + 0.0138 x_f + 0.0003T) \times 10^{-6}. \tag{1.38}$$

Although Equation 1.36 is for liquid foods,[62] it is relatively accurate for solid foods.[9] Equation 1.37 was fitted to more than 430 liquid and solid foods with satisfactory results, but it is not accurate for porous foods containing air (e.g., apples). The temperature effect is not included in Equations 1.36 and 1.37, so they are valid at the fitting region approximately at 25°C.

For heterogeneous foods, the effect of geometry must be considered using structural models.[21] In general, the models assume that foods consist of two different components physically orientated so that heat travels either in parallel or in perpendicular through each of them.[27,58] In dispersed systems, the volume fraction of the dispersed or discontinuous component as well as the thermal conductivity of the dispersed or continuous component are considered.[27] These models are not widely applicable since foods tend to have more than two components, and they are not arranged in simple configurations.[9] The continuous dispersed components model may be expanded to more than two components, and then appears to have application for some food systems.[9]

Saravacos and Maroulis[21] presented another approach to estimate the thermal conductivity as a function of moisture content and temperature, which is given below. To develop the model, it was assumed that a material of intermediate

moisture content consists of a uniform mixture of two different materials — a dried material and a wet material with infinite moisture — and that k can be estimated using a two-phase structural model. The temperature dependence of the thermal conductivity is then modeled by an Arrhenius-type model, and thus, the proposed mathematical model has the following form:

$$k = \frac{1}{1+X} k_0 \exp\left[-\frac{E_0}{R}\left(\frac{1}{T}-\frac{1}{T_r}\right)\right] + \frac{X}{1+X} k_i \exp\left[-\frac{E_i}{R}\left(\frac{1}{T}-\frac{1}{T_r}\right)\right], \quad (1.39)$$

where X (kg/kg db) is the moisture content, T (°C) is the material temperature, T_r is the reference temperature at 60°C, and R is the ideal gas constant (0.0083143 kJ/mol K). The adjustable parameters are as follows: k_0 (W/mK) is the thermal conductivity at $X = 0$ and $T = T_r$, k_i (W/mK) is the thermal conductivity at $X = \infty$ and $T = T_r$, E_0 (kJ/mol) is the activation energy for heat conduction in dry material at $X = 0$, and E_i (kJ/mol) is the activation energy for heat conduction in wet material at $X = \infty$.

Table 1.4 shows the results of the parameter estimation by applying the model to all the data of each material, regardless of the data sources. Since the results are not based on the data of only one source, the accuracy is very high.[21]

1.4.3.1 Thermal Conductivity of Meats

Few data are available on the thermal conductivity of meat in the cooking temperature range. For predictive purposes, Baghe-Khandan et al.[63] developed models to estimate thermal conductivities at temperatures up to 90°C and heating rates of <0.5°C/min based on the initial water (x_{w0}) and fat (x_f) contents at 30°C:[64]

For whole beef:

$$k = 10^{-3}(732 - 4.32x_f - 3.56x_{w0} + 0.636T). \quad (1.40)$$

For minced meat:

$$k = 10^{-3}(400 - 4.49x_f + 0.147x_{w0} + 1.74T). \quad (1.41)$$

For lamb meat:[11,50]

$$k = 0.48534 + 1.0627 \times 10^{-3}T, \quad T \geq -0.9113°C. \quad (1.42)$$

TABLE 1.4
Parameter Estimates of Equation 1.39

Material	k_i (W/mK)	k_0 (W/mK)	E_i (kJ/mol)	E_0 (kJ/mol)	SD (W/mK)
Cereal products					
Corn	1.580	0.070	7.2	5.0	0.047
Fruits					
Apple	0.589	0.287	2.4	11.7	0.114
Orange	0.642	0.106	1.3	0.0	0.007
Pear	0.658	0.270	2.4	1.9	0.016
Vegetables					
Potato	0.611	0.049	0.0	47.0	0.059
Tomato	0.680	0.220	0.2	5.0	0.047
Dairy					
Milk	0.665	0.212	1.7	1.9	0.005
Meat					
Beef	0.568	0.280	2.2	3.2	0.017
Baked products					
Dough	0.800	0.273	2.7	0.0	0.183
Model foods					
Amioca	0.718	0.120	3.2	14.4	0.037
Starch	0.623	0.243	0.3	0.4	0.006
Hylon	0.800	0.180	9.9		0.072
Other					
Rapeseed	0.239	0.088	3.6	0.6	0.023

Note: SD = standard deviation.

Source: From Saravacos, G.D. and Maroulis, Z.B., in *Transport Properties of Foods*, Marcel Dekker, New York, 2001, pp. 269–358.

Thermal conductivity for meat products and for heat transfer parallel or perpendicular to muscle fiber can be correlated as[65]

$$k = 0.1075 + 0.501x_w + 5.052\times10^{-4}x_wT \quad \text{Parallel to fiber} \tag{1.43}$$

$$k = 0.0866 + 0.501x_w + 5.052\times10^{-4}x_wT \quad \text{Perpendicular to fiber.} \tag{1.44}$$

The correlation given below is proposed for surimi paste for temperatures in the cooking range of 25 to 90°C:[51]

$$k = 1.33 - 4.82\times10^{-3}T + 5\times10^{-5}T^2 - 2.45\times10^{-2}x_w + 1.7\times10^{-4}x_w^2 + 2.4\times10^{-5}x_wT, \tag{1.45}$$

where x_w is in percent wet basis, and T is in degrees Centigrade (°C). The standard deviations of Equation 1.45 ranged from 0.1 to 5%, with higher deviations found at higher temperatures.

1.4.3.2 Thermal Conductivity and Thermal Diffusivity of Juices, Fruits and Vegetables, and Others

The thermal conductivity of clarified apple juice as a function of the concentration (Bx) in °Brix and temperature (T) in K can be expressed as[47]

$$k = 0.27928 - 3.5722 \times 10^{-3} Bx + 1.1357 \times 10^{3} T \tag{1.46}$$

Thermal conductivity of Golden Delicious and Granny Smith apples can be evaluated as[11]

$$k = 0.0159 x_w + 0.0025T - 0.994, \tag{1.47}$$

and for the thermal diffusivity:

$$\alpha = (-0.00278T - 1.39) \times 10^{-7} \quad \text{Golden Delicious} \tag{1.48}$$

$$\alpha = (-0.00556T - 1.31) \times 10^{-7} \quad \text{Granny Smith} \tag{1.49}$$

for a temperature range from the initial freezing point up to 60°C; x_w and T are the water content on percent wet basis and temperature in °C, respectively.

Quadratic and multiple form correlations are also used to model k in an attempt to cover a wide range of moisture contents.[10] Rahman et al.[59] improved a general model developed previously for fruits and vegetables, and obtained the following general power law correlation, which is valid for a wide range of temperatures (from 5 to 100°C), water contents (from 14 to 88%, wet basis), and porosities (from 0 to 0.56):

$$\frac{\alpha_0}{1 - \varepsilon_a + \dfrac{k_a}{\left(k_w\right)_r}} = 0.996 \left(\frac{T}{T_r} \right)^{0.713} x_w^{0.285}, \tag{1.50}$$

where α_0 is the Rahman–Chen structural factor, which includes the effective value of the thermal conductivity (k_e) and accounts for the effect of temperature and structure of a food item as

$$\alpha_0 = \frac{k_e - \varepsilon_a k_a}{\left(1 - \varepsilon_a - \varepsilon_w\right) k_s + \varepsilon_w k_w}. \tag{1.51}$$

Equation 1.50 gives a mean percent deviation from 6.8 to 15.1%, so the model can be applied in process design and control purposes, where around 15% maximum allowable error in data is permitted.[59]

Califano and Calvelo[66] measured the thermal conductivity of potatoes between 50 and 100°C and obtained a quadratic equation, which fitted experimental values within a mean absolute deviation of 2.3%; the fitted equation is given as[11]

$$k = 1.05 - 1.96 \times 10^{-2} T + 1.90 \times 10^{-4} T^2. \tag{1.52}$$

For extruded Durum wheat pasta, k for the range 20 to 60°C can be predicted from[67]

$$k = 0.305 + 0.285 x_w, \tag{1.53}$$

with an error in the order of 1% in the extreme temperatures.[11] For the thermal diffusivity, the following general relationship is proposed, involving moisture content and temperature with an error of 4%:[11]

$$\alpha = (1.73 - 0.9 x_w - 0.003T) \times 10^{-7}. \tag{1.54}$$

1.4.4 Density

In most engineering design, it is assumed that density moderately changes with temperature and pressure.[10] Pretreatments (heating, cooking, drying, etc.) and product preparation are factors that can also influence the value of density. Rahman[10] presented one of the most comprehensive books related to food properties. Experimental values and models to predict density are reviewed and discussed by the author.[10]

The density of materials also influences their electrical properties.[68] This can be seen in Equation 1.17, which shows that density is inversely proportional to the temperature increase (ΔT).

Some of the many equations that exist in literature for density are given here. The most commonly used model to predict density is

$$\rho = \frac{1}{\sum \frac{x_i}{\rho_i}}. \tag{1.55}$$

Since the porosity (ε) of a food material can strongly influence its density, Equation 1.55 should be modified to incorporate porosity (ε):

$$\rho = (1 - \varepsilon) \frac{1}{\sum \frac{x_i}{\rho_i}}, \tag{1.56}$$

where *i* denotes the *i*th component of the food system. A rule of thumb, regarding densities of major food components, states that values of fats, proteins, and carbohydrates fall within narrow ranges; consequently, average values of 920, 1250, and 1550 kg/m^3 can be taken for most of the calculations.[11]

A general correlation for density of fruit juices, which is claimed to agree with values calculated from the Choi and Okos model and fits experimental values obtained for 30 different juices, is presented below.[69] The following equation is valid for temperatures above freezing and for soluble solids concentrations up to 30°Brix:[11]

$$\rho = (1002 + 4.61Bx) - 0.460T + 7.001 \times 10^{-3} T^2 - 9.175 \times 10^{-6} T^3. \quad (1.57)$$

For sour cherry, apple, and grape juices, correlations as a function of temperature (T) in K and concentration (Bx) are obtained as[11,70]

$$\rho = 0.79 + 0.35 \exp(0.0108Bx) - 5.41 \times 10^{-4} T \quad \text{Sour cherry juice} \quad (1.58)$$

$$\rho = 0.83 + 0.35 \exp(0.01Bx) - 5.64 \times 10^{-4} T \quad \text{Apple juice} \quad (1.59)$$

$$\rho = 0.74 + 0.43 \exp(0.01Bx) - 5.55 \times 10^{-4} T \quad \text{Grape juice.} \quad (1.60)$$

In general, density of food materials varies nonlinearly with moisture content. The density of fruits and vegetables during drying can be correlated as[71]

$$\rho = g + h\frac{x_w}{x_{w0}} + p\left[\exp\left(-u\frac{x_w}{x_{w0}}\right)\right], \quad (1.61)$$

where g, h, p, and u are constants for each specific product considered (e.g., carrot, garlic, pear, potato, sweet potato, etc.).

For meat products, a density equal to 1053 kg/m^3 for temperatures above freezing point can be used.[40] AbuDagga and Kolbe[51] represented by the following straight line regression in two variables for the density of Pacific whiting surimi paste:

$$\rho = 1511.2 - 1.16T - 5.4x_w. \quad (1.62)$$

The moisture content for Equation 1.62 ranges from 74 to 84%, and T from 30 to 90°C; x_w is in percent wet basis. Equation 1.62 indicates that density decreases with increased moisture content and temperature. Protein denaturation during cooking is likely to be responsible for the decrease in ρ with temperature.

Pasta density as a function of moisture content (%) can be correlated as follows:[11,67]

$$\frac{1}{\rho} = (3.02x_w + 6.46)10^{-4}. \quad (1.63)$$

1.4.5 Dielectric Properties

Electrical properties of foods have generally been of interest for two reasons. One relates to the possibility of using the electrical property as a means for determining moisture content or some other quality factor. The other has to do with the absorption of energy in high-frequency dielectric heating or microwave heating applications in food processing.[68] Primary determinants of electrical properties of foods are frequency, temperature, chemical composition, and physical structure.[26] The effect of composition on dielectric properties is complex. For example, the dielectric constant increases with moisture content for most foods, but studies report different trends for the dielectric loss factor.[72]

Extensive experimentally obtained data for the dielectric properties of various foods are reported in the literature; however, values of dielectric properties above 100°C for both microwave and RF ranges are scarce.[30] Furthermore, data extrapolation from low temperatures up to the sterilization region should not be done.[37]

Efforts have been made to relate dielectric properties to food composition, temperature, and frequency.[30] The responses of different components in a system (e.g., salt or ash content and carbohydrates) depend upon the manner in which they are bound to the other components in a food matrix; the particle geometry in a food mixture is also an important parameter.[73] Therefore, for food mixtures, the prediction of dielectric properties from data for the individual components is difficult.[73] On the other hand, prediction from composition can potentially avoid costly measurements and can provide valuable insight into the behavior of individual components in the food.[31]

A series of polynomial equations have been developed to estimate ε' and ε'' for cereal grains, fatty/low moisture content, fruits and vegetables, and meat products.[73] The predictive equations include the influence of food composition and temperature (below 70°C in general) at microwave frequencies between 0.9 and 3 GHz for all the products, and up to 10 GHz for grains. Table 1.5 shows the predictive equations that give coefficients of determination of $R^2 \geq 0.9$.

Datta et al.[31] performed a regression analysis for the dielectric constant and loss data set of about 100 experimental points in the frequency range of 2400 to 2500 MHz and the temperature range of 5 to 65°C. The most important factors proposed for use in the predictive equations were moisture (moisture content greater than 60%), salt, and temperature. After fitting to the reported data in the literature, the authors[31] concluded that it was difficult to develop a generic composition-based model for all products; then they separated meat products from those of fruits and vegetables. The different methods of measurement and the

TABLE 1.5
Predictive Equations for the Dielectric Constant and Loss Factor of Foods

Food Type	f (GHz)	T (°C)	x_w (%)	x_a (%)	x_f (%)	R^2
Fatty/low-moisture-content foods						
$\varepsilon' = 2.63 - 0.0015T + 0.162x_w$	1–3	0–100	0–30	0–5	70–100	0.98
Fruits/vegetables						
$\varepsilon' = 2.14 - 0.104T + 0.808x_w$	≈2.45	0–70	50–90	—	—	0.98
$\varepsilon'' = 3.09 - 0.0638T + 0.213x_w$	≈2.45	0–70	50–90	—	—	0.90
Meat products						
Pork						
$\varepsilon' = -70 - 0.1T + 1.7x_w + (1.5 + 0.02T)x_{as}$	2–3	0–70	60–80	0–6	0–20	0.89
Poultry						
$\varepsilon' = -87.3 - 0.051T + 1.91x_w + (2 + 0.02T)x_{as}$	2–3	0–70	60–80	0–5	≈10	0.90

Source: Adapted from Calay, R.J. et al., *Int. J. Food Sci. Technol.*, 29, 699–713, 1995.

lack of composition data could have probably led to the significant variability observed. For a restricted data set containing about 30 data points for raw beef, beef juice, raw turkey, and turkey juice, the best correlation for the dielectric constant contains two components — water and ash:[31]

$$\varepsilon' = x_w(1.0707 - 0.0018485T) + x_{as}(4.7947) + 8.5452. \quad (1.64)$$

Equation 1.64 has a correlation coefficient of 0.94, and the maximum error in the prediction is 5%. The dielectric loss for this restricted data set was modeled as a function of the mass percentage of water and temperature. The addition of a temperature-dependent ash term resulted in the final correlation, which has a high correlation coefficient ($R^2 = 0.989$) and an error lower than 10%:

$$\varepsilon'' = x_w(3.447 - 0.0187T + 0.000025T^2) + x_{as}(-57.093 + 0.231T) - 3.599. \quad (1.65)$$

ε' and ε'' of ham as a function of temperature (0 to 70°C), moisture (38.2 to 68.9%), and ash contents (1.78 to 6.80%) at 2450 MHz can be predicted from[72]

$$\varepsilon' = -25.49 + 1.063x_w - 1.041x_{as} + 0.03452T \quad (1.66)$$

$$\varepsilon'' = -150.2 + 5.243x_w + 6.220x_{as} - 0.2845T - 0.04322x_w^2 - 0.4732x_{as}^2 + 0.002245T^2 + 0.1090x_{as}T \quad (1.67)$$

TABLE 1.6
Predictive Equations for Vegetables and Fruits at 2450 MHz

Dielectric Constant	
Overall	$\varepsilon' = 38.57 + 0.1255T + 0.4546x_w - 14.54x_{as} - 0.0037x_wT + 0.07327x_{as}T$
Vegetables	$\varepsilon' = -243.6 + 1.342T + 4.593x_w - 426.9x_{as} + 376.5x_{as}^2 - 0.01415x_wT - 0.3151x_{as}T$
Fruits	$\varepsilon' = 22.12 + 0.2379T + 0.5532x_w - 0.0005134T^2 - 0.003866x_wT$
Dielectric Loss Factor	
Overall	$\varepsilon'' = 17.72 - 0.4519T + 0.001382T^2 - 0.07448x_w + 22.93x_{as} - 13.44x_{as}^2 + 0.002206x_wT + 0.1505x_{as}T$
Vegetables	$\varepsilon'' = -100.02 - 0.1611T + 0.001415T^2 + 2.429x_w - 378.9x_{as} + 316.2x_{as}^2$
Fruits	$\varepsilon'' = 33.41 - 0.4415T + 0.001400T^2 - 0.1746x_w + 1.438x_{as} + 0.001578x_wT + 0.2289x_{as}T$

Source: From Sipahioglu, O. and Barringer, S.A., *J. Food Sci.*, 68, 234–239, 2003.

where x_w and x_{as} are the percentages of moisture and ash, respectively, T is in °C, and the adjusted coefficients of determination R^2 are equal to 0.817 and 0.852, respectively.

Sipahioglu et al.[38] obtained dielectric constant and loss factor predictive equations for turkey meat with the addition of sodium chloride, sodium tripolyphosphate, glycerol, lactic acid, and sodium lactate as a function of temperature (5 to 130°C), moisture, water activity, and ash content at both 915 and 2450 MHz.

Sipahioglu and Barringer[74] developed predictive equations at 2450 MHz for 15 vegetables and fruits at 5 to 130°C as a function of temperature, ash content (0.26 to 1.56%), and moisture content (57.30 to 95.89%). It was found that separating vegetables from fruits increased the correlation between dielectric properties and food composition and temperature. Predictive equations for each vegetable and fruit as a function of temperature were also reported. The average percent error of prediction was 6.20% for the dielectric constant and 13.22% for the dielectric loss. Table 1.6 lists the predictive equations at 2450 MHz. The units for temperature and moisture and ash contents are °C and percent wet basis, respectively.

Dielectric properties of mashed potatoes relevant to microwave and radio frequency pasteurization and sterilization processes have been measured over 1 to 1800 MHz and 20 to 120°C, and regressed with polynomial relationships as a function of moisture content (81.6 to 87.8% wet basis) and salt content (0.8 to 2.8% wet basis).[30] The regression equations are shown in Table 1.7 at four frequencies: 27, 40, 433, and 915 MHz. All the regression equations have R^2 values equal to or above 0.91. The calculated data for ε' differ from measured values by less than 10%, and the calculated data for ε'' differ by 1 to 25%, except

TABLE 1.7
Predictive Equations for the Dielectric Properties of Mashed Potatoes

Dielectric Constant		**R^2**
27 MHz	$\varepsilon' = 54 + 98.5x_{as} - 81.2x_{as}^2 + 0.000019T^3 + 0.00121T^2x_{as} - 0.000026T^2x_w + 18.6x_{as}^3$	0.95
40 MHz	$\varepsilon' = 37.5 + 114x_{as} - 86.4x_{as}^2 + 0.000020T^3 + 0.000683T^2x_{as} - 0.000035T^2x_w + 18.6x_{as}^3$	0.91
433 MHz	$\varepsilon' = -59.2 + 0.940x_w + 115x_{as} - 0.00138Tx_w - 82.4x_{as}^2 + 16.8x_{as}^3$	0.92
915 MHz	$\varepsilon' = -85.5 + 1.26x_w + 105x_{as} - 76.3x_{as}^2 + 0.000012T^3 - 0.000025T^2x_w + 15.7x_{as}^3$	0.91
Dielectric Loss Factor		
27 MHz	$\varepsilon'' = -285 + (636 + 0.0893T^2)x_{as}$	0.98
40 MHz	$\varepsilon'' = -187 + (426 + 0.0601T^2)x_{as}$	0.98
433 MHz	$\varepsilon'' = -9.51 + (39.1 + 0.0053T^2)x_{as}$	0.97
915 MHz	$\varepsilon'' = 0.12 + (19.3 + 0.00234T^2)x_{as}$	0.96

Source: From Guan, D. et al., *J. Food Sci.*, 69, FEP30–FEP37, 2004.

that the discrepancies are up to 40% at 20°C. The literature shows that it is more difficult to the predict loss factor than the dielectric constant.[74]

1.5 CONCLUSIONS

Extensive data on experimental values and predictive equations for thermal properties of foods have been reported in the literature; in some areas, e.g., dielectric properties, the data are very limited. Although the data are sometimes incomplete, they are of great value for preliminary design, heat transfer calculations, and food quality assessment. There are few databases available at present, and in some cases (e.g., Nelfood), the databases available give a score indicating the quality of the method specification and food definition. These databases can be very helpful tools when there is not enough expertise. In general, data or predictive equations for the upper temperature range of interest to food engineers are rather scarce. Mathematical models for predicting properties are very useful, but if more accuracy is desired, experimental determination should be carried out. The data analysis shows that when experimental values are compared with the ones obtained from predictive models, the less water there is in the material, the higher are the discrepancies between predicted and measured values. The reason seems to be the treatment of water as bulk water, without taking into account the interactions with the food components. Future work, as suggested by many researchers, should be addressed to study the influence of the state of water on thermal and electrical properties.

NOMENCLATURE

Symbols

a, b	Constants in Equation 1.11
A	Area (m^2)
Bx	Concentration (°Brix)
c	Specific heat (J/kg °C)
c_0	Speed of light in vacuum (m/sec)
c_1, c_2	Constants in Equation 1.34
d	Penetration depth (cm)
E_0	Activation energy in dry material (kJ/mol)
E_i	Activation energy in wet material (kJ/mol)
f	Frequency (Hz)
g, h	Constants in Equation 1.61
H	Enthalpy (J/kg)
k	Thermal conductivity (W/mK)
m	Mass (kg)
p	Constant in Equation 1.61
q	Heat transfer rate (W)
Q	Heat (kJ)
t	Time (sec)
T	Temperature (K or °C)
u	Constant in Equation 1.61
V	Electric field (V/cm)
V_S	Sample volume (m^3)
V_w	Water volume (m^3)
x	Mass fraction
z	Thickness (m)

Greek Letters

α	Thermal diffusivity (m^2/sec)
α_0	Rahman–Chen structural factor
β	Constant in Equation 1.14
δ	Dielectric loss angle (°)
ΔT	Temperature increase (°C)
ε	Porosity or volume fraction
ε_0	Dielectric constant of vacuum (8.85419×10^{-12} F/m)
ε'	Dielectric constant of the material (F/m)
ε''	Dielectric loss factor of the material (F/m)
ε_d''	Dipole loss component (F/m)
ε_σ''	Ionic loss component (F/m)
γ	Constant in Equation 1.14

λ_0	Free space microwave wavelength (m)
ρ	Density (kg/m^3)
σ	Electrical conductivity (S/m)

Subscripts

a	Air
as	Ash
c	Carbohydrate
e	Effective value
f	Fat
i	*i*th component in a food system
ns	Nonfat solids
p	Protein
r	Reference temperature (°C)
s	Solids
w	Water
w_0	Initial water content

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2 Heat and Mass Transfer in Thermal Food Processing

Lijun Wang and Da-Wen Sun

CONTENTS

2.1 INTRODUCTION

Thermal processing techniques are widely used to improve eating quality and safety of food products, and to extend the shelf life of the products. These thermal processing techniques involve the production, transformation, and preservation of foods. Sterilization and pasteurization are heating processes to inactivate or destroy enzyme and microbiological activity in foods. Cooking (including baking, roasting, and frying) is a heating process to alter the eating quality of foods and to destroy microorganisms and enzymes for food safety. Dehydration and drying are heating processes to remove the majority of water in foods by evaporation (or by sublimation for freeze drying) for extending the shelf life of foods due to a reduction in water activity.

When a food is placed in contact with a liquid or solid medium of different temperatures or concentrations, a potential for a flux of energy or mass appears. The principles of many food thermal processes are based on heat and mass exchanges between the food and processing medium. There is a need for qualitative and quantitative understanding of the heat *and* mass transfer mechanisms underlying various unit operations of food thermal processes. This is important for the development of new food sources and food products, for more economical and efficient processing of foods, and for better food quality and safety. If the mechanism of a process is well understood, mathematical models can be developed to present the process. Experiments can virtually be carried out on mathematical models under broad experimental conditions in an economical and timesaving manner. With process models, quantitative calculations and predictions can be made for more reliable design, optimization of design and operating conditions, and evaluation of process performance. Therefore, advances of food thermal processes may become possible on the basis of improved understanding of heat and mass transfer mechanisms.

This chapter first briefly presents the fundamental mechanisms and physical laws of heat and mass transfer. A review is then conducted on the applications of the engineering principles and physical laws of heat and mass transfer for analyzing the unit operations of thermal processes in the food industry. Finally, future improvements in understanding of heat and mass transfer mechanisms in food thermal processes and development of heat and mass transfer models for describing food thermal processes are discussed.

2.2 FUNDAMENTALS OF HEAT AND MASS TRANSFER

2.2.1 Heat Transfer

2.2.1.1 Basic Heat Transfer Modes

Many unit operations of thermal food processes involve the transfer of heat into or out of a food. Heat may be transferred by one or more of the three mechanisms of conduction, convection, and radiation. Most industrial heat transfer operations involve a combination of these, but it is often the case that one mechanism is dominant.

Conduction is the transfer of heat through solids or stationary fluids due to lattice vibration or particle collision. The heat flux due to conduction in the x direction through a uniform homogeneous slab of materials, as shown in Figure 2.1a is given by Fourier's first law of conduction:

$$q = -kA\frac{dT}{dx} \tag{2.1}$$

Fourier's law of heat conduction may be solved for a rectangular, cylindrical, or spherical coordinate system, depending on the geometrical shape of the object being studied.

Convection uses the movement of fluids to transfer heat. The movement, which causes heat transfer, may occur in natural or forced form. Natural convection creates the fluid movement by the difference between fluid densities due to the temperature difference. Forced convection uses external means such as agitators and pumps to produce fluid movement. Convection heat transfer is the major mode of heat transfer between the surface of a solid material and the surrounding fluid. For analyzing convection heat transfer, a boundary layer is normally assumed near the surface of the solid material, as shown in Figure 2.1b. Heat is transferred by conduction through this layer. The layer contains almost all of the resistance to heat transfer because of relatively low thermal conductivities and rapid heat transfer from the outer edge of the boundary layer into the bulk of the fluid. Using the boundary layer concept, the rate of convective heat transfer may be written as

$$q = kA\frac{(T_s - T_\infty)}{\delta} = A\frac{(T_s - T_\infty)}{\delta/k} \tag{2.2}$$

However, as the thickness of the boundary layer, δ, can neither be predicted nor measured easily, the thermal resistance of the boundary layer cannot be determined. δ/k is thus replaced with the term $1/h_c$, in which h_c is a film heat transfer coefficient. Equation 2.2 can then be rewritten as

$$q = h_c A(T_s - T_\infty) \tag{2.3}$$

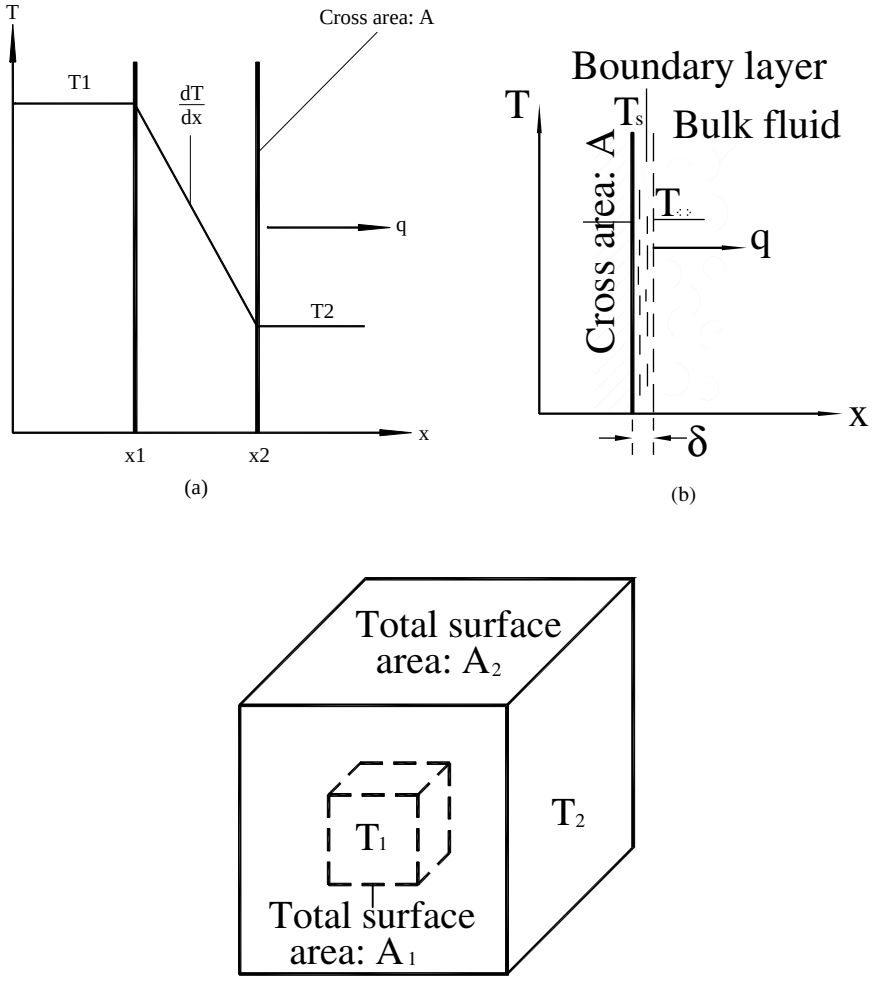

FIGURE 2.1 Schematic of three basic heat transfer modes. (a) Heat conduction through a uniform slab. (b) Heat convection through a vertical wall. (c) Heat radiation between a surface, 1, of a body and the surroundings, 2.

Radiation does not require a medium for transferring heat but uses electromagnetic waves emitted by an object for exchanging heat. The energy emitted from a surface depends on the temperature of the surface, which can be described using the Stefan–Boltzmann law:

$$q = \sigma A \varepsilon T_K^4 \tag{2.4}$$

When the energy exchanges between two bodies by radiation, the energy emitted by one is not completely absorbed by the other, as it can only absorb the portion that it intercepts. Therefore, a shape factor, F, is defined. The radiative energy exchange between a surface, 1, of a body and the surroundings, 2, can be determined by

$$q = \sigma F_{12} A_1 e(T_{K1}^4 - T_{K2}^4) \tag{2.5}$$

If the surface, 1, is enclosed by the surroundings, 2, as shown in Figure 2.1c, there is $F_{12} = 1$. Similar to the convective heat transfer coefficient, a radiative heat transfer coefficient may be expressed as

$$q = h_r A(T_{K1} - T_{K2}) \tag{2.6}$$

where

$$h_r = \sigma e(T_{K1}^2 + T_{K2}^2)(T_{K1} + T_{K2}) \tag{2.7}$$

2.2.1.2 Heat Transfer with Phase Changes

Most foods, such as raw meats and vegetables, have high moistures. Water itself is widely used as a processing medium in food processes. Water normally exists in one of three states: solid, liquid, or gas. The transition between two states is called a *phase transformation* or *phase change*. During phase transformation, the temperature of pure water keeps constant with added energy because all energy is used to transform water from one state to another. Because water is widely present in foods and is used as a processing medium, it is necessary to discuss the heat transfer with phase changes of water in the food industry.

During food thermal processes, the water in the food may experience phase changes. Frying and grilling of foods involve phase change from liquid water to vapor. There is an evaporation front, which divides the food body into two parts of the outer crust and the internal core regions, as shown in Figure 2.2. The evaporation front moves toward the center as frying and grilling processes proceed. If a frozen food is used during frying and grilling, there will be two moving boundaries: the thawing front and the evaporation front.

The heat transfer mechanisms across the moving boundary must account for the latent heat of phase change of water. The moving front of phase change in the food can be tracked by the energy balance on the front, which is given by[1]

$$-k_1\left(\frac{\partial T}{\partial x}\right)_1 + k_2\left(\frac{\partial T}{\partial x}\right)_2 = \lambda \rho X_w \frac{dS(t)}{dt} \tag{2.8}$$

$$t > 0, x = S(t) \tag{2.9}$$

Water is also widely used as processing medium. Boiling and condensation involve a phase change between liquid water and vapor. Boiling heat transfer is particularly important in processing operations such as evaporation, in which the

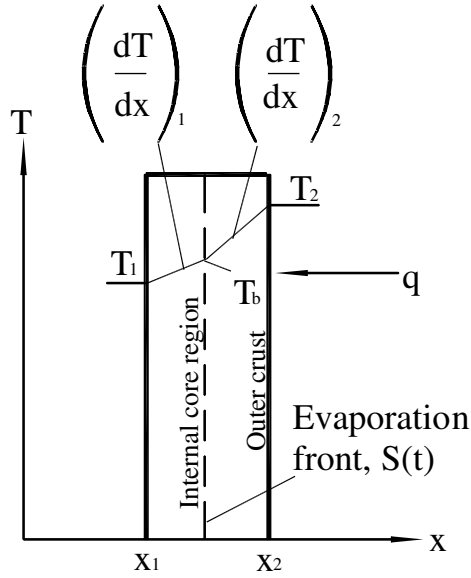

FIGURE 2.2 Schematic of heat transfer with phase changes (frying).

boiling of liquids takes place either at submerged surfaces or on the inside of vertical tubes, as in a climbing film evaporator. The heat flux changes dramatically as a function of the temperature difference between the surface and the boiling liquid, rising to a peak value and falling away sharply. This is caused by the strong dependence between the heat transfer coefficient and the temperature difference, which is shown in Figure 2.3. In order to avoid the danger of overheating and damaging the walls of the heater, equipment should ideally be operated in the nucleate boiling zone, just below the critical temperature difference, as shown in Figure 2.3.[2] Vapor condensation is also used in food thermal processes. Consider the food sterilization process used in canned foods: if steam is used as a heating medium, the condensing vapors on the metal surface of the container result in a significantly higher heat transfer than if hot water were used to heat the cans. A vapor condenses on a cold surface in one of two distinct ways: film condensation and drop condensation. The presence of noncondensable gases affects the rate of condensation, and the film heat transfer coefficient may be reduced considerably.[2]

The heat flux due to phase change of boiling and condensation can be expressed as

$$q = hA(T_s - T_\infty) \tag{2.10}$$

The heat transfer coefficients experienced when a liquid is vaporized or when a vapor is condensed are considerably greater than that for heat transfer without a phase change. However, it is much more difficult to measure heat transfer coefficients of phase changes.

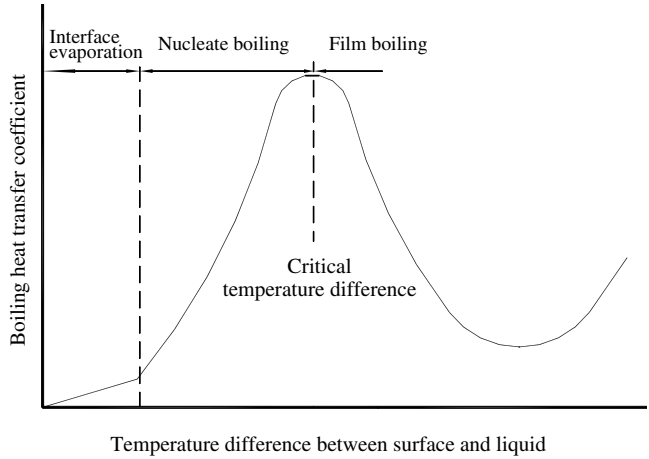

FIGURE 2.3 Relationship between boiling heat transfer coefficient and temperature difference.

The heat transfer coefficient in nucleate boiling may be calculated by a correlation. Kutateladze's correlation is a commonly used one, which is given by[2]

$$\left(\frac{h_b}{k}\right)\psi^{0.5} = 0.0007\left[\frac{q_{\max}}{\alpha\lambda\rho_v}\frac{P}{\sigma}\Psi\right]^{0.7}\mathrm{Pr}^{-0.35} \tag{2.11}$$

where

$$\Psi = \frac{\sigma}{g(\rho_l - \rho_v)} \tag{2.12}$$

$$q_{\max} = 0.16\lambda\rho_v\left(\frac{\sigma g(\rho_l - \rho_v)}{\rho_v^2}\right)^{0.25} \tag{2.13}$$

The film heat transfer coefficient for condensation can be predicted from the Nusselt theory, which gives the mean film coefficient by[2]

$$h_{cd} = 0.943\left(\frac{\rho^2 k^3 g\lambda}{\mu L\Delta T}\right)^{0.25}, \quad \text{for a vertical surface} \tag{2.14}$$

$$h_{cd} = 0.725\left(\frac{\rho^2 k^3 g\lambda}{\mu d\Delta T}\right)^{0.25}, \quad \text{for a horizontal tube} \tag{2.15}$$

2.2.1.3 Heat Transfer with Electromagnetic Waves

Microwave energy is an electromagnetic energy widely used in the food thermal industry. Microwaves are transmitted as waves, which can penetrate foods and interact with the polar molecules such as water in the foods to be converted to heat. The electromagnetic spectrum is normally characterized by wavelength (λ) and frequency (v). Microwaves are nonionizing electromagnetic waves, and commercial microwave heating applications use frequencies of 2450 MHz, sometimes 915 MHz in the U.S. and 896 MHz in Europe. The depth of penetration into a food is directly related to frequency, and the lower-frequency microwaves penetrate more deeply. Because the microwave can penetrate into foods, it can heat foods quicker than the food is heated through conduction from the outer surface. Once microwave energy has been absorbed by foodstuffs, heat is then transferred throughout the food mass by conduction or convection. The rate of energy conversion per unit volume can be considered a source term in a heat transfer model.

The conversion of microwave energy to heat depends on the properties of the energy source and the dielectric properties of the foodstuffs. The power dissipation or rate of energy conversion per unit volume, S, is given by[2,3]

$$S = 5.56 \times 10^{-15} E^2 v \varepsilon'' \tag{2.16}$$

where

$$\varepsilon'' = \varepsilon' \tan\beta \tag{2.17}$$

However, the suitability of a food for microwave heating is crucially dependent on the penetration characteristics. The microwave electrical field strength is a function of penetration depth, which can be given by

$$E = E_0 e^{-2\alpha' x} \tag{2.18}$$

where

$$\alpha' = \frac{2\pi}{\lambda}\left[\frac{\varepsilon'}{2}\left(\sqrt{1+\tan^2\beta}-1\right)\right]^{0.5} \tag{2.19}$$

2.2.2 Mass Transfer

Mass transfer is concerned with the movement of materials in fluid systems, including gases or liquids. Mass transfer may take place according to two mechanisms: *molecular diffusion* or *convective mass transfer*. When there is a concentration gradient of the considered component between two points of the system, mass transfer is produced by molecular diffusion. When the entire mass moves from one point to another, the transfer is produced by convection.

2.2.2.1 Molecular Diffusion

Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motion. Although no molecule has a preferred direction of motion, observation indicated that molecules transfer from a region of higher concentration to a region of lower concentration. The mass flux can be described by Fick's first law:

$$J_A = -D_A \frac{dC_A}{dx} \tag{2.20}$$

where D is diffusivity, which is defined as the constant of proportionality in Fick's law.

The diffusion of fluids within the pore spaces of a porous solid is of some interest to food processing such as drying. It is possible to quantify an effective diffusivity that describes the transfer of gas or liquid within a solid porous food. Effective diffusivities of moisture in some solid foods are listed in Table 2.1.[4]

In Equation 2.20, concentrations can be expressed in a number of ways, such as molar concentration, partial pressure, mass concentration, and mass and mole fractions. The corresponding units of different concentrations differ considerably.

2.2.2.2 Convective Mass Transfer

During food processes, mass may be transferred between distinct phases across a phase boundary. Whitman assumed that two laminar films exist on each side of the interface when a gaseous solute transfers from a gas phase to a liquid phase or mass transfers between two liquid phases, as shown in Figure 2.4.[2] According to Whitman's theory, the resistance to mass transfer is contained within the two

TABLE 2.1
Effective Diffusities in Solid Foods

	Moisture Content (%, by dry base)	Temperature (K)	Diffusivity $\times 10^{11}$ (m^2/sec)
Starch gel	10	298	0.1
Starch gel	30	298	2.3
Blached potato	60	327	26.0
Air-dried apple	12	303	0.65
Freeze-dried apple	12	303	12.0
Fish muscle	30	303	34.0
Raw minced beef	60	333	10.0
Cooked minced beef	60	333	12.0

Source: Saravacos, G.D., in *Engineering Properties of Foods*, 2nd ed., Rao, M.A. and Rizvi, S.S.H., Eds., Marcel Dekker, New York, 1994, pp. 169–221. With permission.

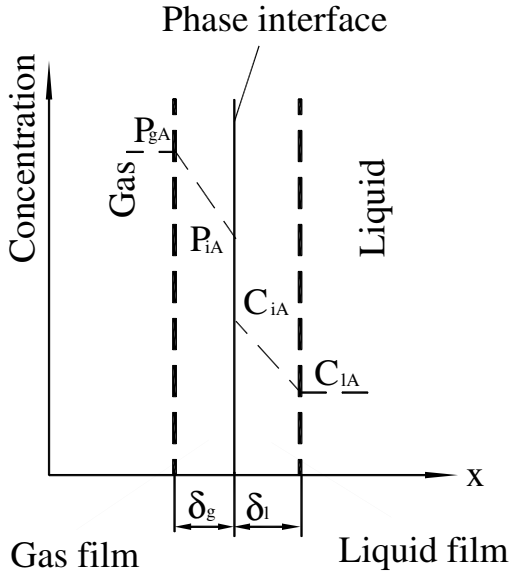

FIGURE 2.4 Whitman's two-film diffusion theory. (From Smith, P.G., *Introduction to Food Process Engineering,* Kluwer Academic/Plenum Publishers, New York, 2003, pp. 163–170, 179–186, 191–217.)

films and the concentration gradients across each film are linear. Whitman's two-film theory is the earliest and most general one to account for interphase mass transfer. Mass transfer within the films is assumed to be due solely to molecular diffusion, and thus Fick's law can be applied directly to each film. Integrating over the linear concentration gradient, Fick's law can be expressed as[2]

$$J_A = -\frac{D_{g_A}}{\delta_g}(P_{iA} - P_{gA}) = -\frac{D_{lA}}{\delta_l}(C_{lA} - C_{iA}) \tag{2.21}$$

However, the thicknesses δ_g and δ_l cannot be measured or predicted independently. In order to overcome this difficulty, the terms D_{gA}/δ_g and D_{lA}/δ_l are replaced by a gas film mass transfer coefficient, k_g, and a liquid film mass transfer coefficient, k_l, respectively.

The partial pressure and molar concentration on the interface cannot be determined independently because of the uncertainty of the interface position and the impossibility of measurement of interfacial concentration. Therefore, overall gas and liquid mass transfer coefficients are introduced based on the concentration differences that can be determined. Equation 2.21 can be rewritten as

$$J_A = -K_g(P_A^* - P_{gA}) = -K_l(C_{lA} - C_A^*) \tag{2.22}$$

where P_A^* is the partial pressure of A in the gas phase, which is in equilibrium with the bulk liquid concentration, C_{lA}, and C_A^* is the molar concentration of A in the liquid phase, which is in equilibrium with the bulk partial pressure, P_{gA}. The equilibrium relationships are determined by Henry's law and are expressed as

$$P_A^* = HC_{lA} \tag{2.23}$$

$$C_A^* = P_{gA}/H \tag{2.24}$$

2.2.3 Unsteady-State Heat and Mass Transfer

For steady-state heat and mass transfer, there is no change in temperature or concentrate of the material with time. However, in the majority of food thermal processing applications, the food temperature or concentrate of a food component is constantly changing, and unsteady-state heat and mass transfer is more commonly found. Heat and mass transfer follows the same pattern, which can be described in a generalized manner. The generalized governing equation of unsteady-state heat and mass transfer can be expressed as

$$\frac{\partial \phi}{\partial t} + u_x \frac{\partial \phi}{\partial x} + u_y \frac{\partial \phi}{\partial y} + u_z \frac{\partial \phi}{\partial z} = \frac{\partial}{\partial x}\left(\alpha \frac{\partial \phi}{\partial x}\right) + \frac{\partial}{\partial y}\left(\alpha \frac{\partial \phi}{\partial y}\right) + \frac{\partial}{\partial z}\left(\alpha \frac{\partial \phi}{\partial z}\right) + S \tag{2.25}$$

where ϕ is temperature for heat transfer and concentration for mass transfer, and α is diffusivity (for heat transfer $\alpha = k/(\rho c)$ and for diffusion $\alpha = D$).

In order to find the solution of Equation 2.25, it is necessary to know the initial and boundary conditions. The initial conditions give what happens at the start. The initial conditions may be the same initial temperature or concentration, $\phi|_{t=0} = \phi_0$. The initial conditions may also be an initial profile of temperature or concentration, $\phi|_{t=0} = \phi_0(x, y, z)$. The boundary conditions give what happens at the boundaries of the phase to be investigated. The boundary conditions may be (1) a constant, $\phi|_\Gamma = \phi_s$; (2) a flux, $\phi|_\Gamma = q_s$; (3) a convection, $\phi|_\Gamma = h(\phi_s - \phi_\infty)$; or (4) a combination of flux and convection, $\phi|_\Gamma = q_s + h(\phi_s - \phi_\infty)$.

Sometimes, depending on the geometry of the product to be studied, it is useful to consider alternative coordinate systems, such as the cylindrical coordinate and spherical coordinate systems. However, whichever system is used, the intrinsic mechanisms and physical laws of heat and mass transfer remain the same.

2.2.4 Overview of Solution Methods

Variables such as temperature and moisture used in modeling the unsteady-state thermal processes depend on time and position. The equations governing the physical mechanism of unsteady-state heat and mass transfer are thus of a partial differential type, as shown in Equation 2.25. An analytical solution of the partial differential equation is continuous. However, the possibility of analytical solution

is restricted to rather simple forms of the governing equations, boundary, and initial conditions. *Numerical methods* have been widely used to solve the partial differential equations governing the heat and mass transfer. Numerical methods can generate discretized solutions for the partial differential equations.

The finite difference (FD) method is simple to formulate a set of discretized equations from the transport differential equations in a differential manner.[5] The FD method is normally used for simple geometries such as sphere, slab, and cylinder. The FD method has been widely used to solve heat and mass transfer models of many food processes.[6–24] There are a number of important publications that have improved the knowledge of the finite difference scheme for predicting the heat and mass transfer during food processes.[25,26] Additional information can be found in a review paper by Wang and Sun.[27] Table 2.2 gives a summary of recent development of FD models for simulating food thermal processes. However, for foods with irregular shapes, the surface temperature predictions by the FD method are less satisfactory due to geometric simplification.

The finite element (FE) method may perform better than the finite difference method for irregular geometries, complex boundary conditions, and heterogeneous materials. The FE method involves discretizing a large domain into a large number of small elements, developing element equations, assembling the element equations for the whole domain, and solving the assembled equations. The FE discretization of the governing differential equations is based on the use of interpolating polynomials to describe the variation of a field variable within an element. Although the spatial discretization is different for the FE method than for the FD method, it is usual to employ an FD method for the time progression in a transient problem.[28,29] The FE method has been successfully used to solve the heat and mass transfer models of food processes.[30–56] Additional information can be found in two review papers by Wang and Sun[27] and Puri and Anantheswaran.[57] A summary of various finite element methods developed recently for analyzing food thermal processes is listed in Table 2.3. However, the FE method is complex and computationally more expensive than the FD method.

Computational fluid dynamics (CFD) is a simulation tool for the solution of fluid flow and heat transfer problems. In CFD calculation, the continuity equation, momentum conservation equation (also known as the Navier–Stockes transport equations), and energy conservation equation are numerically solved to give predictions of velocity, temperature, shear, pressure profiles, and other parameters in a fluid flow system.[58] In the last few years, there has been continuous progress in the development of CFD codes. Some of the common commercial codes include CFX (http://www.software.aeat.com/cfx/), Fluent (http://www.fluent.com/), Phoenics (http://www.cham.co.uk/), and Star-CD (http://www.cd.co.uk). The computational procedure of most commercial CFD packages is based on the *finite volume* (FV) numerical method. In fact, the FV method was derived from the finite difference method. In the FV method, the domain is divided into discrete control volumes. The key step of the FV scheme is the integration of the transport equations over a control volume to yield a discretized equation at its nodal points.[59] Although CFD has been applied to industries such as aerospace, automotive, and nuclear for several

TABLE 2.2
Summary of Finite Difference Method in Thermal Food Processing

Processes	Authors	Affiliation	Heat Model	Mass Model	Dimension	Temperature Dependent Properties	Foods
Dehydration and drying	Rovedo et al. (1995)[82]	Ciudad University, Argentina		√	One dimension	√	Potato
	Simal et al. (2000)[84]	University of Illes Balears, Spain		√	Three dimensions	√	Aloe vera
	Ben-Yoseph et al. (2000)[83]	University of Wisconsin–Madison, U.S.		√	Three dimensions	√	Sugar film
	Wang and Brennan (1995)[7]	University of Reading, U.K.	√	√	One dimension	√	Solid foods
	Thorvaldsson and Janestad (1999)[22]	Swedish Institute for Food and Biotechnology	√	√	One dimension	√	Bread
	Wang and Chen (1999)[21]	Hong Kong University of Science and Technology	√	√	One dimension	√	Vegetables
Pasteurization and sterilization	Akterian (1995, 1997)[9,13]	Higher Institute of Food and Flavour Industries, Bulgaria	√		One dimension		Mushroom
	Ghazala et al. (1995)[6]	Memorial University of Newfoundland and McGill University, Canada	√		Three dimensions		Various
	Fasina and Fleming (2001)[24]	North Carolina State University, U.S.	√		One dimension, axisymmetric		Cucumber

(*Continued*)

TABLE 2.2 (Continued)
Summary of Finite Difference Method in Thermal Food Processing

Processes	Authors	Affiliation	Heat Model	Mass Model	Dimension	Temperature Dependent Properties	Foods
Cooking and frying	Erdogdu et al. (1998a,b)[18,19]	University of Florida, U.S.	√		Two dimensions, axisymmetric	√	Shrimp
	Farkas et al. (1996a,b)[11,12]	North Carolina State University and University of California, Davis, U.S.	√	√	One dimension		Potato
	Pan et al. (2000)[23]	Archer Daniels Midland Co. and University of California, Davis, U.S.	√	√	One dimension, axisymmetric	√	Hamburger patty
Others	Schmalko et al. (1997)[121]	University Nacional de Misiones, Argentina	√		One dimension, axisymmetric	√	Twigs of yerba mate
	Sahin et al. (1999)[109]	Middle East Technology University, Turkey, and Ohio State University, U.S.	√		One dimension	√	Potato

Source: Adapted from Wang, L.J. and Sun, D.-W., *Trends Food Sci. Technol.*, 14, 408–423, 2003.

TABLE 2.3
Summary of Finite Element Method in Thermal Food Processing

Processes	Authors	Affiliation	Heat Model	Mass Model	Dimension	Temperature-Dependent Properties	Foods
Dehydration and drying	Wu and Irudayaraj (1996)[85]	University of Saskatchewan, Canada, and Utah State University, U.S.	√	√	Two dimensions	√	Starch
	Jia et al. (2000a–d, 2001)[43–47]	University College Dublin, Ireland, and China Agricultural University	√	√	Two dimensions, axisymmetric	√	Grain
	Ahmad et al. (2001)[48]	Purdue University, U.S.	√	√	Two dimensions, axisymmetric	√	Biscuits
Pasteurization and sterilization	Varga et al. (2000a,b),[105,106] Varga and Oliveira (2000)[110]	University Catolica Portuguesa, Portygal. and University College Cork, Ireland	√		Two dimensions, axisymmetric		Various
Cooking and frying	Chen et al. (1999)[41]	University of Arkansas, U.S.	√		Two dimensions, axisymmetric	√	Chicken
	Ikediala et al. (1996)[37]	Technical University of Nova Scotia, Canada	√		Two dimensions, axisymmetric	√	Meat
	Zhang and Datta (2000),[42] Zhang et al. (2001)[95]	Cornell University, U.S.	√		Two dimensions, axisymmetric	√	Various

(*Continued*)

TABLE 2.3 (Continued)
Summary of Finite Element Method in Thermal Food Processing

Processes	Authors	Affiliation	Heat Model	Mass Model	Dimension	Temperature-Dependent Properties	Foods
	Lin et al. (1995),[35] Zhou et al. (1995),[34] Vilayannur et al. (1998a,b)[91,92]	Pennsylvania State University, U.S.	√	√	Two and three dimensions		Solid foods
	Nicolaï and De Baerdemaeker (1996),[100] Verboven et al. (2001),[107] Nicolaï et al. (1998, 1999a,b, 2000)[101–104]	Katholieke University Leuven, Belgium	√		Two dimensions, axisymmetric		Various
	Wang and Singh (2004)[56]	University of California, Davis, U.S.	√	√	Two dimensions, axisymmetric	√	Hamburger patty
Others	Hulbert et al. (1997)[111]	University of Tennessee, U.S.	√		Two dimensions		Carrot
	Nahor et al. (2001)[119]	Katholieke University Leuven, Belgium	√		Three dimensions	√	Various

Source: Adapted from Wang, L.J. and Sun, D.-W., *Trends Food Sci. Technol.*, 14, 408–423, 2003.

decades, it has only recently been applied to the food processing industry due to the rapid development in computer and commercial software packages. A review of CFD in the food industry has been given by Scott and Richardson[60] and Xia and Sun.[61] Langrish and Fletcher[62] reviewed the applications of CFD in spray drying. Applications of CFD in the food industry include analyses of airflow in ovens and chillers, fluid flow of particle foods in processing systems, and convection flow patterns in containers during thermal processing such as sterilization, and modeling of the vacuum cooling process.[63–78] The transport equations of CFD can be applied to both laminar and turbulent flow conditions. The eddy viscosity models such as the κ-ε approach and second-order closure models are used to describe the flow turbulence if the effects of turbulence on the effective viscosity need to be considered. A summary of various CFD models developed recently for analyzing food thermal processes is presented in Table 2.4.

TABLE 2.4
Summary of CFD in Thermal Food Processing

Processes	Authors	Affiliation	Foods
Drying	Straatsma et al. (1999)[88]	NIZO Food Research, Netherlands	Particle foods
	Mathioulakis et al. (1998)[86]	National Centre for Scientific Research, Greece	Fruits and vegetables
	Mirade and Daudin (2000)[67]	INRA, France	Sausage
Pasteurization and sterilization	Ghani et al. (1999a,b, 2001)[63,64,69]	University of Auckland, New Zealand	Canned liquid foods
	Jung and Fryer (1999)[65]	University of Birmingham, U.K.	Various
Heating	Verboven et al. (2000a,b)[89,90]	Katholieke University Leuven, Belgium	Various
Others	Verboven et al. (1997)[113]	Katholieke University Leuven, Belgium	Various
	Kondjoyan and Boisson (1997)[112]	INRA, IMFT, France	Various

Note: INRA = Institut National de la Recherche Agronomique; IMFT = Institut de Mécanique des Fluides de Toulouse.

Source: Adapted from Wang, L.J. and Sun, D.-W., *Trends Food Sci. Technol.*, 14, 408–423, 2003.

2.3 HEAT AND MASS TRANSFER APPLIED TO THERMAL FOOD PROCESSING

During thermal food processing, heat must be transferred between a heat source or sink and the inside zone of the food usually through an interface such as a food surface or container wall. External heat transfer between the source or sink and the interface may occur by any heat transfer mechanism (including conduction, convection, radiation, and phase changes). Internal heat transfer from the interface to the inside zone of foods is usually by conduction for solid foods or by conduction and convection for liquid foods. If a microwave is used, heat can also travel to the inside zone by penetrating radiation. Moisture, water vapor, nutrients, and flavor must first travel to the food surface by any of internal mass transfer mechanisms, such as diffusion. Then they must travel from the food surface to the ambient by external mass transfer processes such as convective mass transfer. For a series of the mechanisms of external heat transfer, internal heat transfer, internal mass transfer, and external mass transfer, the step with the greatest effect on the rate will be the slowest one, which is the rate-determining step.[79]

Heat transfer through solid foods is normally modeled by Fourier's equation of heat conduction, and mass transfer is generally described by Fick's law of diffusion.[80] For thermal processes of fluid foods, the conservation of mass, momentum, and energy in a fluid should be considered together. The continuity equation and Navier–Stokes equations are used to describe fluid flow.[59] The actual conditions imposed by the processing equipment are considered as the boundary conditions of the governing equations. Most heat and mass transfer models can only be solved analytically for simple cases. Numerical methods are useful for estimating the thermal behavior of foods under complex but realistic conditions such as variation in initial temperature, nonlinear and nonisotropic thermal properties, irregular-shaped bodies, and time-dependent boundary conditions. In solving the models, the finite difference and finite element methods are widely used. In recent years, the finite volume method was the main computational scheme used in commercial computational fluid dynamics (CFD) software packages. CFD has been increasingly used to simulate thermal processes of foods for analyzing complex flow behavior.[27,58]

2.3.1 Pasteurization and Sterilization

Pasteurization and sterilization are widely used in the food industry to inactivate microorganisms present in foods for ensuring food safety and extending the shelf life of foods. In aseptic processing, the products are first thermally treated, then carried to a previously sterilized container and sealed under sterile environment conditions. The thermal processing of packed products is carried out in equipment that uses steam or hot water as the heating fluid. The pasteurization and sterilization techniques are initially used in liquid foods such as milk and fruit juices. Recently, they have also been applied to particulate food products.[81]

2.3.1.1 Pasteurization and Sterilization of Liquid Foods

The sterilizing process of canned liquid foods is a typical example of fluid flow with heat transfer. The CFD model can thus be used to predict transient flow patterns and temperature profiles in a can filled with liquid foods. For simulating the sterilizing process of canned liquid foods, the energy equation needs to be solved simultaneously with the continuity and momentum equations in a CFD model.[63,64,69] Continuous sterilization processes of single-phase mixtures such as milks and fruit juices have become more and more common. The continuous process is called the high-temperature short-time (HTST) sterilization process, which gives the same level of sterility but a reduced quality loss, compared to batch sterilization process. For optimizing the quality of foods during continuous sterilization, the laminar flow of liquid foods in circular pipes with uniform wall temperature can be described by a CFD model.[65]

2.3.1.2 Pasteurization and Sterilization of Particle–Liquid Foods

Sterilization of canned solid particle foods with a brine solution in a container is a typical liquid–solid thermal process. Blanching of fresh vegetables and *sous vide* processing of particle foods are also heating practices in a liquid–solid system. In this system, the low-viscosity brine liquid is heated by convection and the solid particle foods by conduction. A heat conduction model can be used to simply determine the temperature distribution in a canned particle body. Meanwhile, the temperature of brine liquid in the heated cans, which is variable with the temperature outside of the cans, can be simply described by the regular regime differential equation:

$$\frac{dT_l}{dt} = \frac{T_m - T_l}{\Phi} \tag{2.26}$$

where the thermal inertia, Φ, which characterizes the temperature lag of the brine liquid from the temperature of heating medium, is experimentally determined by monitoring the temperature of the brine with linearly increasing, holding, and linearly decreasing the temperature of the medium.[9,13]

For the liquid–solid thermal process, because the heat transfer coefficient of surface convection is normally very large due to good circulation of brine liquid in the container, the effect of the coefficient on the temperature profiles of foods is normally assumed to be negligible. This means that if the coefficient is big enough, the total heat transfer rate is controlled by conduction through the particle food body. For this reason, the heat transfer coefficient can arbitrarily be set at a very high value in a simulation, for example, 5000 W/m^2 K.[6,24]

2.3.2 Dehydration and Drying

Dehydration, or *drying*, is a unit operation of food thermal processing most commonly used for food preservation. Reduction of water in foods during drying can

achieve better microbiological preservation and retard many undesirable reactions. Drying can also decrease packaging, handling, storage, and transport costs due to the decrease of food weight. The drying process is mainly characterized by moisture loss of foods. In most cases, the removal of water from a food is achieved by blowing a dry airflow, which transports water from the surface of the product to the airstream. However, spray drying, freeze drying, microwave drying, and other methods are also used for drying some special products. Drying of food materials is normally a complex process involving simultaneously coupled heat and mass transfer in the materials. It is important to know the mechanisms related to the movements of water inside and outside the food.[81]

2.3.2.1 Air Drying

Air drying is the most popular drying method in the food industry. For a drying process with a small Biot number, a uniform temperature profile in foods can be assumed in simulation. This uniform temperature can be determined by a heat balance between the dried food body and drying medium,[82,83] or be assumed to be the air temperature.[84] The moisture transfer through the foods is normally described by the differential equation of Fick's law of diffusion, which is expressed as

$$\frac{\partial X_w}{\partial t} = \nabla \cdot (D \nabla X_w) \tag{2.27}$$

The diffusion coefficient is important for the accuracy of model prediction. The diffusion coefficient can be regressed as a function of temperature and concentration by using data in the literature.[83] Alternatively, the diffusion coefficient can be determined by Arrhenius's law as[7,82,84]

$$D = D_0 \exp\left(-\frac{E_a}{RT_K}\right) \tag{2.28}$$

and E_a and D_0 are varied during simulation until a reasonable agreement between predicted and experimental results is obtained.

However, for a drying process with a big Biot number, a coupled mass and heat transfer should be taken into account in the simulation. For drying of a composite food system, simulation found that the predicted temperature, moisture, and pressure distributions in the composite food system by the coupled model agreed with experimental data. However, there was a big difference between the predicted values by the uncoupled model and experimental data.[85]

In most cases, it is often assumed that moisture diffuses to the outer boundaries in a liquid form and evaporation takes place only on the surface. The diffusion models do not separate liquid water and water vapor diffusion.[7] However, in some cases, inner water evaporation during drying is significant, and therefore, simultaneous heat, water, and vapor diffusion should be considered in simulation.[22] For example,

for predicting the drying process of breads, simultaneous heat, water, and vapor diffusion through breads was described by using three governing equations, respectively. The three governing equations of heat, moisture, and vapor were connected by the equilibrium of local moisture evaporation and vapor condensation, which is determined by the relationship between saturated vapor pressure and local temperature.[22] Simulations on the drying process of vegetables and fruits using the coupled heat, water, and vapor diffusion model confirmed that the assumption of an evaporation–condensation front in the drying model was valid for drying of porous moisture materials with big permeability, such as banana. However, the assumption of an evaporation–condensation front was invalid and more comprehensive analysis was necessary if the permeability of dehydrated foods and vegetables was below 10^{-19} m^2.[21]

On the surface of a food body, external mass transfer is normally assumed to be proportional to the vapor pressure difference between the surface and the drying media.[7] The surface mass transfer coefficients are affected by the properties of air, operating conditions, design of the dryer, and the product. Pressure profiles and velocity of heated air above products in an air dryer can be determined by a CFD model.[86] In this case, the turbulent flow, which is characterized by relatively high velocity and the presence of many obstacles in the air dryer, can be described by the Chen–Kim κ-ε model.[87]

2.3.2.2 Spray Drying

During spray drying, a coupled heat, mass, and pressure transfer phenomenon occurs. The drying of droplets is influenced by external and internal transport phenomena alike. For simulating gas flow in a spray dryer and calculating the trajectories and the course of the atomized particles, CFD is widely used.[62] The κ-ε turbulence model is used to calculate the gas flow field. The differential equation that describes the diffusion process in spherical particles is then solved simultaneously with equations for external heat and mass transfer.[88]

2.3.2.3 Microwave Drying

A microwave is used in drying of some heat-sensitive foods.[39,48] The heat and moisture transfer during microwaving can be described by Fourier's equation of heat conduction with inner heat generation and Fick's law of diffusion, respectively.[48] In modeling the coupled heat and moisture transfer through porous materials during microwave-assisted vacuum drying, a combination of liquid water and vapor transfer should be taken into account in the equation of mass transfer. Meanwhile, heat transfer can be described by Fourier's equation of heat conduction with an inner heat generation term covering latent heat of water evaporation and source heat of microwave power. However, as moisture transfer is caused by the temperature gradient in foods, the equation of moisture transfer can even be simplified into an isothermal equation if the temperature gradient is too small.[39]

2.3.3 Cooking and Frying

2.3.3.1 Air Convection Cooking

An air convection-heating oven is popular cooking equipment. For predicting transient temperature and moisture distribution in chicken patties of regular shapes in a cooking oven, a coupled heat and mass transfer model was found to give better prediction than that of single heat transfer model.[41] In some cases, if it is difficult to find data for the mass diffusivity and mass transfer coefficient, a volumetric moisture loss rate due to evaporation can be experimentally determined and the heat removed due to moisture loss can then be incorporated into Fourier's equation of heat conduction as inner heat generation.[37]

With powerful computers available, heating and cooking of solid foods in an industrial convection-type oven can be modeled as a fluid flow and heat transfer problem. CFD offers an efficient and effective tool to analyze the performance of an industrial convection-type oven such as hot-air electrical forced convection ovens. In the CFD models, the electrical heating coils and the fan can be modeled in the momentum equation (the Navier–Stockes equations) as a distributed resistance and a distributed body force in the region of the flow domain where the coils and fan are positioned. The value of turbulent viscosity in the momentum equation can be obtained by using the standard and renormalization group version of the κ-ε turbulence model.[89,90]

2.3.3.2 Microwave Cooking

Microwave-heated and -cooked foods are becoming increasingly popular in the food market and at home. For modeling the microwave heating process, the heat transfer through a solid food body can also be described by Fourier's equation of heat conduction with inner heat generation due to the microwave energy absorbed by the food components. The microwave power density absorbed at any location in foodstuffs can be derived as a function of dielectric properties and geometry of the food. Meanwhile, heat losses on the surface of the food body by convention and evaporation can be included in the boundary conditions. For simulating microwave heating of solid food with rectangular and cylindrical shapes, finite element analysis may be a powerful tool to numerically solve the model.[35] During microwave heating, a big moisture loss sometimes occurs. In this case, a coupled heat and mass transfer model should be developed and additional moisture transfer through a solid food body can be modeled by the diffusion equation of Fick's law.[34] The moisture evaporation rate on the surface can be obtained by using a drying experiment and regressed as a function of temperature.[91,92]

2.3.3.3 Frying

When foods are fried, crust formation is easily observed in many foods. The crust layer increases in thickness as the frying process proceeds, and the interface between the crust and the core region becomes a moving boundary. For a phase

change problem in frying, one side of the interface is crust and the other is the core region. Fourier's law of heat conduction can be used to describe the heat transfer on both sides of the interface:

$$\rho_1 c_1 \frac{\partial T_1}{\partial t} = \nabla \cdot (k_1 \nabla T_1) \quad \text{(for frozen)} \tag{2.29}$$

$$\rho_2 c_2 \frac{\partial T_2}{\partial t} = \nabla \cdot (k_2 \nabla T_2) \quad \text{(for unfrozen)} \tag{2.30}$$

The interface between two phases is tracked by Equation 2.8. It should be stressed that the crust and core regions have significantly different thermophysical properties. Because the phase change in foods occurs over a range of temperature, the thermophysical properties of foods experience extreme discontinuities at the phase change temperatures. These discontinuities cause instability in the numerical solutions. Alternatively, the enthalpy formulation technique, based on the relationship between enthalpy and temperature, is used to model the phase change problem. One advantage of the enthalpy formulation is that it is not necessary to track the moving interface. Other advantages include the relative stability and simplicity of the method. Using the enthalpy method, Equations 2.29 and 2.30 can be replaced by one single equation as[93]

$$\rho \frac{\partial H}{\partial t} = \nabla \cdot (k \nabla T) \tag{2.31}$$

During frying, there occurs significant mass transfer as the movement of fat/oil and moisture into or out of the food. A set of mass transfer models based on Fick's law of diffusion is widely used to describe the moisture and oil/fat movement during frying. Both mass and heat transfer models are coupled for simulating the frying process of foods.[56,93]

2.4 CHALLENGES IN MODELING HEAT AND MASS TRANSFER

Although continuous progress has been made in recent years in improving the accuracy of modeling, much research work still needs to be carried out. The following identifies several possible areas where further research could be performed in order to further improve the accuracy of model prediction.

2.4.1 Mechanisms in Heat and Mass Transfer

Drying of moisture and porous foods is widely used in the food industry. Drying involves coupled heat and mass transfer through a porous media. It is still difficult to predict the moisture transfer rate through a porous medium because the mechanisms

involved are complex and not completely understood. As a result, the design of the drying process remains largely an art based on experience gained from trial-and-error testing. Often, the controlling resistance is from internal mass transfer and the internal mass transfer may occur through the solid phase or within the void spaces. Several mechanisms of internal mass transfer, including vapor diffusion, moisture diffusion, surface evaporation, hydrodynamic flow, and capillary flow, have been proposed. However, modeling of drying processes is complicated because there is nearly always more than one mechanism to the total flow.[94]

During microwave heating, the heating patterns can be uneven. Food factors such as dielectric properties, size, and shape play a more important role than conventional heating because they affect not only the magnitude of heat generation but also its spatial distribution.[95] Modeling of the microwave heating process involves solutions of the electromagnetic equation and the energy equation. *Lambert's law* is a simple and commonly used power formulation, according to which the microwave power is attenuated exponentially as a function of distance of penetration into the sample.[96,97] Although Lambert's law is valid for samples thick enough to be treated as infinitely thick, it is a poor approximation in many practical situations. In such cases, a rigorous formulation of the heating problem requires solving Maxwell's equations, which govern the propagation of electromagnetic radiation in a dielectric medium.[96,97] During microwave heating, a large temperature change may cause significant variations in dielectric properties, resulting in big changes in the heating pattern. Therefore, a coupled Maxwell's equation with the heat transfer model is necessary to descibe the microwave heating process. Besides, the potential for nonuniformity in the microwave heating process should be comprehensively described. Also, there occurs moisture accumulation at the food surface during microwave heating.[98] Therefore, the challenge is to understand the mechanism of microwave heating, gain insight into the changes in heating patterns, verify the temperature distribution during microwave heating, and develop a coupled heat, moisture, and electromagnetic transfer model.

Turbulence is a phenomenon of great complexity and has puzzled theoreticians for over a hundred years. What makes turbulence so difficult to tackle mathematically is the wide range of length and timescales of motion even in flows with very simple boundary conditions. No single turbulence model is universally accepted as being superior for all classes of problems. The standard k-ε model is still highly recommended for general-purpose CFD computation. The mechanism of k-ε models is derived for equilibrium flows in which the rates of production and destruction of turbulence are nearly balanced.[59] This assumption has been proven to be valid only in flows with a high Reynolds number and relatively far from the wall in the boundary layer. At low Reynolds numbers (smaller than 30,000), simplified turbulence models, such as k-ε models or even the modified k-ε models by the near-wall treatment, based either on a wall function or on Wolfshtein's low Reynolds number, are rough approximations of reality. In many cases, these semiempirical models will fail to predict the correct near-wall limiting behavior near the product surface. However, k-ε models remain popular because of their availability in user-friendly codes, which allows a straightforward implementation of the models, and because

they are cheap in terms of computation time. Predictions by general codes based on the k-ε model are often very different from experimental data. Because the shape of many food products is very complex, the experimental determination of heat transfer coefficients remains at the time quicker and much more reliable than predictions. The calculation based on the current CFD codes has to be used with caution, and more research is needed to improve near-wall modeling, particularly around blunt bodies placed in a turbulent flow. A full treatment of turbulence would require more complex models, such as large eddy simulations (LESs) and Reynolds stress models (RSMs). However, LES models require large computing resources and are not of use as general-purpose tools. Because the RSM accounts for the effects of streamline curvature, swirl, rotation, and rapid changes in strain rate in a more rigorous manner than the k-ε models, it has greater potential to give accurate predictions for complex flows. However, the fidelity of RSM predictions is still limited by the closure assumptions used to model various terms in the exact transport equations for the Reynolds stresses. The modeling of the pressure strain and dissipation rate terms is particularly challenging. Therefore, the RSM with additional computational expense might not always yield results that are clearly superior to simpler models in all cases of flows. The mathematical expressions of turbulence models may be quite complicated, and they contain adjustable constants that need to be determined as best-fit values from experimental data. Therefore, any application of a turbulence model should not go beyond the data range. Besides, the current turbulence models can be used to guide the development of other models through comparative studies.

2.4.2 Judgment of Assumptions in Models

Accurate modeling of a thermal process of foods is complex. For simplification and saving of computational time, some assumptions made in the modeling are necessary. Most assumptions come from the geometrical dimension and shape, surface heat, and mass transfer coefficients, food materials properties, and volume change during thermal processes. Before simulation, whether or not to use a model of coupled heat and mass transfer or coupled heat transfer and fluid flow should also be determined.

Sensitivity analysis can make a judgment for the acceptability of an assumption in the modeling. Some research has been carried out to investigate the sensitivity of variables of interest, such as temperature on operating conditions of a thermal system and thermal properties of foods.[99–107] Findings from the research include that the time- and location-dependent variations in operating conditions, such as variable temperature and surface heat transfer coefficient, cause the detachment of the thermal and geometric centers during processing of foods.[99] For simulating a thermal process with a low heat transfer coefficient, small deviations in the coefficient may result in large deviations in the core temperature of foods.[100,107] The disturbances of different means, but with the same scale of fluctuation in processing the medium temperature, resulted in comparable center temperature variation.[103] For a typical sterilization process, it was found that thermal-physical properties

were the most important sources of variability.[101,102,104] It is stressed from the findings of sensitivity analyses in the publications that more efforts should be made to judge the acceptability of an assumption in the modeling.

2.4.3 Surface Heat and Mass Transfer Coefficients

Heat and mass transfer coefficients are important parameters in modeling heat and mass transfer during food thermal processes. The heat transfer coefficients of surface convection are mostly calculated using a correlation between a set of dimensionless numbers: *Nusselt number* ($\mathrm{Nu} = h_c L/k$), *Prandtl number* ($\mathrm{Pr} = c\mu/k$), *Reynolds number* ($\mathrm{Re} = \rho Lu/\mu$), and *Grashof number* ($\mathrm{Gr} = L^3\rho^2 g\beta\Delta T/\mu^2$) for flow across a body.[14,32,49–51] The surface mass transfer coefficient can be determined by using the Lewis relationship of heat and mass transfer coefficients, which is expressed as[108]

$$\frac{h}{K_p \lambda} = 64.7 Pa/K \tag{2.32}$$

It should be noted that such correlations are normally restricted to a given range of operating conditions, and reasonable accuracy can only be ensured under the given range of operating conditions. More attention should be paid to select a suitable correlation for a given case.

The heat transfer coefficients of surface convection can also be determined by fitting predicted temperatures to experimental data. The coefficient is determined by a trial-and-error method until the predicted model gives a good fit with experimental data.[109,110] For an aseptic system of fluid–particle foods, the coefficient of each particle can be determined by a trial-and-error matching of predicted temperature contours from a numerical heat transfer model with magnetic resonance imaging (MRI) images.[111]

For simplicity, an average heat transfer coefficient of surface convection is used in most simulations. However, with the advance of CFD technology, a CFD model can offer an effective and efficient tool to calculate the average and local heat transfer coefficients of surface convection with an acceptable cost.[112] Verboven et al.[113] used a two-dimensional CFD model (CFX package) to investigate the variation in heat transfer coefficient around the surface of foods. Their simulations found that around the rectangular-shaped foods, there was a large variation in the local surface heat transfer coefficients. Using the local coefficients instead of the average surface coefficient caused changes in temperature in the foods to be considerably slower, especially for slab-shaped foods, and the coldest point was also no longer at the geometric center.[113]

2.4.4 Food Properties

The food is introduced into a model through its properties. These properties, including thermal conductivity, density, specific heat capacity, diffusivity, and porosity, can identify the uniqueness of the food to the model. Food products are complicated materials. Their properties vary with species, process treatment,

temperature, concentration, etc. All these factors will increase difficulties in describing and predicting the properties of a product in modeling heat and mass transfer.

Thermal properties are another one of the most important factors determining the accuracy of model predictions. Part of thermal properties of food products can be found in publications available (e.g., see references 108, 114–118).

The thermal properties of foods can be directly measured by experiments.[6,24] For measuring physical properties, heat transfer models can be used to optimize the experimental design.[119] The prediction accuracy of a model can be significantly improved by including temperature- and composition-dependent thermal properties.[41,120] However, it is difficult for experimental measurement to obtain a detailed description of the relationship between thermal properties and temperature and compositions of foods. Alternatively, thermal properties of foods can be calculated from the compositions of foods and the thermal properties of each composition.[10,14,49–51] The compositions of foods can be measured before or after processing, and the variation in the compositions during processing can be determined by mass transfer models. The main compositions of foods usually are water, protein, and fat; other compositions such as salt and ash are very small. The temperature-dependent thermal properties of these compositions can be measured or found in the literature (e.g., see reference 108). It should be noted that the calculations for thermal properties from food compositions are based on an empirical or semiempirical relationship. More attention should be paid to select suitable correlation equations for a given case.

Thermal properties of foods can also be inversely found by using analytical or numerical heat transfer models and experimental temperature history. For determining a thermal property, an assumed value of the thermal property is first used to solve the numerical model. The predicted temperatures for given locations are compared with their corresponding measured values. The value of the thermal property is acceptable if the minimum difference between the predicted and measured temperatures is achieved.[121]

2.4.5 Shrinkage of Solid Foods during Thermal Processes

Shrinkage in foods occurs due to moisture loss during thermal processes. Effects of shrinkage on the accuracy of models are sometimes significant.[122] Shrinkage is normally taken into account in models of drying processes.[7,82,84] Shrinkage can be expressed as functions of moisture, and the functions are determined by experiments.[7,122]

2.5 CONCLUSIONS

Changes in temperature and concentration during thermal processes are always initiated by a transfer to or from the surface of the product. The transfer rate may be controlled by internal resistance, external resistance, or both. Transfer of both heat and mass takes place according to several mechanisms. In most cases, more

than one of these mechanisms is involved. In some processes, both heat and mass transfers occur simultaneously. It is important to understand the heat and mass transfer mechanism for the improvement of existing food thermal processes and for the development of new and better processes.

The physical laws of heat and mass transfer have widely been used to describe food thermal processes, producing a large number of mathematical models. Some assumptions, such as simplified geometrical shape, constant thermal physical properties, constant surface heat, and mass transfer coefficients, and no volume change during processing, were widely used in modeling. However, more research should be conducted to justify the acceptability of those assumptions and to improve the accuracy of models by finding more information on surface heat and mass transfer coefficients, food properties, and shrinkage during processing. Before heat and mass transfer models can become a quantitative tool for correctly analyzing thermal processes, determination of thermal physical propensities and surface mass and heat transfer coefficients remains an important area to be studied.

NOMENCLATURE

A	Area (m^2)
C	Concentration (kg/m^3 or $kmol/m^3$)
c	Specific heat capacity (kJ/kg K)
C^*	Concentration in equilibrium with the bulk gas partial pressure (kg/m^3 or $kmol/m^3$)
d	Diameter (m)
D	Mass diffusivity (m^2/sec)
D_0	Preexponential factor in Arrhenius equation (m^2/sec)
D_g	Mass diffusivity in the gas phase (kmol/N m sec)
D_l	Mass diffusivity in the liquid phase (m^2/sec)
E	Electrical field strength (V/m)
e	Emissivity (–)
E_a	Activation energy (J/kg mol)
F_{12}	View factor, fraction of radiation leaving surface 1 and arriving at surface 2 (–)
g	Acceleration due to gravity (m/sec^2)
H	Enthalpy (J/kg) or Henry's constant (J/kmol)
h	Heat transfer coefficient (W/m^2 K)
h_b	Boiling heat transfer coefficient (W/m^2 K)
h_c	Convection heat transfer coefficient (W/m^2 K)
h_{cd}	Condensation heat transfer coefficient (W/m^2 K)
h_r	Radiation heat transfer coefficient (W/m^2 K)
J	Diffusive flow rate (kg/m^2 sec or $kmol/m^2$ sec)
k	Thermal conductivity (W/mK)
K_g	Gas mass transfer coefficient (kmol/N sec)

K_l	Liquid mass transfer coefficient (m/sec)
K_p	Surface mass transfer coefficient related to pressure (kg/Pa m^2 sec)
L	Length (m)
P	Pressure (Pa)
P^*	Partial pressure in equilibrium with the bulk liquid concentration (Pa)
Pr	Prandtl number (–)
q	Heat rate (W)
q_{max}	Peak heat flux (W/m^2)
q_s	Heat flux (W/m^2) or mass flux on the surface (kg/m^2 sec or kmol/m^2 sec)
R	Gas constant (8.314 J/mol K)
S	Source term (W/m^3)
$S(t)$	Position of moving boundary at time, t (m)
T	Temperature (°C)
t	Time (sec)
T_K	Absolute temperature (K)
ΔT	Temperature difference (°C)
u	Velocity (m/sec)
X	Moisture content (%)
x, y, z	Orthogonal coordinates (m)

Greek Symbols

ρ	Density (kg/m^3)
ν	Frequency (Hz)
ψ	Group defined by Equation 2.12
λ	Latent heat (J/kg) or wavelength (m)
β	Loss angle (–) or thermal expansion (1/K)
σ	Stefan–Boltzmann constant (W/m^2 K^4) or surface tension (N/m)
ϕ	Temperature or concentration (–)
α	Thermal diffusivity (m^2/sec)
Φ	Thermal inertia (sec)
δ	Thickness (m)
∇	Vector operator
μ	Viscosity (Pa sec)
α'	Attenuation factor (1/m)
ε''	Capacitive part of permittivity (–)
e'	Resistive part of permittivity (–)
$\nabla\cdot$	Divergence of a vector

Subscripts

Γ	Boundary
∞	Processing medium
0	Initial
1	Surface or phase 1
2	Surface or phase 2
A	Component *A*
b	Boiling
c	Convection
cd	Condensation
g	Gas
i	Interface
K	Temperature in Kelvin
l	Liquid
m	Medium
max	Maximum
s	Surface
v	Vapor
w	Water
x, *y*, *z*	Orthogonal coordinates

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3 Simulating Thermal Food Processes Using Deterministic Models

Arthur A. Teixeira

CONTENTS

3.1 INTRODUCTION

Thermal processing of canned foods has been one of the most widely used methods of food preservation during the 20th century and has contributed significantly to the nutritional well-being of much of the world's population. Thermal processing consists of heating food containers in pressurized retorts at specified temperatures for prescribed lengths of time. These process times are calculated

on the basis of achieving sufficient bacterial inactivation in each container to comply with public health standards and to ensure that the probability of spoilage will be less than some minimum. Associated with each thermal process is always some undesirable degradation of heat-sensitive vitamins and other quality factors. Because of these quality and safety factors, great care is taken in the calculation of these process times and in the control of time and temperature during processing to avoid either under- or overprocessing. The heat transfer considerations that govern the temperature profiles achieved within the container of food are critical factors in the determination of time and temperature requirements for sterilization. This chapter will focus on the development and application of determinist heat transfer models capable of accurately predicting internal product temperature in response to retort operating conditions, and coupling these with deterministic models that mathematically describe the thermal inactivation kinetics of bacterial spores and food quality factors for thermal process simulation.

3.2 THERMAL DEATH TIME RELATIONSHIPS

An understanding of two distinct bodies of knowledge is required to appreciate the basic principles involved in thermal process calculation. The first of these is an understanding of the thermal inactivation kinetics (heat resistance) of pathogenic spoilage-causing organisms. The second body of knowledge is an understanding of heat transfer considerations that govern the temperature profiles achieved within the food container during the process, commonly referred to in the canning industry as heat penetration.

Figure 3.1 conceptually illustrates the interdependence between the thermal inactivation kinetics of bacterial spores and the heat transfer considerations in the food product. Thermal inactivation of bacteria generally follows first-order kinetics and can be described by logarithmic reduction in the concentration of bacterial spores with time for any given lethal temperature, as shown in the upper family of curves in Figure 3.1. These are known as *survivor curves*. The decimal reduction time, D, is expressed as the time required to achieve one log cycle of reduction in concentration, C. As suggested by the family of curves shown, D is temperature dependent and varies logarithmically with temperature, as shown in the second graph. This is known as a *thermal death time* curve and is essentially a straight line over the range of temperatures employed in food sterilization. The slope of the curve that describes this relationship is expressed as the temperature difference, Z, required for the curve to transverse one log cycle. The temperature in the food product in turn is a function of the retort temperature (T_R), initial product temperature (T_I), location within the container (x), thermal diffusivity of the product (α), and time (t) in the case of a conduction-heating food.

Thus, the concentration of viable bacterial spores during thermal processing decreases with time in accordance with the inactivation kinetics, which are a function of temperature. The temperature, in turn, is a function of the heat transfer considerations involving time, spacial location, combined thermal and physical

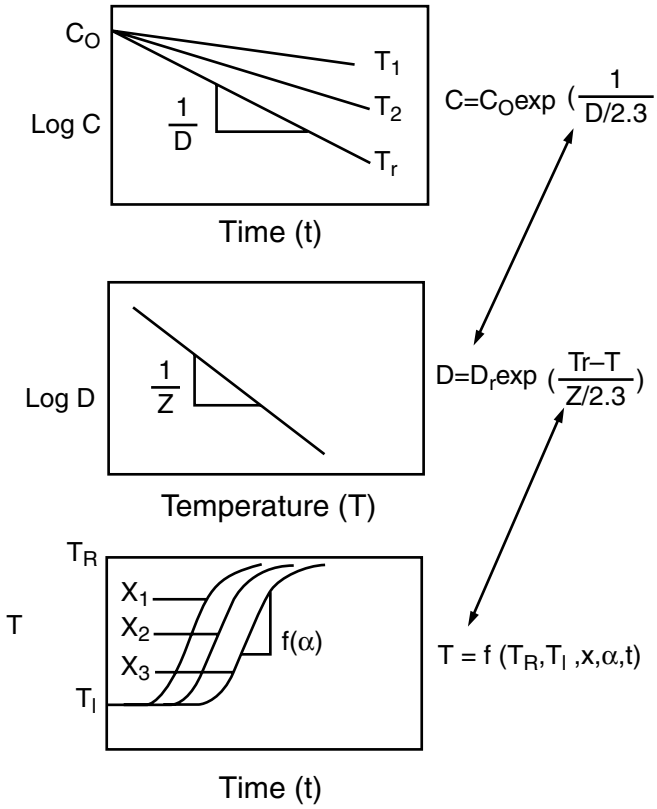

FIGURE 3.1 Time and temperature dependence of thermal inactivation kinetics of bacterial spores in thermal processing of canned foods.

properties (thermal diffusivity), and initial and boundary conditions (initial product temperature and retort temperature, respectively).

3.3 PROCESS LETHALITY AND STERILIZING VALUE

3.3.1 Time at Temperature for Isothermal Process

Once the thermal death time (TDT) curve (Figure 3.2) has been established for a given microorganism in a specific substrate, it can be used to calculate the time–temperature requirements for any idealized thermal process (isothermal process) in which a product is heated instantly and uniformly to the treatment temperature, held there for a specified time, and likewise cooled instantly and uniformly. For example, assume a process is required that will achieve a six-log cycle reduction in the population of bacterial spores whose kinetics are described by the TDT curve in Figure 3.2 at a specified process temperature (T). The D value at that temperature

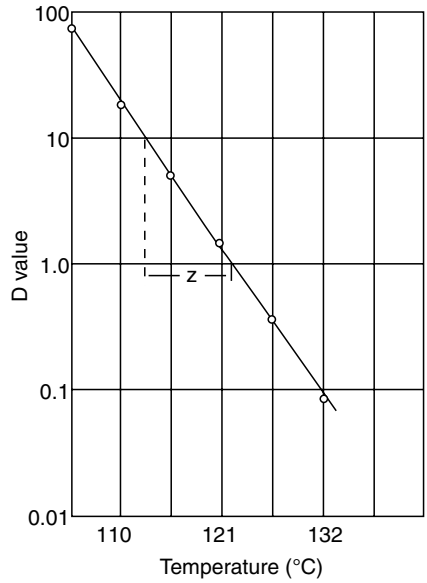

FIGURE 3.2 Thermal death time (TDT) curve showing temperature dependency of D value given by temperature change (Z) required for 10-fold change in D value.

is taken from the curve and simply multiplied by the number of log cycles of spore reduction required to determine the process time needed.

Since the TDT curve is a straight line on a semilog plot, all that is needed to specify such a curve is its slope and a single reference point on the curve. The slope of the curve is specified by the Z value, and the reference point is the D value at a reference temperature. For sterilization of low-acid foods (pH above 4.5), in which thermophilic spores of relatively high heat resistance are of concern, this reference temperature is usually taken to be 121°C (250°F). For high-acid foods or pasteurization processes in which microorganisms of much lower heat resistance are of concern, lower reference temperatures are used, such as 100 or 66°C. In specifying a reference D value for a microorganism, the reference temperature is shown as a subscript, such as D_{121}. Ranges of D values for different classifications of bacteria are given in Table 3.1, and $D_{121(250F)}$ values for specific organisms in selected food products are given in Table 3.2.

3.3.2 Process Lethality

The example process calculations carried out in the preceding subsection show that for a given Z value, the specification of any one point on the straight line drawn parallel to the TDT curve but intersecting the process time at process temperature is sufficient to specify the sterilizing value of any process combination of time and temperature on that line. The reference point that has been adopted for this purpose is the time in minutes at the reference temperature of

TABLE 3.1
***D* Values for Different Classifications of Food-Borne Bacteria**

Bacterial Groups	*D* Value
Low-acid and semiacid foods (pH above 4.5)	D_{250}
Thermophiles	
Flat-sour group (*B. stearothermophilus*)	4.0–5.0
Gaseous-spoilage group (*C. thermosaccharolyticum*)	3.0–4.0
Sulfide stinkers (*C. nigrigicans*)	2.0–3.0
Mesophiles	
Putrefactive anaerobes	
C. botulinum (types A and B)	0.10–1.20
C. sporogenes group (including PA 3679)	0.10–1.5
Acid foods (pH 4.0–4.5)	
Thermophiles	
B. coagulans (facultatively mesophilic)	0.01–0.07
Mesophiles	D_{212}
B. polymyxa and *B. macerans*	0.10–0.50
Butyric anaerobes (*C. pasteurianum*)	0.10–0.50
High-acid foods (mesophilic non-spore-bearing bacteria)	D_{150}
Lactobacillus spp., *Leuconostoc* spp., yeast and molds.	0.50–1.00

Source: Stumbo, C.R., *Thermobacteriology in Food Processing*, Academic Press, New York, 1965. With permission.

TABLE 3.2
Comparison of $D_{121(250F)}$ Values for Specific Microorganisms in Selected Food Substrates

Organism	Substrate	TDT Method	D_{250} (min)
PA 3679	Cream-style corn	Can	2.47
PA 3679	Whole-kernel corn	Can	1.52
PA 3679	Whole-kernel corn (replicate)	Can	1.82
PA 3679	Phosphate buffer	Tube	1.31
FS 5010	Cream-style corn	Can	1.14
FS 5010	Whole-kernel corn	Can	1.35
FS 1518	Phosphate buffer	Tube	3.01
FS 617	Whole milk	Can	0.84
FS 617	Evaporated milk	Tube	1.05

Note: PA = putrefactive anaerobe; FS = facultative spore.

Source: Stumbo, C.R., *Thermobacteriology in Food Processing*, Academic Press, New York, 1965. With permission.

121°C, or the point in time where the equivalent process curve crosses the vertical axis drawn at 121°C, and is known as the F value for the process. This is often referred to as the lethality of a process, and since it is expressed in minutes at 121°C, the unit of lethality is 1 min at 121°C. Thus, if a process is assigned an F value of 6, then the integrated lethality achieved by whatever time–temperature history is employed by the process must be equivalent to the lethality achieved from 6 min of exposure to 121°C, assuming an idealized process of instantaneous heating to 121°C followed by instantaneous cooling after the 6-min hold.

All that is required to specify the F value is to determine how many minutes at 121°C will be necessary to achieve the specified level of log cycle reduction. The D_{121} value is used for this purpose, since it represents the number of minutes at 121°C to accomplish one log cycle reduction. Thus, the F value is equal to D_{121} multiplied by the sterilizing value (number of log cycles required in population reduction):

$$F = D_{121}(\log a - \log b) \tag{3.1}$$

where a is the initial number of viable spores, and b is the final number of viable spores (or survivors).

In the example given earlier, assume the value $D_{121} = 1.5$ min was taken from the TDT curve in Figure 3.2 and multiplied by the required sterilizing value (six log cycles). Thus, $F = 1.5\ (6) = 9$ min, and the lethality for this process has been specified as $F = 9$ min. This is normally the way in which a thermal process is specified for subsequent calculation of a process time at some other temperature. In this way, proprietary information regarding specific microorganisms of concern or numbers of log cycles reduction can be kept confidential and replaced by the F value (lethality) as a process specification.

Note also that this F value serves as the reference point to specify the equivalent process design curve discussed earlier. By plotting a point at 9 min on the vertical line passing through 121°C on a TDT graph, and drawing a line parallel to the TDT curve through this point, the line will pass through all combinations of process time and temperature that deliver the same level of lethality. The equation for this straight line can be used to calculate the process time (t) at some other constant temperature (T) when F is specified.

$$F = 10^{[(T-121)/Z]_t} \tag{3.2}$$

The following equation becomes important in the general case when the product temperature varies with time during a process, and the F value delivered by the process must be integrated mathematically,

$$F = \int_0^t 10^{[(T-121)/Z]t} \tag{3.3}$$

At this point Equations 3.1 and 3.3 have been presented as two clearly different mathematical expressions for the process lethality, *F*. It is most important that the distinction between these two expressions be clearly understood. Equation 3.1 is used to determine the *F* value that should be *specified* for a process, and is determined from the log cycle reduction in spore population required of the process (sterilizing value) by considering factors related to safety and wholesomeness of the processed food, as discussed in the following section. Equation 3.3 is used to determine the *F* delivered by a process as a result of the time–temperature history experienced by the product during the process. Another observation is that Equation 3.1 makes use of the D_{121} value in converting log cycles of reduction into minutes at 121°C, while Equation 3.3 makes use of the *Z* value in converting temperature–time history into minutes at 121°C. Because a *Z* value of 10°C (18°F) is so commonly observed or assumed for most thermal processing calculations, *F* values calculated with a *Z* of 10°C and reference temperature of 121°C are designated F_o.

3.3.3 Specification of Process Lethality

Establishing the sterilizing value to be specified for a low-acid canned food is undoubtedly one of the most critical responsibilities taken on by a food scientist or engineer acting on behalf of a food company in the role of a competent thermal processing authority. In this section we outline briefly the steps normally taken for this purpose.[1]

There are two types of bacterial populations of concern in canned food sterilization. First is the population of organisms of public health significance. In low-acid foods with pH above 4.5, the chief organism of concern is *Clostridium botulinum*. A safe level of survival probability that has been accepted for this organism is 10^{-12}, or one survivor in 10^{12} cans processed. This is known as the *12 D concept for botulinum cook*. Since the highest D_{121} value known for this organism in foods is 0.21 min, the minimum lethality value for a botulinum cook assuming an initial spore load of one organism per container is

$$F = 0.21 \times 12 = 2.52$$

Essentially all low-acid foods are processed far beyond the minimum botulinum cook in order to avoid economic losses from spoilage-causing bacteria of much greater heat resistance (the second type). For these organisms, acceptable levels of spoilage probability are usually dictated by marketing or economic considerations. Most food companies accept a spoilage probability of 10^{-5} from mesophilic spore formers (organisms that can grow and spoil food at room temperature, but are nonpathogenic). The organism most frequently used to characterize this classification of food spoilage is a strain of *Clostridium sporogenes*, a putrefactive anaerobe (PA) known as PA 3679, with a maximum D_{121} value of 1 min. Thus, a minimum lethality value for a mesophilic spoilage cook assuming an initial spore load of one spore per container is

$$F = 1.00 \times 5 = 5.00$$

TABLE 3.3
Lethality Values (F_o) for Commercial Sterilization of Selected Canned Food Products

Product	Can sizes	F_o (min)
Asparagus		2
Green beans, brine packed	No. 2	3.5
	No. 10	3.5
Chicken, boned	All	6–8
Corn, whole kernel, brine packed	All	9
	No. 10	15
Cream-style corn	No. 2	5–6
	No. 10	2.3
Dog food	No. 2	12
	No. 10	6
Mackerel in brine	301 × 411	2.9–3.6
Meat loaf	No. 2	6
Peas, brine packed	No. 2	7
	No. 10	11
Sausage, Vienna, in brine	Various	5
Chili con carne	Various	6

Source: Lopez, A.A., *Complete Course in Canning*, Book 1, *Basic Information on Canning*, 11th ed., The Canning Trade, Baltimore, 1987. Courtesy of American Can Company, Inc.

Where thermophilic spoilage is a problem, more severe processes may be necessary because of the high heat resistance of thermophilic spores. Fortunately, most thermophiles do not grow readily at room temperature and require incubation at unusually high storage temperatures (45 to 55°C) to cause food spoilage. Generally, foods with no more than 1% spoilage (spoilage probability of 10^{-2}) upon incubation after processing will meet the accepted 10^{-5} spoilage probability in normal commerce. Therefore, when thermophilic spoilage is a concern, the target value for the final number of survivors is usually taken as 10^{-2}, and the initial spore load needs to be determined through microbiological analysis since contamination from these organisms varies greatly. For a situation with an initial thermophilic spore load of 100 spores per can, and an average D_{121} value of 4.00, the process lethality required would be

$$F = 4.00\,(\log 100 - \log 0.01)$$
$$= 4.00(4) = 16$$

The procedural steps above are only preliminary guidelines for average conditions, and often need to be adjusted up or down in view of the types of contaminating

bacteria that may be present, the initial level of contamination or *bioburden* of the most resistant types, the spoilage risk accepted, and the nature of the food product from the standpoint of its ability to support the growth of the different types of contaminating bacteria that are found. Table 3.3 contains a listing of process lethalities (F_o) specified for the commercial processing of selected canned foods.[2]

3.4 HEAT TRANSFER CONSIDERATIONS

3.4.1 Unsteady (Nonisothermal) Heat Transfer

In the previous sections on thermal inactivation kinetics of bacterial spores, frequent reference was made to an idealized process in which the food product was assumed to be heated instantaneously to a lethal temperature, then cooled instantaneously after the required process time. These idealized processes are important to gain an understanding of how the kinetic data can be used directly to determine the process time at any given lethal temperature. There are in fact commercial sterilization processes for which this method of process time determination is applicable. These are *high-temperature short-time* (*HTST*) *pasteurization* and *ultra-high-temperature* (*UHT*) sterilization processes for liquid foods that make use of flow-through heat exchangers or steam injection heaters and flash cooling chambers for instantaneous heating and cooling. The process time is accomplished through the residence time in the holding tube between the heater and cooler as the product flows continuously through the system. This method of product sterilization is most often used with aseptic filling systems, discussed in other chapters.

In traditional thermal processing of most canned foods, the situation is quite different from the idealized processes described above. Cans are filled with relatively cool unsterile product, sealed after headspace evacuation, and placed in steam retorts, which apply heat to the outside can wall. The product temperature can then only respond in accordance with the physical laws of heat transfer, and will gradually rise in an effort to approach the temperature at the wall, followed by a gradual fall in response to cooling at the wall. In this situation, the lethality delivered by the process will be the result of the transient time–temperature history experienced by the product at the slowest-heating location in the can; this is usually the geometric center. Therefore, the ability to determine this time–temperature history accurately is of paramount importance in the calculation of thermal processes. In this section we review the various modes of heat transfer found in canned foods, and describe methods of temperature measurement and recording and how these data are treated for subsequent use in thermal process calculation.

3.4.2 Heat Transfer Modes

Solid-packed foods in which there is essentially no product movement within the container, even when agitated, heat largely by conduction heat transfer. Because of the lack of product movement and the low thermal diffusivity of most foods, these products heat very slowly and exhibit a nonuniform temperature distribution during heating and cooling caused by the temperature gradient that is set up between the

can wall and geometric center. For conduction-heating products, the geometric center is the slowest-heating point in the container. Therefore, process calculations are based on the temperature history experienced by the product at the can center. Solid-packed foods such as canned fish and meats, baby foods, pet foods, pumpkin, and squash fall into this category. These foods are usually processed in still-cook or continuous hydrostatic retorts that provide no mechanical agitation.

Thin-bodied liquid products packed in cans, such as milk, soups, sauces, and gravies, will heat by either natural or forced convection heat transfer, depending on the use of mechanical agitation during processing. In a still-cook retort that provides no agitation, product movement will still occur within the container because of natural convective currents induced by density differences between the warmer liquid near the hot can wall and the cooler liquid near the can center.[3,4] The rate of heat transfer in nearly all convection-heating products can be increased substantially by inducing forced convection through mechanical agitation. For this reason, most convection-heating foods are processed in agitating retorts designed to provide either axial or end-over-end can rotation. Normally, end-over-end rotation is preferred and can be provided in batch retorts, while continuous agitating retorts can provide only limited axial rotation.

Unlike conduction-heating products, because of product movement in forced convection-heating products, the temperature distribution throughout the product is reasonably uniform under mechanical agitation. In natural convection the slowest-heating point is somewhat below the geometric center and should be located experimentally in each new case. The two basic mechanisms of conduction and convection heat transfer in canned foods are illustrated schematically in Figure 3.3.[5]

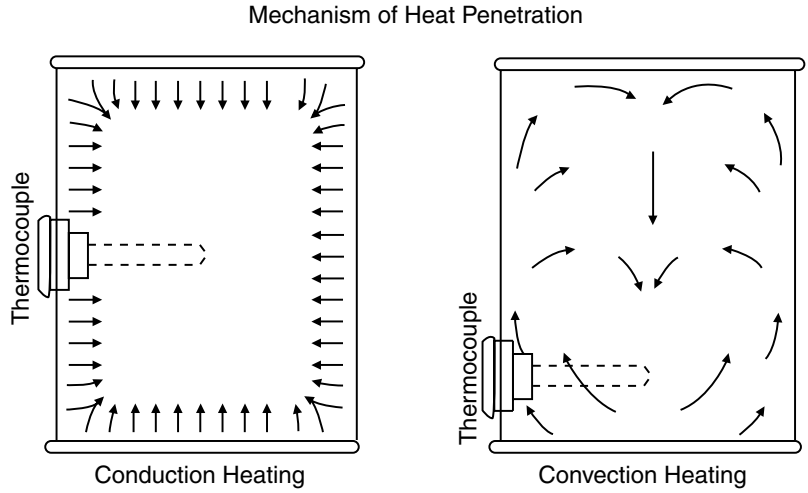

FIGURE 3.3 Conduction and convection heat transfer in solid and liquid canned foods, respectively. (From Lopez, A.A., *Complete Course in Canning*, Book 1, *Basic Information on Canning*, 11th ed., The Canning Trade, Baltimore, 1987. Courtesy CTI Publications, Inc.)

3.4.3 Heat Penetration Measurement

The primary objective of heat penetration measurements is to obtain an accurate recording of the product temperature at the can cold spot over time while the container is being treated under a controlled set of retort processing conditions. This is normally accomplished through the use of copper–constantan thermocouples inserted through the can wall, so as to have the junction located at the can geometric center. Thermocouple lead wires pass through a packing gland in the wall of the retort for connection to an appropriate data acquisition system in the case of a still-cook retort. For agitating retorts, the thermocouple lead wires are connected to a rotating shaft for electrical signal pickup from the rotating armature outside the retort. Specially designed thermocouple fittings are commercially available for these purposes.[1,2,5]

The precise temperature–time profile experienced by the product at the can center will depend on the physical and thermal properties of the product, size and shape of the container, and retort operating conditions. Therefore, it is imperative that test cans of product used in heat penetrations tests be truly representative of the commercial product with respect to ingredient formulation, fill weight, headspace, can size, and so on. In addition, the laboratory or pilot plant retort being used must accurately simulate the operating conditions that will be experienced by the product during commercial processing on the production-scale retort systems intended for the product. If this is not possible, heat penetration tests should be carried out using the actual production retort during scheduled breaks in production operations.

During a heat penetration test, both the retort temperature history and product temperature history at the can center are measured and recorded over time. A typical test process will include venting of the retort with live steam to remove all atmospheric air, then closing the vents to bring the retort up to operating pressure and temperature. This is the point at which process time begins, and the retort temperature is held constant over this period. At the end of the prescribed process time, the steam is shut off and cooling water is introduced under overriding air pressure to prevent a sudden pressure drop in the retort. This begins the cooling phase of the process, which ends when the retort pressure returns to atmosphere and the product temperature in the can has reached a safe low level for removal from the retort. A typical temperature–time plot of these data is shown in Figure 3.4 and illustrates the degree to which the product center temperature in the can lags behind the retort temperature during both heating and cooling.

3.4.4 Heat Penetration Curves and Thermal Diffusivity

The response of the product temperature at the can center to the steam retort temperature applied at the can wall is governed by the physical laws of heat transfer and can be expressed mathematically. This mathematical expression is a deterministic model that serves as a basis for obtaining effective values for thermal properties of canned foods in order to use numerical computations on high-speed

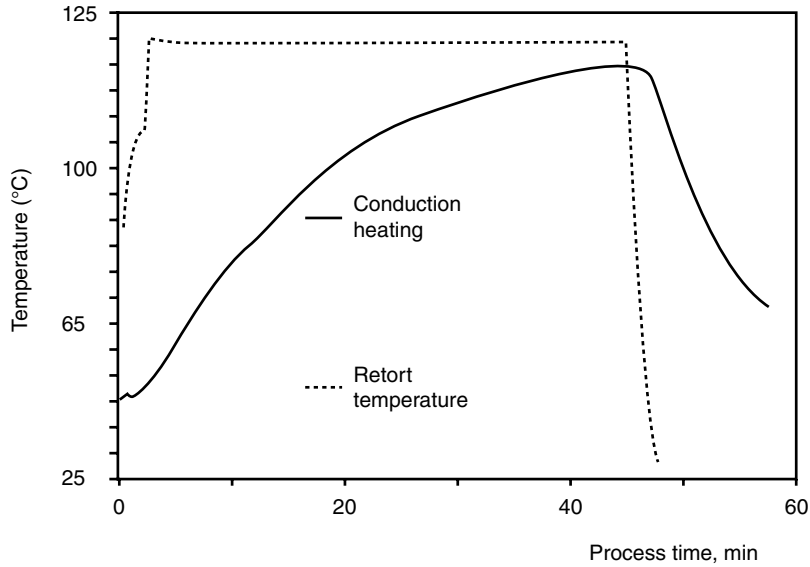

FIGURE 3.4 Generic heat penetration curve for a conduction-heating food during a thermal process.

computers that are capable of simulating the heat transfer in thermal processing of canned foods.

A heat balance between the heat absorbed by the product and the heat transferred across the can wall from the steam retort could be expressed as follows for an element of food volume facing the can wall of surface area A and thickness L:

$$\rho LAC_p \frac{dT}{dt} = \frac{k}{L} A(T_r - T) \tag{3.4}$$

where T is product temperature, T_r is retort temperature, and ρ, C_p, and k are density, specific heat, and thermal conductivity of the product, respectively. Because of the high surface heat transfer coefficient of condensing steam at the can wall and high thermal conductivity of the metal can, the overall surface resistance to heat transfer can be assumed negligible, in contrast to the product's resistance to heat transfer. After rearranging terms, Equation 3.4 can be written in the form of an ordinary differential equation:

$$\frac{dT}{dt} = \frac{k}{\rho C_p} L^2 (T_r - T) \tag{3.5}$$

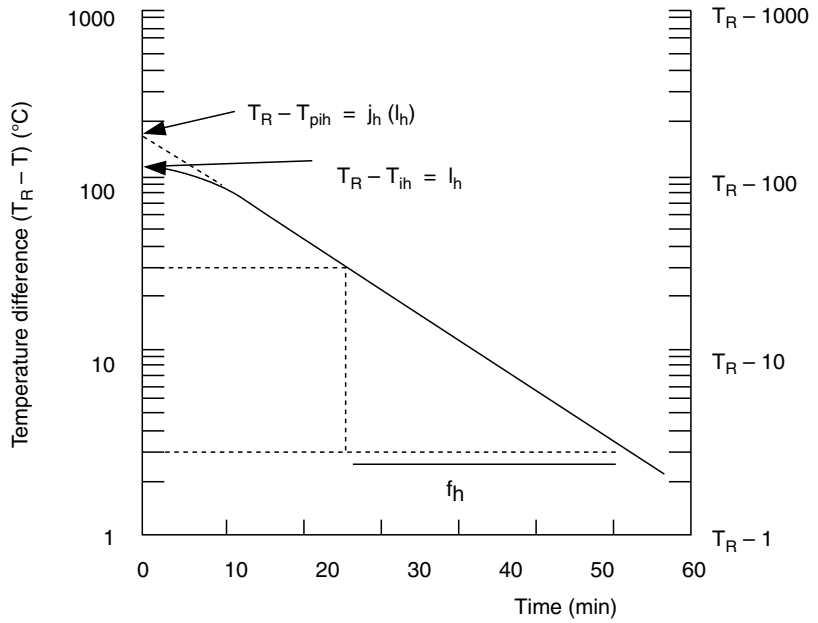

FIGURE 3.5 Semilog heat penetration curve showing unaccomplished temperature difference (on log scale) vs. time, from which heating rate (f_h) and heating lag (j_h) factors can be estimated.

By letting the *thermal diffusivity* (α) represent the combination of thermal and physical properties ($k/\rho C_p$), and letting T_o represent the initial product temperature, the solution to Equation 3.5 becomes

$$\frac{T_r - T}{T_r - T_o} = \exp\left(\frac{\alpha}{L^2} t\right) \tag{3.6}$$

Thus, the product center temperature can be seen to be an exponential function of time; a semilog plot of the temperature difference ($T_r - T$) against time would produce a straight line sloping downward, having a slope related to the product's thermal diffusivity and can dimensions (Figure 3.5). The *heat penetration rate factor* (f_h) is the reciprocal slope of the heat penetration curve (time required for one log cycle temperature change). Therefore, it can be related to the overall apparent thermal diffusivity of the product and container dimensions for a given container shape. For a finite cylinder, the following relationship can be used to obtain the thermal diffusivity, α, from the heating rate factor taken from a heat penetration curve:[1,6]

$$\alpha = \frac{0.398}{1/R^2 + (0.427/H^2) f_h} \tag{3.7}$$

where R is the can radius in inches, H is one half the can height in inches, f_h is the heating curve slope factor in minutes, and α is the product thermal diffusivity in compatible units. This relationship is also useful to determine the heating rate factor for the same product in a different size container, since thermal diffusivity is a combination of thermal and physical properties that characterize the product and its ingredient formulation, and remains unaffected by container size or shape. Similar relationships appropriate for other regular geometries can be found in the published literature.[6]

Another important heat penetration parameter obtained from the semilog heat penetration curve is the heating *lag factor*, j_{ch}, which is taken as the ratio of the difference between the retort temperature (T_r) and *pseudo-initial temperature* (T_o), the temperature at which an extension of the straight-line portion of the heating curve intersects the ordinate axis ($T_r - T_o$) over the difference between retort temperature and actual initial product temperature ($T_r - T_i$). The heating lag factor can be used with deterministic conduction heat transfer models to account for heat transfer mechanisms other than pure conduction that often take place in most canned foods.[6,7]

3.5 PROCESS CALCULATION

Once a heat penetration curve has been obtained from laboratory heat penetration data or predicted by a computer model, there are essentially two widely accepted methods for using these data to perform thermal process calculations. The first of these is the general method of process calculation,[8] and the second is the Ball formula method of process calculation.[6] Only the general method is described in this chapter because of its connected use with deterministic heat transfer models.

As the name implies, the general method is the most versatile method of process calculation because it is universally applicable to essentially any type of thermal processing situation. It makes direct use of the product temperature history at the can center obtained from a heat penetration test (or predicted by a mathematical model) to evaluate the integral shown in Equation 3.3 for calculating the process lethality delivered by a given temperature–time history. A straightforward numerical integration of Equation 3.3 can be expressed as follows with reference to Figure 3.6:

$$F_o = \sum_{i=1}^{n} \Delta Fi = \sum_{i=1}^{n} 10^{[(Ti-121)/Z]\Delta t} \tag{3.8}$$

Figure 3.6 is a direct plot of the can center temperature experienced during a heat penetration test. Since no appreciable lethality can occur until the product temperature has reached the lethal temperature range (above 105°C), Equation 3.8 need only be evaluated over the period during which the product temperature remains above 105°C. By dividing this period into small time intervals (Δt) of

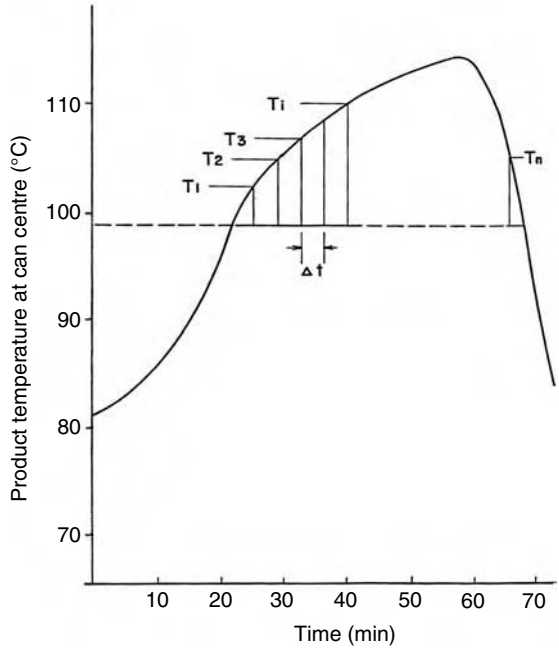

FIGURE 3.6 Temperature history at center of canned food during thermal process for calculation of process lethality by general method.

short duration, as shown in Figure 3.6, the temperature T_i at each time interval can be read from the curve and used to calculate the incremental lethality (ΔF_i) accomplished during that time interval. Then the sum of all these incremental sterilizing values equals the total lethality, F_o, delivered by the test process. To determine the process time required to deliver a specified lethality, the cooling portion of the curve in Figure 3.6 is shifted to the right or left and the integration is repeated until the delivered lethality, so what is calculated agrees with the value specified for the process.

When first introduced in 1920, this method was sometimes referred to as the graphical trial-and-error method because the integration was performed on specially designed graph paper to ease the tedious calculations that were required. The method was also time consuming, and soon gave way in popularity to the historically more convenient (but less accurate) Ball formula method. With the current widespread availability of low-cost programmable calculators and desktop computers, these limitations are no longer of any consequence, and the general method is currently the method of choice because of its accuracy and versatility.

The general method is particularly useful in taking maximum advantage of computer-based data logging systems used in connection with heat penetration tests. Such systems are capable of reading temperature signals received directly from thermocouples monitoring both retort and product center temperature, and

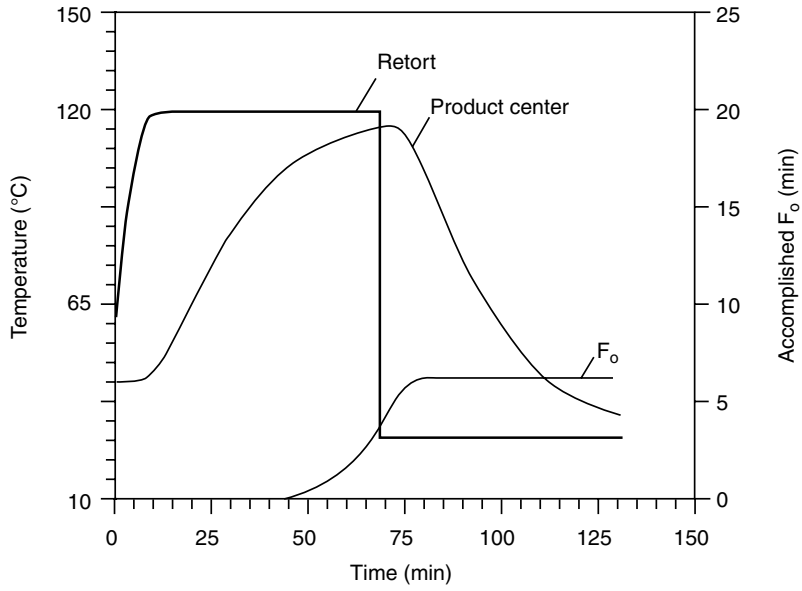

FIGURE 3.7 Computer-generated plot of retort temperature, can center temperature, and accomplished lethality (F_o) over time for thermal processing of a conduction-heated food. (From Datta, A.K. et al., *J. Food Sci.*, 51, 480–483, 507, 1986. With permission.)

processing these signals through the computer. Through programming instructions, both retort temperature and product center temperature are plotted against time without any data transformation. This allows the operator to see what has actually happened throughout the duration of the process test. As the data are being read by the computer, additional programming instructions call for calculation of the incremental process lethality (ΔF_i) at each time interval between temperature readings and summing these over time as the process is under way. As a result, the accumulated lethality (F) is known at any time during the process and can be plotted on the graph, along with the temperature histories, to show the final value reached at the end of the process.

An example of the computer printout from such a heat penetration test is shown in Figure 3.7. Another test can be repeated quickly for a longer or shorter process time, with instant results on the F_o achieved. By examining the results from both tests, the desired process time for the target F value can be closely estimated and then quickly tested for confirmation. The results of two such heat penetration tests are shown superimposed on each other in Figure 3.8. These results show that test 1, with a process time of 68 min, produced an F value of 6, and test 2, with a process time of 80 min, produced an F value of 8, suggesting that a target F value of 7 will be achieved by an intermediate process time. This can be confirmed by running a test at the suggested process time, and examining the resulting F value.

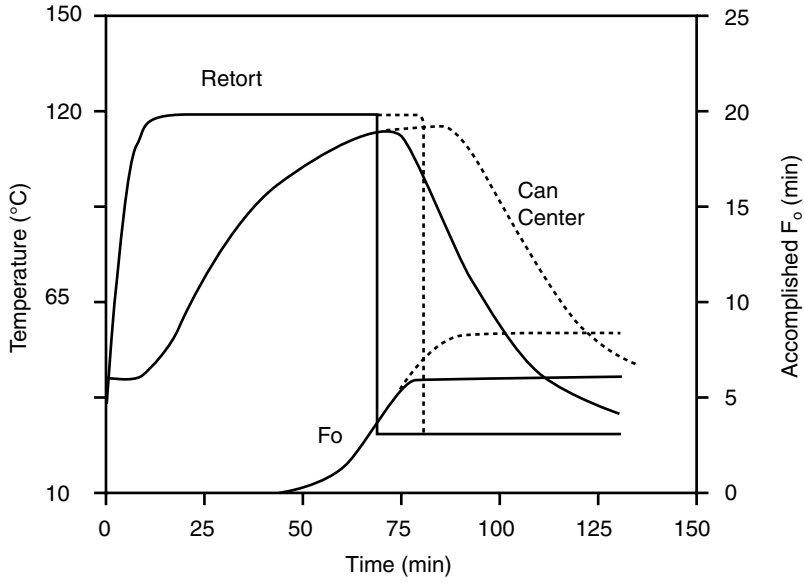

FIGURE 3.8 Computer-generated plot of retort temperature, can center temperature, and accomplished lethality (F_o) over time for two different process times superimposed on each other.

3.6 DETERMINISTIC MODEL FOR HEAT TRANSFER

A *deterministic model* of a process is a mathematical equation derived from mathematical expressions describing the relationships of fundamental scientific principles known to be responsible for the observed process behavior. As such, deterministic models yield a unique solution and produce the same result when repeated under the same conditions. The scientific principles governing heat transfer are well established and understood. Therefore, deterministic models are an appropriate means for mathematically simulating heat transfer in canned foods (as opposed to *stochastic models*, which deal with uncertainty using probability functions). One of the primary advantages of these models is that once the apparent thermal diffusivity has been determined from heat penetration tests, the model can be used to predict the product temperature history at any specified location within the can for any set of processing conditions and container size/shape specified. Thus, with the use of such models, it is unnecessary to carry out repeated heat penetration tests in the laboratory or pilot plant to determine the heat penetration curve for a different retort temperature or can size.

A second advantage, of even greater importance, is that the retort temperature need not be held constant but can vary in any prescribed manner throughout the process, and the model will predict the correct product temperature history at the can center in response to such dynamic (or transient) boundary conditions. Use of these

models has become invaluable for simulating the process conditions experienced in continuous sterilizer systems, in which containers pass from one chamber to another, experiencing a changing boundary temperature as they pass through the system. Another important application of these models is the rapid evaluation of an unscheduled process deviation, such as when an unexpected drop in retort temperature occurs during the course of the process. The model can quickly predict the product center temperature profile in response to such a deviation and calculate the delivered lethality value, F_o, for comparison with the lethality value specified for the product.

The development and use of such a deterministic model for stimulating the thermal processing of canned foods has been well documented in published scientific literature.[9–12] The model makes use of a numerical solution by finite differences of the two-dimensional partial differential equation that describes conduction heat transfer in a finite cylinder. During conduction heating, heat is applied only at the can surface; temperatures will rise first only in regions near the can walls, while temperature near the can center will begin to respond only after a considerable time lag. Mathematically, the temperature is a distributed parameter in that at any point in time during heating, the temperature takes on a different value with location in the can; and in any one location, the temperature changes with time as heat gradually penetrates the product from the can walls toward the center.

The mathematical expression that describes this temperature distribution pattern over time is shown in Figure 3.9 and lies at the heart of the numerical

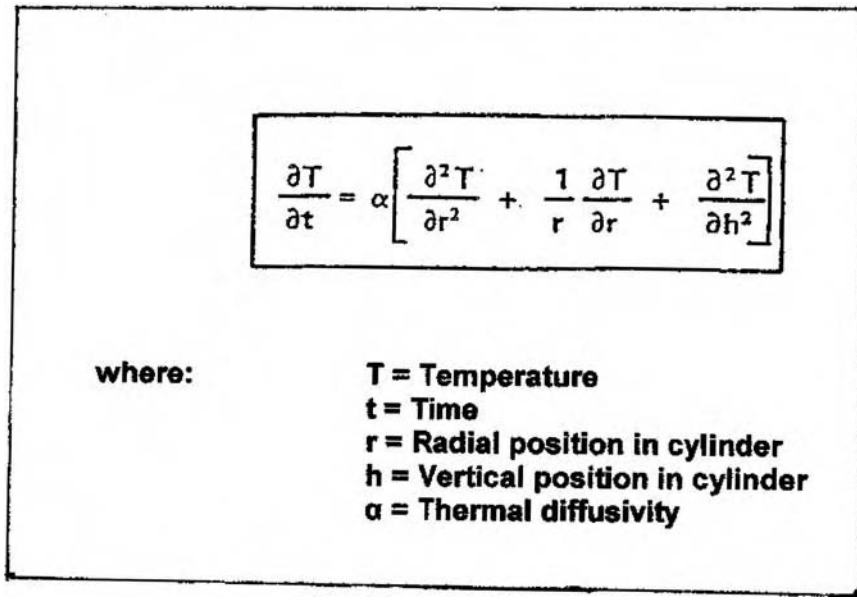

FIGURE 3.9 Two-dimensional second-order partial differential equation for conduction heat transfer (heat conduction equation) in a finite cylinder. (From Teixeira, A.A. and Manson, J.E., *Food Technol.*, 36, 85–90, 1982. With permission.)

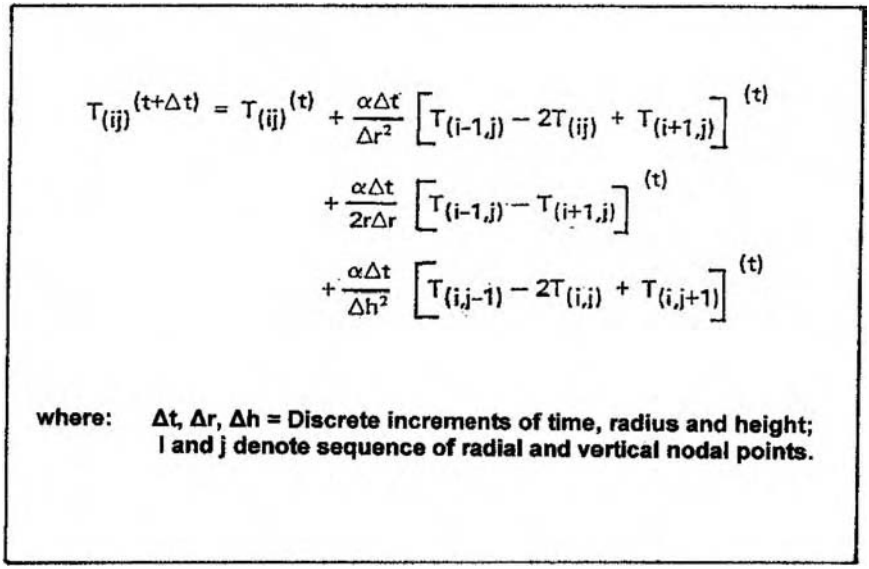

FIGURE 3.10 Heat conduction equation for finite cylinder expressed in finite differences for numerical solution by computer iteration. (From Teixeira, A.A. and Manson, J.E., *Food Technol.*, 36, 85–90, 1982. With permission.)

computer model. This expression is the classic partial differential equation for two-dimensional unsteady heat conduction in a finite cylinder and can be written in the form of finite differences for numerical solution by digital computer, as shown in Figure 3.10. The finite differences are discrete increments of time and space defined as small intervals of process time and small increments of container height and radius (Δt, Δh, and Δr, respectively).

As a framework for computer iterations, the cylindrical container is imagined to be subdivided into volume elements that appear as layers of concentric rings having rectangular cross sections, as illustrated in Figure 3.11 for the upper half of the container. Temperature nodes are assigned at the corners of each volume element on a vertical plane, as shown in Figure 3.12, where I and J are used to denote the sequence of radial and vertical volume elements, respectively. By assigning appropriate boundary and initial conditions to all the temperature nodes (interior nodes set at initial product temperature, and surface nodes set at retort temperature), the new temperature reached at each node can be calculated after a short time interval (Δt) that would be consistent with the thermal diffusivity of the product obtained from heat penetration data (f_h). This new temperature distribution is then taken to replace the initial one, and the procedure repeated to calculate the temperature distribution after another time interval. In this way, the temperature at any point in the container at any instant in time is obtained. At the end of process time, when steam is shut off and cooling water is admitted to

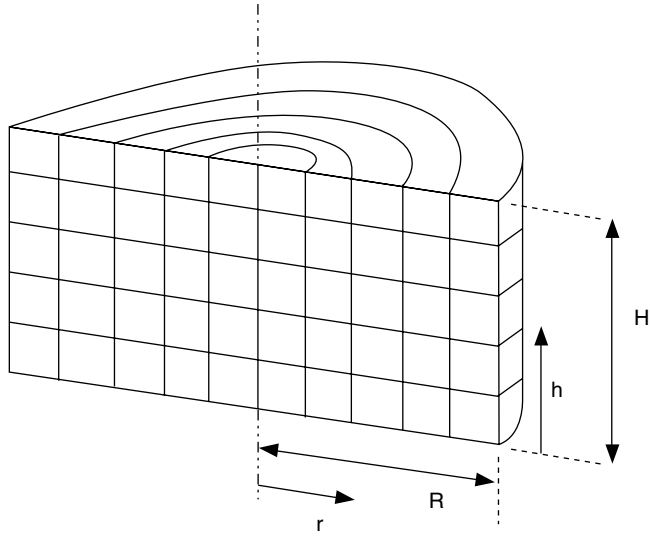

FIGURE 3.11 Subdivision of a cylindrical container for application of finite differences. (From Teixeira, A.A. et al., *Food Technol.*, 23, 137–143, 1969.)

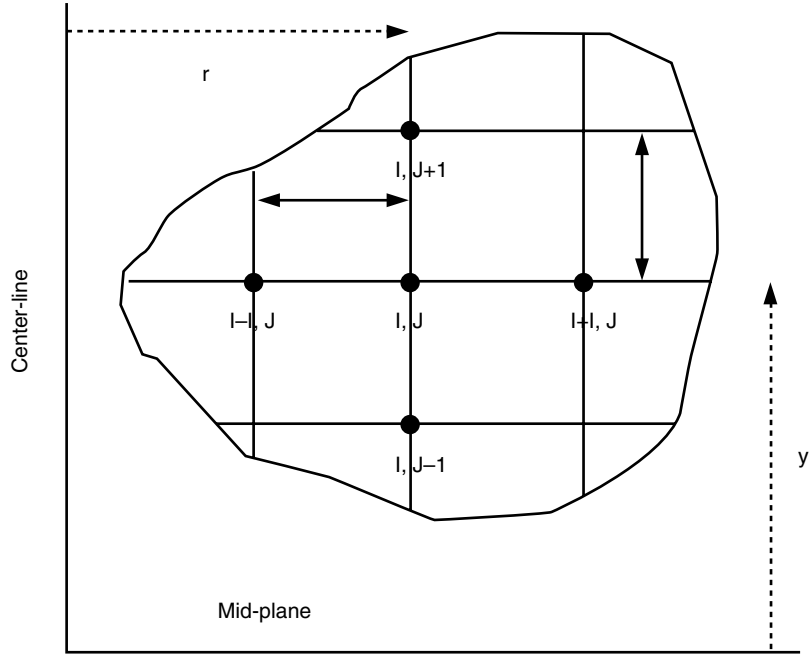

FIGURE 3.12 Labeling of grid nodes in matrix of volume elements on a vertical plan for application of finite differences. (From Teixeira, A.A. et al., *Food Technol.*, 23, 137–143, 1969.)

the retort, the cooling process is simulated by simply changing the boundary conditions from retort temperature T_R to cooling temperature T_C at the surface nodes and continuing with the computer iterations described above.

The temperature at the can center can be calculated after each time interval to produce a predicted heat penetration curve upon which the process lethality, F, can be calculated. When the numerical computer model is used to calculate the process time required at a given retort temperature to achieve a specified lethality, F, the computer follows a programmed search routine of assumed process times that quickly converges on the precise time at which cooling should begin in order to achieve the specified F value. Thus, the model can be used to determine the process time required for any given set of constant or variable retort temperature conditions.

3.7 PROCESS OPTIMIZATION

3.7.1 Objective Functions

The principle objective of thermal process optimization is to maximize product quality and profits while minimizing undesirable changes and cost. At all times, a minimal process must be maintained to exclude the danger from microorganisms of public health and spoilage concern. Five elements common to all optimization problems are performance or objective function (quality factors, nutrients, texture, and sensory characteristics), decision variables (retort temperature and process time), constraints (practical limits for temperatures and required minimal lethality), mathematical model (analytical, finite differences, and finite element), and optimization technique (search, response surface, and linear or nonlinear programming).

Optimization theory makes use of the different temperature sensitivities of microbial and quality factor destruction rates. Microorganisms have lower decimal reduction times (less resistant to heat) and a lower Z value (more sensitive to temperature) than most quality factors. Hence, a higher temperature will result in preferential destruction of microorganisms over the quality factor. Especially applied to liquid product, either in a batch mode (in-container) or in continuous aseptic systems, the higher temperature with shorter time offers a great potential for quality optimization. However, for conduction-heating foods, one of the major limitations is the slower heating. All higher temperatures do not necessarily favor the best quality retention because they also expose the product nearer the surface to more severe temperatures than the product at the center, which might result in diminished overall quality.

3.7.2 Thermal Degradation of Quality Factors

Optimum combinations of retort temperature and process time that maximize quality or nutrient retention can be found if the kinetic parameters describing the thermal degradation kinetics of the quality factors are known. Using the numerical computer simulation (deterministic) models described earlier, process times

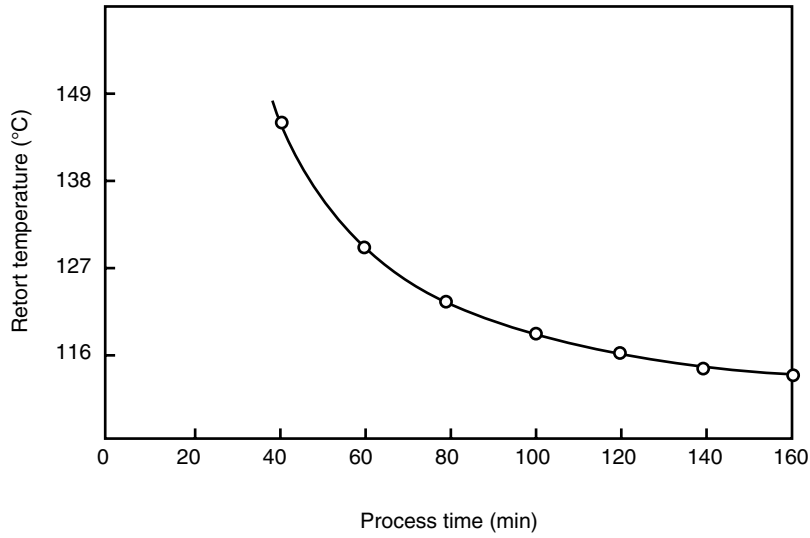

FIGURE 3.13 Isolethality curve showing combinations of retort temperature and process time that deliver the same level of lethality for pea puree in No. 2 cans. (From Teixeira, A.A. et al., *Food Technol.*, 23, 137–143, 1969.)

needed at different retort temperatures to achieve the same process lethality can be quickly calculated over a range of retort temperatures that fall within the operating performance limitations of the retort. A plot of these equivalent retort temperature–process time combinations produces an isolethality curve, such as the one shown in Figure 3.13 for the case of pea puree in No. 2 cans.[9]

The total level of nutrient/quality retention can be quickly calculated for each set of equivalent process conditions by replacing the kinetic parameters in the model for microbial inactivation with those for quality degradation. Table 3.4 gives examples of such kinetic parameters for the thermal degradation of selected quality

TABLE 3.4
Kinetic Parameters for Thermal Degradation of Quality Factors in Selected Thermally Processed Foods

Quality Factor in Food System	$D_{121°C}$ (min)	$K_{121°C}$ (min^{-1})	Z (°C)	E_a (kcal/mol)
Thiamine in beans	329.77	6.9837×10^{-3}	27.95	25.416
Lysine in beans	178.28	9.051×10^{-2}	25.44	27.32
Texture in beans	101.68	2.260×10^{-2}	20.62	35.44

Source: Thermobacteriology Laboratory, Food Science Department, Food Engineering Faculty, UNICAMP, Campinas, Sao Paulo, Brazil.

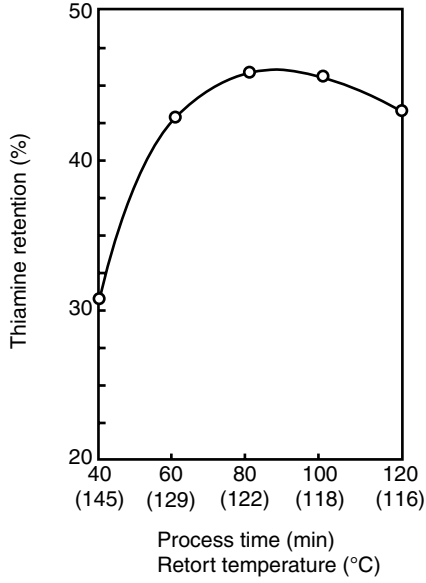

FIGURE 3.14 Optimization curve showing percent thiamine retention for pea puree in No. 2 cans after various retort temperature and process time combinations that deliver the same level of lethality. (From Teixeira, A.A. et al., *Food Technol.*, 23, 137–143, 1969.)

factors in specific food systems. A plot of nutrient retention vs. equivalent process conditions reveals the range of process conditions that result in maximum nutrient retention, as shown in Figure 3.14 for the case of pea puree in No. 2 cans. Note that the same exercise is also useful when seeking to minimize process time, because these results reveal the price that is paid in lower quality retention caused by the higher surface temperatures needed to allow for shorter process time.

3.7.3 Volume Average Determination of Quality Retention

Quality retention in thermally processed conduction-heated foods is a nonuniformly distributed parameter. Relatively long exposure to the higher temperatures near the product surface causes much more quality degradation in products near the surface than will occur in products near the cold spot, or center. This is because temperature distribution throughout the food container is nonuniformly distributed as heating and cooling proceed during the process. For this reason, quality retention must be calculated by volume integration of the different levels of retention at different locations. This is done by taking advantage of the finite element feature of the numerical simulation model. As the computer iterations make each sweep across the finite element nodes in carrying out the heat transfer calculations, the small change in nutrient concentration that occurs in that time

interval can be calculated from the momentary value of rate constant, which prevails at the local temperature at that time. When the process simulation is ended, a different final nutrient/quality concentration will exist within each volume element. Recall that the volume elements are in the shape of concentric rings with known dimensions, from which the volume of each different-size ring can be calculated. Total nutrient retention within each ring is calculated by multiplying the final nutrient concentration within the ring by the volume of that ring. Total nutrient retention in the product is the summation of final retention in all the rings and is known as volume average retention.

3.8 PROCESS DEVIATIONS

Control of thermal process operations in food canning factories has consisted of maintaining specified operating conditions that have been predetermined from product and process heat penetration tests, such as the process calculations for the time and temperature of a batch cook. Sometimes unexpected changes can occur during the course of the process operation or at some point upstream in a processing sequence such that the prespecified processing conditions are no longer valid or appropriate, and an off-specification product is produced that must be either reprocessed or destroyed at appreciable economic loss. These types of situations are known as process deviations and can be of critical importance in food processing operations because the physical process variables that can be measured and controlled are often only indicators of complex biochemical reactions that take place under the specified process conditions.

Because of the important emphasis placed on the public safety of canned foods, processors operate in strict compliance with the Food and Drug Administration's low-acid canned food regulations. Among other things, these regulations require strict documentation and record keeping of all critical control points in the processing of each retort load or batch of canned product. Particular emphasis is placed on product batches that experience an unscheduled process deviation, such as when a drop in retort temperature occurs during the course of the process, which may result from loss of steam pressure. In such a case, the product will not have received the established scheduled process and must be either destroyed, fully reprocessed, or set aside for evaluation by a competent processing authority. If the product is judged to be safe, then batch records must contain documentation showing how that judgment was reached. If judged unsafe, then the product must be fully reprocessed or destroyed. Such practices are costly.

In recent years food engineers knowledgeable in the use of engineering mathematics and scientific principles of heat transfer have developed deterministic computer models capable of simulating thermal processing of conduction-heated canned foods, such as described in this chapter. These models make use of numerical solutions to mathematical heat transfer equations capable of predicting accurately the internal product cold-spot temperature in response to any dynamic temperature experienced by the retort during the process. As such, they are very useful in the rapid evaluation of deviations that may unexpectedly occur.

Accuracy of such models is of paramount importance, and the models must work equally as well for any mode of heat transfer or size and shape container. Recall that the deterministic model described earlier in this chapter was derived for the case of pure conduction heat transfer in a solid body of finite cylinder shape. It would not be applicable to the many food products that heat by convection or to varying degrees of combined convection and conduction, or to different shapes. Recent work reported in the literature has described effective modification and simplification of the model to overcome these limitations.[7,13] These reports confirmed that food containers need not be of the same shape as the solid body assumed by the heat transfer model. They could be of any shape so long as temperature predictions were required only at the single cold-spot location within the container from which heat penetration data were determined.

The improved model assumed the product was a pure conduction-heating solid in the form of a sphere. An apparent thermal diffusivity was obtained for the solid sphere that would produce the same heating rate as that experienced by the product cold spot. Similarly, the precise radial location where the heating *lag factor* (j_h) was the same as that at the product cold spot would be used as the location at which temperature would be calculated by the model (Figure 3.15 and Figure 3.16). Thus, for any product with empirical parameters (f_h and j_h) known from heat penetration tests, it would be possible to simulate the thermal response at the product cold spot to any dynamic boundary condition (time-varying retort temperature) regardless of container size or shape or process conditions (mode of heat transfer).

Recall that heat penetration test data normally produce straight-line semilog heat penetration curves from which the empirical heat penetration parameters (f_h and j_h) can be determined. Incorporation of the parameters into the heat transfer model is accomplished by the relationship between thermal diffusivity (α) and *heating rate factor* (f_h) for a sphere (Equation 3.9), and the relationship between *heating lag factor* (j_h) and radial location (r) within the sphere (Equation 3.10). These and similar relationhips for other regular solid body shapes can be found in the literature.[6,13]

$$f_h = 0.233\ (R^2/\alpha) \tag{3.9}$$

$$j(r) = 0.637\ (R^2/r)\ \sin(\pi r/R) \tag{3.10}$$

Results from heat penetration tests on five products[7] are presented in Table 3.5. All products exhibited straight-line (log-linear) heat penetration curves on semilogarithmic plots of unaccomplished temperature differences vs. time. Can-to-can variation in the heating rate factor (f_h) and lag factors derived from direct analysis of the heat penetration curve (j_h, analyzed) were determined by the maximum and minimum values found over all six cans from two replicate tests. The true heating lag factor found by trial-and-error simulation (j_h, simulated) was also compared. This was the value chosen for use in the heat transfer model along with the maximum f_h values (slowest heating) for a conservative routine

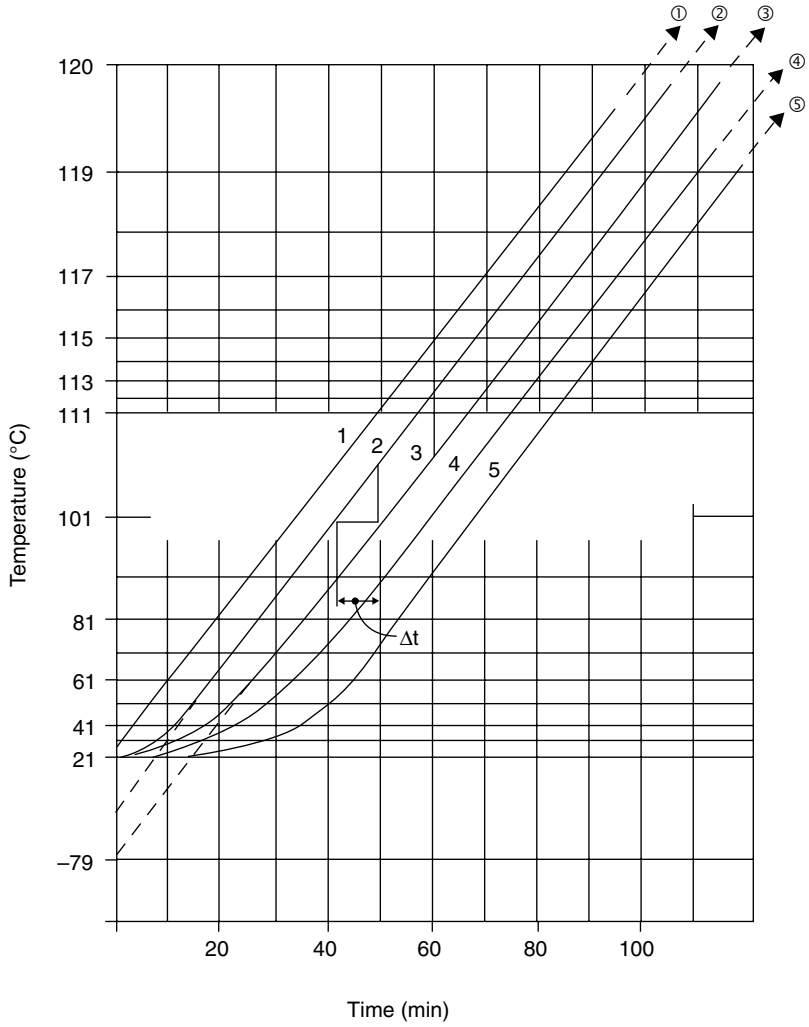

FIGURE 3.15 Heat penetration curves for five different locations along the radius on the midplane of a cylindrical container (see Figure 3.16), illustrating relationship between location and heating lag factor (j_h).

simulation of each product. The range of lethality values calculated from the temperatures measured by thermocouples in each can (F_o, actual) were also compared. Lethality was calculated from the simulated temperature profile (F_o, simulated) predicted by the heat transfer model in response to the retort temperature data file from each heat penetration test as input. Figure 3.17 compares internal cold-spot temperatures predicted by model simulation with profiles measured by thermocouples in response to multiple retort temperature deviations

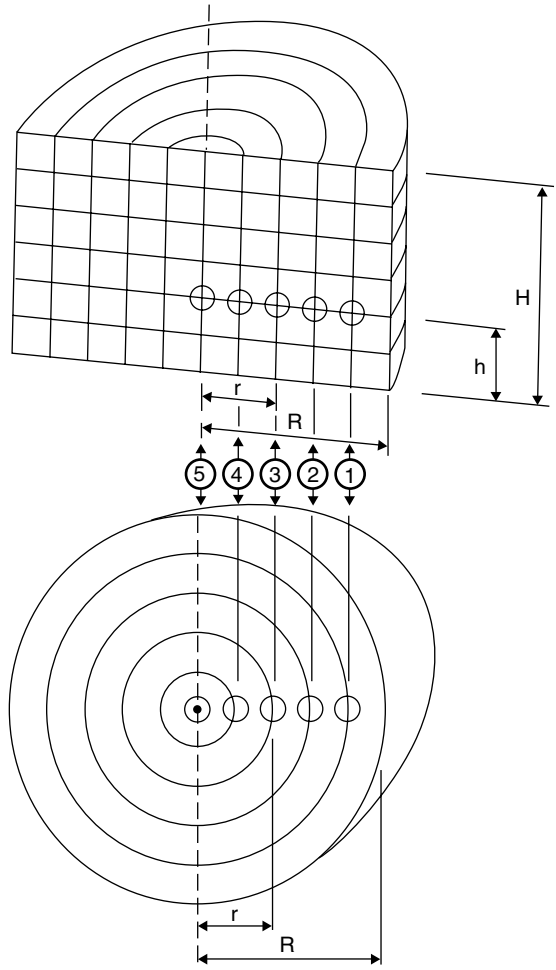

FIGURE 3.16 Replacement of solid body shape from finite cylinder to perfect sphere for simplification of numerical heat transfer model, with choice of radial location based upon heating lag factor from heat penetration tests.

during a heat penetration test.[7] The simulated profiles follow the measured profiles quite closely in response to relatively severe and twice repeated deviations.

The final test of model performance in the simulation and evaluation of process deviations was a comparison of lethalities accomplished by actual and simulated temperature profiles (Table 3.6). Recall that the accomplished lethality (F_o) for any thermal process is easily calculated by numerical integration of the measured or predicted cold-spot temperature over time, as explained previously. Thus, if the cold-spot temperature can be accurately predicted over time, so can

TABLE 3.5
Heat Penetration Results on Products Using Two Replicated Heat Penetration Tests with Six Instrumented Cans for Each Product

Product and Process	f_h Range (min)	j_h Range, Analyzed	j_h, Simulated	F_o Range, Actual	F_o, Simulated
5% bentonite, 1-kg cans (98 × 110 mm), static cook	70.4–73.0	1.9–2.0	2.0	6.0–7.0	6.2
5% bentonite, tuna cans (86 × 45 mm), static cook	20.0–22.0	1.4–1.6	1.4	7.5–9.8	7.4
Water, 1-kg cans (98 × 110 mm), static cook	3.0–3.1	1.8–2.3	1.0	9.8–10.8	9.9
Water, tuna cans (86 × 45 mm), static cook	1.7–1.9	2.5–3.9	1.0	7.9–10.6	7.7
Peas in brine, ∫-kg cans (74 × 88 mm), agitated cook	2.5–3.0	2.6–3.4	1.0	10.8–12.0	11.0

Source: Teixeira, A.A., *J. Food Sci.*, 64, 488–493, 1999. With permission.

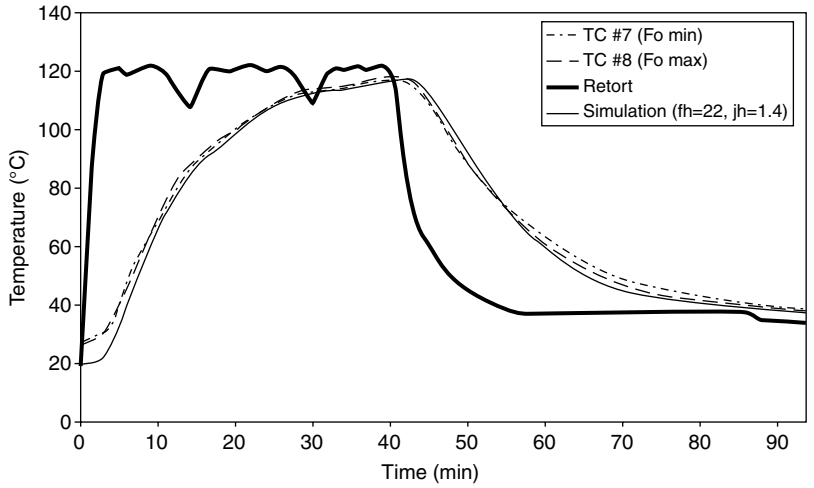

FIGURE 3.17 Comparison of internal cold-spot temperatures predicted by model simulation with those measured by thermocouples in response to multiple retort temperature deviations during a heat penetration test with 5% bentonite suspension in a 6-ounce tuna can. (From Teixeira, A.A., *J. Food Sci.*, 64, 488–493, 1999. With permission.)

TABLE 3.6
Process Deviation Test Results Showing Lethalities Calculated from Temperatures Predicted by Model Simulation (F_o Simulated) and Those Calculated from Actual Measured Temperatures (F_o Actual) in Slowest- and Fastest-Heating Cans of the Same Product in Response to Different Types of Retort Temperature Deviations during Processing

Product/Process	Deviation Type (A, B, C)	F_o, Simulated	F_o, Actual	
			Minimum	Maximum
5% bentonite, 1 kg, static	A	5.5	5.5	6.4
	B	3.0	3.3	5.3
	C	1.7	1.6	2.4
5% bentonite, tuna, static	A	6.5	6.6	7.6
	B	5.6	5.7	7.0
	C	4.8	4.7	5.7
Water, 1 kg, static	A	7.4	7.4	8.2
	B	7.8	8.8	10.3
	C	7.1	7.4	8.8
Water, tuna, static	A	4.4	5.4	6.2
	B	6.0	6.6	7.7
	C	5.5	6.7	8.0
Peas in brine, ∫ kg, agitated	C	9.1	9.2	10.0

Source: Teixeira, A.A., *J. Food Sci.*, 64, 488–493, 1999. With permission.

accumulated process lethality. In all cases, the simulated lethality predicted agreed most closely with the minimum actual lethality calculated from measured temperature profiles. Model predictions that tend toward the minimum side of the range are always desirable for conservative decision making.

3.9 ONLINE REAL-TIME COMPUTER CONTROL

Computer-based intelligent online control systems make use of these deterministic models as part of the decision-making software in a computer-based online control system. Instead of specifying the retort temperature as a constant boundary condition, the actual retort temperature is read directly from sensors located in the retort and is continually updated with each iteration of the numerical solution. Using only the measured retort temperature as input to the control system, the model operates as a subroutine calculating the internal product cold-spot temperature after small time intervals for computer iteration in carrying out the numerical solution to the heat conduction equation by finite differences. At the same time, the model also calculates the accomplishing process lethality associated with increasing cold-spot temperature in real time as the process is under way. At each

time step, the subroutine simulates the additional lethality that will be contributed by the cooling phase if cooling were to begin at that time. In this way, the decision of when to end heating and begin cooling is withheld until the model has determined that final target process lethality will be reached at the end of cooling.

By programming the control logic to continue heating until the accumulated lethality has reached some designated target value, the process will always end with the desired level of lethality (F_o), regardless of an unscheduled process temperature deviation. At the end of the process, complete documentation of measured retort temperature history, calculated center temperature history, and accomplished lethality (F_o) can be generated in compliance with regulatory record-keeping requirements. Such documents are shown in Figure 3.18 for a normal process (above) and for the same intended process with an unexpected deviation (below).[12]

3.10 CONCLUSIONS

This chapter has focused on the development and application of determinstc heat transfer models for simulation of thermal processing in the process development and manufacture of heat-sterilized canned foods. The models are capable of accurately predicting internal product temperature over time during heating in response to dynamic retort operating conditions for any degree of combined conduction–convection mode of heat transfer, and for any size or shape container.

Applications of these models to optimization of process design, rapid offline evaluation of process deviations, and real-time online computer control of retort operations were described in detail.

The chapter also presented an appropriate review of underlying principles and concepts of thermal processing important to understanding model development, applications, and limitations. These included:

- Review of thermal death time relationships, which describe how thermal inactivation of bacterial spore populations can be quantified as a function of time and temperature
- Process lethality and sterilizing value, defining concepts for specifying process requirements with respect to public health considerations and spoilage probability
- Heat transfer considerations, describing methods of temperature measurement and recording, and how these data are treated to obtain important heat penetration parameters for subsequent use in thermal process calculation and in deterministic models
- Process calculations, which described the general method for calculating thermal processes, including the process lethality delivered by a specific process, as well as the process time required at a given temperature to deliver a specified lethality value

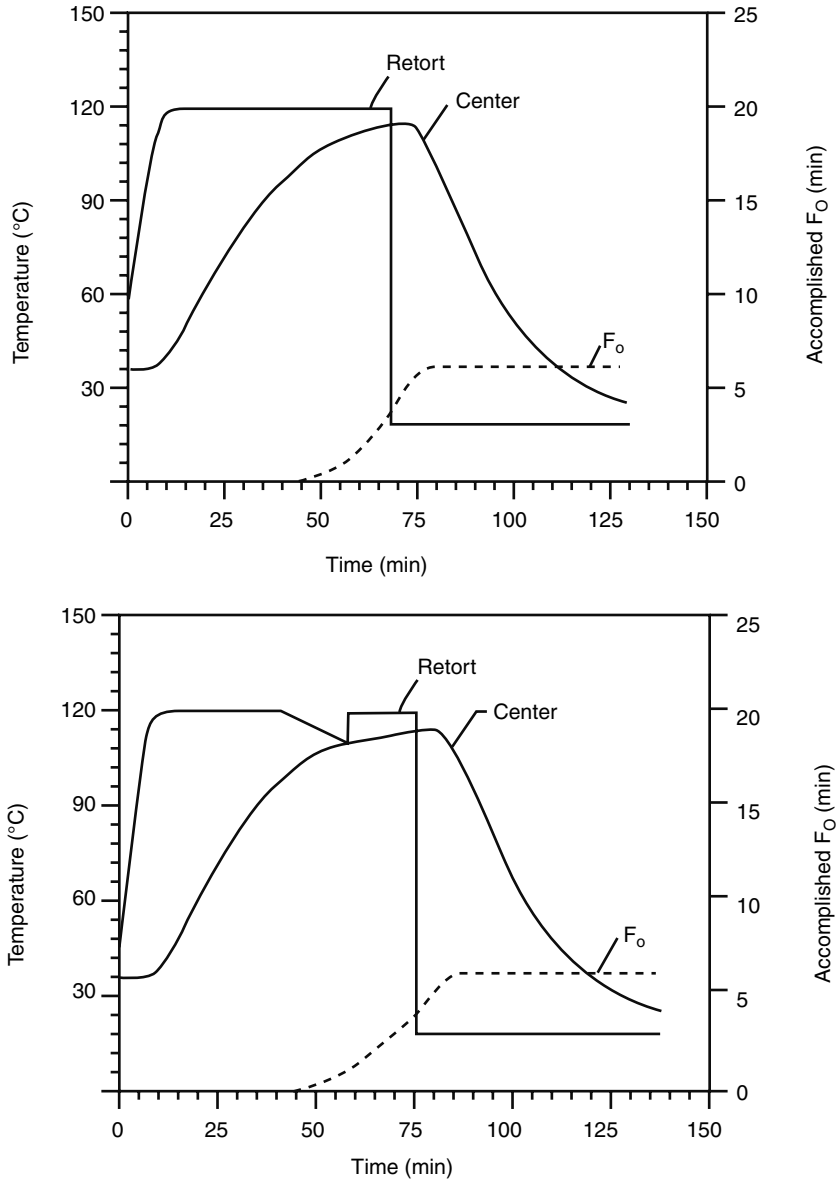

FIGURE 3.18 Computer-generated output from computer-based online control system showing scheduled heating time of 68 min for normal process (above), and heating time extended automatically to 76 min in compensation for unscheduled temporary loss of retort temperature (process deviation) (below).

- Deterministic modeling of heat transfer, which described the development of deterministic heat transfer models for thermal process simulation and application to process design
- Process optimization, showing use of deterministic models to find optimum process conditions that maximize quality retention without compromise of sterility assurance
- Process deviations, describing application of deterministic models to the rapid evaluation of unexpected process deviations
- Online computer control, showing use of deterministic models for online correction of unexpected process deviations.

NOMENCLATURE

A	Area through which heat transfer occurs, m^2
A	Initial number of viable bacterial spores at the beginning of a thermal process
b	Final number of viable bacterial spores (survivors) at the end of a thermal process
C	Concentration of primary component in a first-order reaction, quantity per unit mass or volume (e.g., spores/ml)
C_o	Initial concentration of primary component at beginning of reaction, spores/ml
C_p	Specific heat or heat capacity, kJ/kg·°C
D	Decimal reduction time, time for one log cycle reduction in population during exposure to constant lethal temperature, min
D_r	Decimal reduction time at a specified reference temperature (T_r), min
D_{121}	Decimal reduction time at temperature of 121°C (250°F), min
D_{100}	Decimal reduction time at temperature of 100°C (212°F), min
D_{65}	Decimal reduction time at temperature of 65°C (150°F), min
F	Process lethality, min, at any specified temperature and Z value, applied to destruction of microorganisms
F_o	Lethality value applied to destruction of microorganisms with Z value of 10°C (18°F), minutes at 121°C (250°F)
f_h	Heat penetration factor, time for straight-line portion of semilog heat penetration curve to traverse one log cycle, min
H	Half height of cylindrical food can, m
h	Any distance along vertical dimension (height) from the midplane in a cylindrical can, m

I	Sequence of radial nodal points for numerical iteration
J	Sequence of vertical nodal points for numerical iteration
j_h	Heating lag factor at geometric center of food container, dimensionless
k	Thermal conductivity, W/m·k, with reference to heat transfer
L	Length or thickness, m
R	Radius of cylinder or sphere, m
r	Any distance along radius from centerline, m
T	Temperature, °C
T_c	Temperature of cooling medium, °C
T_I	Initial product temperature, °C
T_o	Pseudo-initial temperature, the temperature at which an extension of the straight-line portion of the heat penetration curve intersects the ordinate axis, °C
T_R	Retort temperature, °C
T_r	Reference temperature at which D_r is measured
T_{ih}	Initial product temperature at beginning of heating, °C
T_{pih}	Pseudo-initial product temperature at beginning of heating (see also T_o), °C
$T_{(ij)}$	Temperature at any grid node (i, j) in finite difference solution to heat transfer equation, °C
$T_{(ij)}^{(t)}$	Temperature at any grid node (i, j) at time t, °C
$T_{(ij)}^{(t+\Delta t)}$	Temperature at any grid node (i, j) at time ($t + \Delta t$), or one time interval (Δt) later, °C
T_w	Cooling water temperature, °C
t	Time, min
x	Spatial location within a food container, m
Z	Temperature dependency factor in thermal inactivation kinetics, temperature difference required for 10-fold change in decimal reduction time (D value), °C thermal diffusivity, m^2/sec
ΔF_i	Incremental lethality accomplished over time interval (Δt), min
Δh	Vertical height of incremental volume element ring in finite difference solution to heat transfer equation, m
Δr	Radial width of incremental volume element ring in finite difference solution to heat transfer equation, m
Δt	Time interval between computational iterations in finite difference solution to heat transfer equation, min product density, kg/m^3

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4 Modeling Food Thermal Processes Using Artificial Neural Networks

C.R. Chen and H.S. Ramaswamy

CONTENTS

4.1 INTRODUCTION

Artificial neural networks (ANNs) are being successfully applied for a wide range of problem domains in diverse areas, including engineering, physics, finance, medicine, and others related to purposes of prediction, classification, or control. This extensive success can be attributed to many factors:

1. *Power of modeling* — Neural networks are very sophisticated techniques capable of modeling extremely complex functions. *A priori* knowledge of the system is not needed for constructing the ANN because the ANN will learn its internal representation from the input/output data of its environment and response.
2. *Ease of use* — Neural networks learn by example. The user of neural networks gathers representative data and then invokes training algorithms to automatically learn the structure of the data. Although the user does need to have some heuristic knowledge of how to select and prepare data, how to select an appropriate neural network, and how to interpret the results, the level of user knowledge needed to successfully apply neural networks is much lower than that needed to use some more traditional nonlinear statistical methods.
3. *High computational speed* — The ANN is an inherently parallel architecture. The result comes from the collective behavior of a large number of simple parallel processing units. Therefore, once trained, ANN can calculate results from a given input very quickly. Because of this feature, ANNs have a greater potential to be used for the online control system than conventional modeling methods.

The concept of neural networks was based on the research in artificial intelligence, which was specifically intended to mimic the fault tolerance and capacity of biological neural systems by modeling the low-level structure of the brain. Warren McCulloch and Walter Pitts[1] in 1943 were the first to open the idea on how neurons might work, and they modeled a simple neural network using electrical circuits. As computers became more advanced in the 1950s, it was finally possible to simulate a hypothetical neural network. In 1959, Bernard Widrow and Marcian Hoff developed models called ADALINE and MADALINE.[2,3] In 1962, the same authors developed a learning procedure that examined the value before the weight adjustment (i.e., 0 or 1), which was one of the important fundamentals to the following success of neural networks.[4] However, the neural network concepts did not result in practical applications until the 1980s, when several new approaches, such as bidirectional lines, the hybrid network, and multilayer neural networks, were developed.[2–6] In addition to these advances in algorithms, the rapid development of computer technologies, including both hardware and software, became an important driving force for neural networks as a computing technique to be used not only in computing science, but also in other areas as a tool for prediction, classification, and optimization.

4.2 THE INSPIRATION FROM BIOLOGICAL NEURONS

The human brain principally consists of over 10 billion neurons, each connected to about 10,000 other neurons. A typical biological neuron, as shown in Figure 4.1, contains neuronal cell bodies (soma), dendrites, and axons. Each neuron receives electrochemical inputs from other neurons at the dendrites. If the sum of these electrical inputs is sufficiently powerful to activate the neuron, it transmits an electrochemical signal along the axon and passes this signal to the other neurons, whose dendrites are attached at any of the axon terminals. These attached neurons may then fire. It is important to note that a neuron fires only if the total signal received at the cell body exceeds a certain level. The entire brain is composed of these interconnected electrochemical transmitting neurons. From a very large number of extremely simple processing units (each performing a weighted sum of its inputs, and then firing a binary signal if the total input exceeds a certain level), the brain manages to perform extremely complex tasks.

This is the model on which artificial neural networks are based. However, it should be noted that artificial neural networks only represent extremely simplified formal models of biological neurons and their interconnections, without making any attempt to model the biological system itself. Their importance lies in the fact that artificial networks are brain-inspired computational tools for solving complex problems.

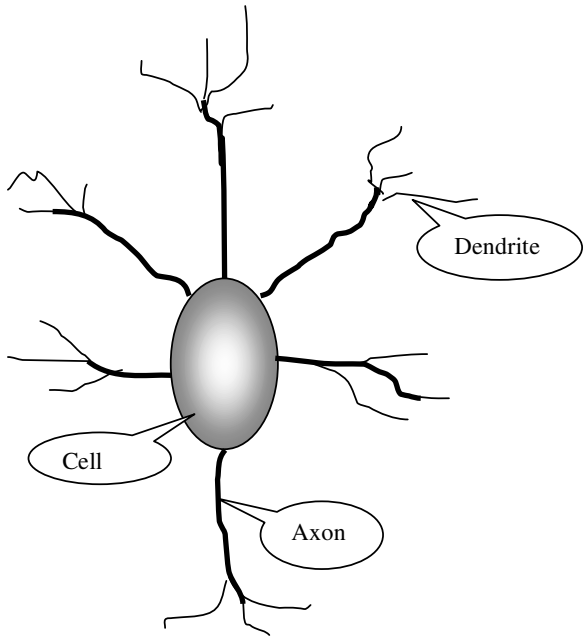

FIGURE 4.1 The structure of a typical biological neuron.

4.3 PRINCIPLES OF A BASIC ARTIFICIAL MODEL

4.3.1 Neural Network Architecture

Neural networks consist of a set of neurons, called processing units, which are arranged in several parallel layers. The most commonly used neural network architecture is the multilayer feed-forward network using back-propagation of error in the learning mechanism, which is shown in Figure 4.2. This neural network has an input layer, two hidden layers, and one output layer. Each layer is essential to the operation of the network. A neural network can be viewed as a black box into which a specific input to each node in the input layer is sent. The network processes this information through the interconnections between nodes, but this entire processing step is hidden. Finally, the network gives an output from the nodes on the output layer. The function of each layer is described as follows:

- *Input layer* — Receives information from an external source and passes this information to the network for processing.
- *Hidden layers* — Receives information from the input layer and does all of the information processing, which is hidden from view. The number of hidden layers can be one to three, dependent on the problem being investigated.
- *Output layer* — Receives processed information from the network and sends the results out to an external receptor.

When the input layer receives the information from an external source, it will be activated and emit signals to its neighbors. The neighbors, which receive excitations from an input layer, in turn emit signals to their neighbors. Depending on the strength

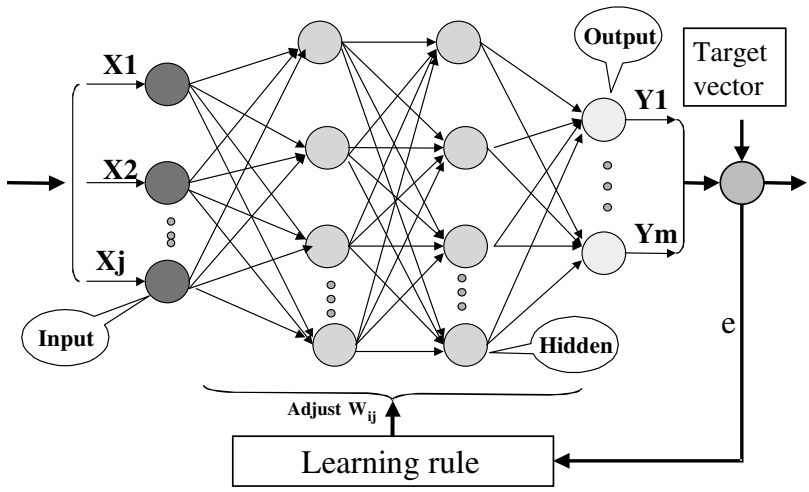

FIGURE 4.2 A typical multilayer neural network with one hidden layer.

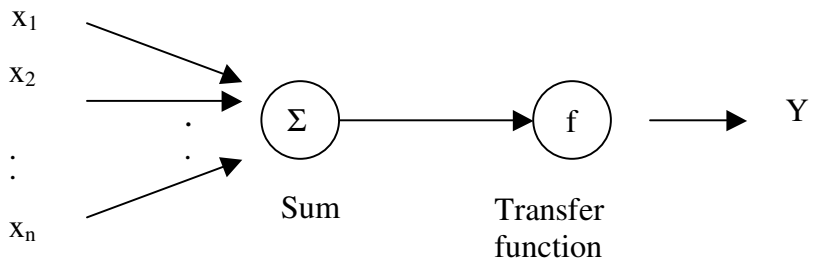

FIGURE 4.3 McCulloch and Pitt neural model. (From McCulloch, W.S. and Pitt, W., *Bull. Math. Biophys.*, 5, 115–133, 1943. With permission.)

of the interconnections (i.e., the magnitude of the so-called weight factor that adjusts the strength of the input signal), these signals can excite or inhibit the nodes. The result is a pattern of activation that eventually manifests itself in the output layer. Finally, the values from the output layer will be compared with the desired values. If the difference between output and desired values is larger than the set error range, then the weight factors are adjusted through the repeated training until the error is within the set error range or the number of learning runs is larger than the set number.

There are other ways for interconnections between neurons to construct different neural network architectures, such as feedback connections, lateral connections, time-delayed connections, and recurrent network.

4.3.2 Artificial Neurons

The artificial neurons are simple processing units similar to the biological neurons: they receive multiple inputs from other neurons but generate only a single output. The generated output may be propagated to several other neurons.

Each neuron has two basic functions: gathering information from the other neurons in the prior layer and sending the signals to the neurons in next layers. The first artificial neuron model proposed in 1943 by McCulloch and Pitt[1] (Figure 4.3) is based on the simplified consideration of the biological model. In this model, $x_1, x_2, \ldots, x_n$ are the binary inputs of the neurons. Zero represents absence, and 1 represents existence. The weight of connection between the i^{th} input x_i and the neuron is represented by w_i. When $w_i > 1$, the input is excitatory and when $w_i < 0$, it is inhibitory.

The net summation, X, of inputs weighted by the synaptic strength w_i at connection i is

$$X = \sum_{i-1}^{n} w_i x_i \tag{4.1}$$

The net value is then mapped through an activation function of neuron output. The activation function used in the model is a threshold function:

$$y = f(X) \tag{4.2}$$

$$f(x) = \begin{cases} 1, & x > \theta \\ 0, & \text{otherwise} \end{cases} \tag{4.3}$$

where θ is the threshold value.

The neuron models used in current neural networks are constructed in a more general way. The input and output signals are not limited to the binary data, and the activation function can be any continuous function other than the threshold function used in the earlier model. The activation function is typically a monotonic nondecreasing nonlinear function. Some of the often used activation functions are (where α and θ are constants):

Sigmoid function:

$$f(x) = \frac{1}{1+e^{-ax}} \tag{4.4}$$

Hyperbolic function:

$$f(x) = \tanh(\alpha x) = \frac{e^{\alpha x} - e^{-\alpha x}}{e^{\alpha x} + e^{-\alpha x}} \tag{4.5}$$

Linear threshold:

$$f(x) = \begin{cases} 1 & x \geq \theta \\ x/\theta & 0 < x < \theta \\ 0 & x \leq \theta \end{cases} \tag{4.6}$$

Gaussian function:

$$f(x) = e^{-ax^2} \tag{4.7}$$

4.3.3 Learning Rules

There are primarily two learning methods used for neural networks: supervised learning and unsupervised learning. For supervised learning, the training data set consists of pairs of input and desired output data. The error signal is generated as difference between the actual output and the desired output, and then used to adjust weights of networks. For unsupervised learning, only input data are fed into the network, because the desired output is not known, and thus no explicit error information is given. The supervised learning networks are the most often used neural networks for the modeling purpose. Therefore, only learning rules used in supervised learning networks are discussed.

The *learning rule* is a method to adjust the weight factors based on trial and error. Many learning rules have been developed to train neural networks. The main training method is error-correction learning,[1] which uses the data to adjust

the network's weights and thresholds so as to minimize the error in its prediction on the training set, mathematically defined as follows:

$$\varepsilon_i = d_i - c_i \tag{4.8}$$

where ε_i is the output error, d_i is the desired output, and c_i is the calculated output, for the i^{th} neuron on the output layer only. The total square error on the output layer can be calculated as

$$E = \sum_i \varepsilon^2 = \sum_i (d_i - c_i)^2 \tag{4.9}$$

The change in the weight factor for the j^{th} connection to the i^{th} neuron is obtained by

$$\Delta w_{ji} = -\eta \left(\frac{\partial E}{\partial w_{ji}} \right) = \eta a_j \varepsilon_i \tag{4.10}$$

where η is a linear proportionality constant, called the learning rate (typically, $0 < \eta << 1$), and a_j is the j^{th} input to neuron i.

In order to speed up the learning during training, the following modification is often implored:

$$\Delta w_{ji}(new) = \eta a_j \varepsilon_i + \lambda_i \Delta w_{ji}(old) \tag{4.11}$$

where λ is the momentum.

There are a number of other approaches developed as learning rules.[1] *Reinforcement learning* is a type of supervised learning closely related to error-correction learning. *Stochastic learning* utilizes statistics, probability, and random processes to adjust connection weights. *Hardwired neural networks* have all connections and weights predetermined (hardwired). These networks have a speed advantage and are used with additional a priori information in speech recognition, language processing vision, and robotics. *Hebbian learning* adjusts weights based on a correlation between the two nodes associated with the weight factor.

4.4 DEVELOPING NEURAL NETWORKS

Neural networks can be developed either based on the principles of neural networks using a specific computer language or by use of commercial neural networks software. Developing neural network codes, which means to turn the theory of a particular network model into a computer simulation implementation, can be a challenging task for most applied scientists and engineers, who do not have both programming and related knowledge of neural networks; so the use of commercial software has been the most popular method to develop a neural network (NN) model. With the rapid development of computer software, several

NN software packages have been developed that can be used for developing NN models for specific purposes, such as NeuralWare Profession, NeuralShell, Neurosolution (NeuroDimension, Inc., Gainesville, FL), Matlab, etc. Developing a neural network by using commercial NN software consists of the following steps: (1) selection of inputs and outputs, (2) data collection, (3) optimization of configurations, (4) training or learning, and (5) testing or generation.

The number of outputs can be determined by the problem being investigated while the number of inputs should be those influencing outputs significantly, which can be decided by comparison of results from different experiments with different inputs. The size of data required for neural network training is dependent on the complexity of the underlying function that the network is trying to model and the variance of the additive noise. Normally, neural networks can only process numeric data in a limited range, but it is also possible for neural networks to handle different types of data, such as an unusual range, missing data, or nonnumeric data, through some methods. For example, numeric data can be scaled into an appropriate range for the network, missing values can be substituted for using the mean value, and nonnumeric data can be represented by a set of numeric values.

For each specific problem, in order to develop an NN model with the best performance, the configuration parameters of the neural network being developed must be determined by trial and error. These parameters include transfer functions, learning rules, learning rate, momentum coefficient, number of hidden layers, number of neurons in each hidden layer, and learning runs.

In the *training* or *learning step*, a set of known input–output data is repeatedly presented to train the network. During this repetition process, the weight factors between nodes are adjusted until the specified input yields the desired output. Through these adjustments, the neural network learns the correct input–output response behavior. In neural network development, this phase is typically the longest and most time consuming, and it is critical to the success of the network.

After the training step, the *recall and generalization step* will be carried out. In the recall step, the network will be subjected to a wide array of input patterns used in training, and adjustments introduced to make the system more reliable and robust. During the generalization step, the network will be subjected to input patterns that it has not seen before, but whose outputs are known, and the system's performance will be monitored. The performance of neural networks can be evaluated visually by graphs or in quantity by different statistic measures. Figure 4.4 shows three kinds of graphs used for the performance of NN modeling. In Figure 4.4a, x and y axes represent desired and predicted results, respectively. The diagonal line is an ideal line and can be easily used for evaluation of the modeling performance. If NN predicted values are equal or close to the desired results, then the points should be located on or close to the ideal line. In Figure 4.4b, the x axis is one input variable, while the y axis is used for outputs, including desired and predicted results. This graph can be used to determine the match ability of the NN model with the specifically input variable. In Figure 4c, the x axis is just representing the number order of data used for training or testing, while the y axis

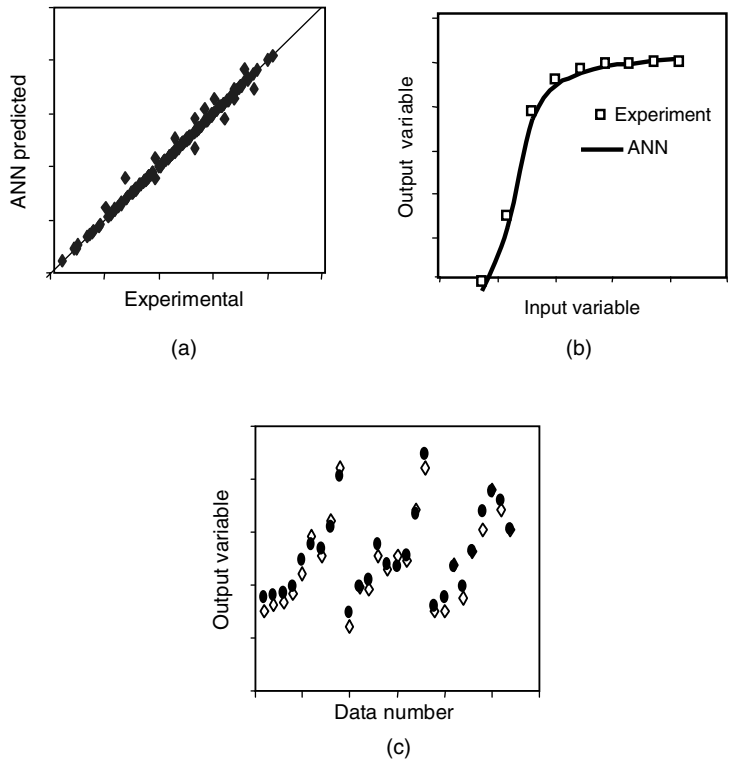

FIGURE 4.4 Graphs for performance of NN modeling.

is used for outputs, as shown in Figure 4.4b. Its emphasis is on comparison of the agreement between each pair of predicted and desired values.

Often used statistical calculations include the regression coefficient R^2 of the relationship between predicted and experimental results and the average relative error (E_r), which are given as

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(y_i - y_{di})^2}{\sum_{i=1}^{n}(y_i - y_m)^2}$$
$$E_r = \frac{\sum_{i=1}^{n}\left|(y_i - y_{di})\right| / n}{y_{\max} - y_{\min}} \tag{4.12}$$

where y_i is predicted by the ANN model, y_{di} is the actual desired value (actual values), n is the number of data, and y_m is the average of actual values.

4.5 APPLICATIONS IN FOOD THERMAL PROCESSING

Thermal processing is one of the major operations in the food processing and preservation system. It has generally been viewed as an energy-intensive preservation technique, but persists as the most widely used method of preservation. One major objective of thermal processing is to destroy pathogenic and spoilage microorganisms present in foods being processed so that they can be stored for extended periods and consumed with no safety concerns. Quality factors in foods are also affected by heat treatments; however, they usually show much higher heat resistance than targeted microorganisms. Therefore, an optimal thermal process procedure for a given food product means that it will result in minimal quality destruction while being sufficient to make the product safe for consumption. In order to solve an optimization problem, the key step is to develop a suitable model capable of describing the relationships between inputs and outputs. To date, a variety of conventional methods have been used for both modeling and optimization purposes in food thermal processing areas, from which different models have been developed, including numerical, analytical, and experimental. These conventional methods applied for optimizing thermal processing operations need specific inputs. First, the models need a knowledge and understanding of relationships between the input and output variables. Second, it is necessary that information of physical and thermal properties of food products being modeled be available. Unlike other disciplines, food processing deals with biomaterials, which show much more complicated thermophysical properties and uncertainties during the processing period. This also results in more complicated relationships between input and output variables. Thus, often it is difficult to use a simple partial differential equation or model to accurately describe the phenomena occurring in food processing operations. In addition, the lower calculation speed of most conventional methods under complex situations of process optimization and control limits them to be optimally applied for online application in industrial processes. Neural network models offer an attractive alternative in such instances. Hence, neural networks are being continually extended to the food thermal processing area as a modeling and optimization technique.

Since the 1980s, neural networks have received more and more interest in food processing areas. So far, the applications of neural networks in food processing have covered various areas, such as drying,[7–12] fermentation,[13,14] extrusion,[15–17] freezing,[18] baking,[19,20] postharvest,[21,22] experimental design,[23] etc. The application in food thermal processing began in the mid-1990s. Sablani et al.[24] published one of the early reports on the application of neural networks in food thermal processing. They developed a four-layer neural network with three inputs and three outputs to predict optimal sterilization temperatures under different processing conditions. Sablani et al.[25] used artificial neural network models for the overall heat transfer coefficient and the fluid-to-particle heat transfer associated with liquid particle mixtures, in cans subjected to end-over-end rotation.

The application of the neural computing approach for prediction of the *residence time distribution* (RTD) under aseptic processing conditions was reported by Chen and Ramaswamy.[26] In this paper, neural networks were explored for modeling two RTD functions: the time-specific (*E*-type distribution) and the cumulative particle concentration function (*F*-type distribution) of carrot cubes in starch solutions in a vertical scraped-surface heat exchanger (SSHE) of a pilot-scale aseptic processing system. Neural networks have been used as an alternative tool to the Ball and Stumbo methods, which are the most often used methods for thermal calculation to predict process time and or process lethality in cans during thermal processing.[27] A more systematic and in-depth application of neural networks in food thermal processing areas was carried out by Chen and Ramaswamy.[28–33] In these studies, separate ANN prediction models were developed involving main input parameters such as retort temperature profile, thermophysical properties of food products, kinetics of microorganisms, and quality factors and outputs, such as the process time, cumulative lethality value, quality retention, unit energy consumption, and transient temperature at the can center. These ANN models were able to be directly used for the process establishment and validation for a given food product, but also could be combined with a search technique to build optimal thermal process conditions in order to meet different optimization objectives. Some details of selected studies in thermal processing based on the ANN approach are given in the following sections.

4.5.1 Neural Network Modeling of Heat Transfer to Liquid Particle Mixtures in Cans Subjected to End-over-End Processing

The *overall heat transfer coefficient* (U) and *fluid-to-particle heat transfer coefficient* (h_{fp}) are fundamental data needed to develop prediction models for the transient temperature of canned foods undergoing agitation thermal processing, which is necessary to establish and optimize the thermal process schedule for the canned liquid–particle food system. Traditionally, the dimensionless correlations are used for development of an experimental model of U and h_{fp} involving other influencing parameters by use of multiple regression analysis. However, selection of appropriate dimensionless groups requires prior knowledge of the phenomena under investigation. Sablani et al.[25] developed an artificial neural network (ANN) model for the overall heat transfer coefficient and the fluid-to-particle heat transfer coefficient associated with liquid particle mixtures, in cans subjected to end-over-end rotation. Experimental data obtained for U and h_{fp} under various test conditions (shown in Table 4.1) were used for both training and evaluation. Multilayer neural networks with seven inputs and two output neurons (for a single particle in a can), and six inputs and two output neurons (for multiple particles in a can) were trained. The optimal network was obtained by initial trials as number of hidden layers = 2, number of neurons in each hidden layer = 10, and learning

TABLE 4.1
Range of System and Product Parameters Used in the Determination of Heat Transfer Coefficients (U and h_{fp})

No.	Parameter	Experimental Range
1	Retort temperature	110, 120, and 130°C
2	Radius of rotation	0, 0.09, 0.19, and 0.27 m
3	Rotation speed	10, 15, and 20 rpm
4	Can headspace	0.0064 and 0.01
5	Test fluid	Water and oil
6	Test particle	Polypropylene, nylon
7	Particle concentration	Single particle, 20, 30, and 40% (v/v)
8	Particle shape and size	
	Cube	0.01905 m
	Cylinder	0.01905 × 0.01905 m
	Sphere	0.01905, 0.02225, and 0.025 m
9	Can dimension	307 × 409 (8.73 × 11.6)

runs = 50,000. By use of trained NN models with optimal configurations, the prediction performance of all NN models for both U and h_{fp} was found to be higher than 0.98, meaning that the developed NN models could safely be used for prediction of U and h_{fp} under the given experimental conditions. The comparison of NN models and dimensionless regression models using the same experimental data is summarized in Table 4.2. Prediction errors using ANN were less than 3 and 5%, respectively, for U and h_{fp}, which were about 50% better than those associated with dimensionless number models, indicating that the predictive performance of the ANN was far superior than that of dimensionless correlations.

TABLE 4.2
Comparison of Error Parameters for Neural Network (NN) Models and Dimensionless Correlation (DC) Models

	Single Particle				Multiple Particle			
	U		h_{fp}		U		h_{fp}	
Error Parameters	DC	NN	DC	NN	DC	NN	DC	NN
MAE	17.1	5.11	31.3	17.2	25.1	9.85	75.4	48.1
SDE	25.4	4.76	43.3	16.0	32.0	11.0	63.4	40.7
MRE (%)	5.00	2.46	16.9	5.82	5.70	2.57	8.26	4.52
SRE (%)	3.76	2.51	11.9	7.00	4.65	1.96	7.12	3.90
R^2	0.99	0.99	0.83	0.98	0.98	0.99	0.96	0.98

4.5.2 A Neuro-Computing Approach for Modeling of Residence Time Distribution of Carrot Cubes in a Vertical Scraped-Surface Heat Exchanger

The residence time distribution (RTD) is one of the important parameters for establishing the aseptic processing of particulate liquids. Although a lot of different models have been developed for describing RTD characteristics using conventional mathematical methods, none of them give a fully satisfactory solution for the RTD covering the wide range of processing conditions. A neuro-computing approach was used by Chen and Ramaswamy[26] for modeling two residence time distribution (RTD) functions: the time-specific (*E*-type distribution) and the cumulative particle concentration function (*F*-type distribution) of carrot cubes in starch solutions in a vertical scraped-surface heat exchanger (SSHE) of a pilot-scale aseptic processing system. In this study, 356 experimental data pairs obtained for $E(t)$ and $F(t)$ under various test conditions, including the concentration of particles, flow rate, particle dimension, and test time, were used for both training and evaluation. The optimal configurations of the neural network model were determined by adjusting the number of hidden layers, the number of neurons in each hidden layer and learning runs, and a combination of learning rule and transfer functions. The results showed that the trained ANN model can accurately map experimental results with R^2 value = 0.98 and 0.99 for *E* and *F* functions, respectively. The prediction performance of the ANN model under several typical processing conditions is shown in Figure 4.5. The ANN models were also compared with conventional models developed based on multiple variable regression techniques. The comparison indicated that average modeling errors associated with the ANN model were 5.7 and 3.0%, respectively, for *E* and *F*, while those for the multiple regression models were 15.5 and 12.3%, meaning that the ANN model had higher precision for predicting *E* and *F* functions.

4.5.3 Modeling and Optimization of Constant Retort Temperature Thermal Processing Using Coupled Neural Networks and Genetic Algorithms

Modeling and optimization of the thermal processing are of considerable interest and are widely based on conventional mathematical methods. Traditionally, solving an optimization problem consists of two steps. First, different objective function models are developed using mathematical approaches that include regression methods, theoretical analysis models, and differential equations; and then the optimal conditions are sought using one of several search methods, such as direct search, grid search, gold-section method, etc., for single variables, and alternating variable search, pattern search, and Powell's method for multivariables. Like traditional modeling methods, neural networks cannot provide direct answers for optimization problems. In order to be used for optimization purposes, neural network models have to be combined with a search technique.

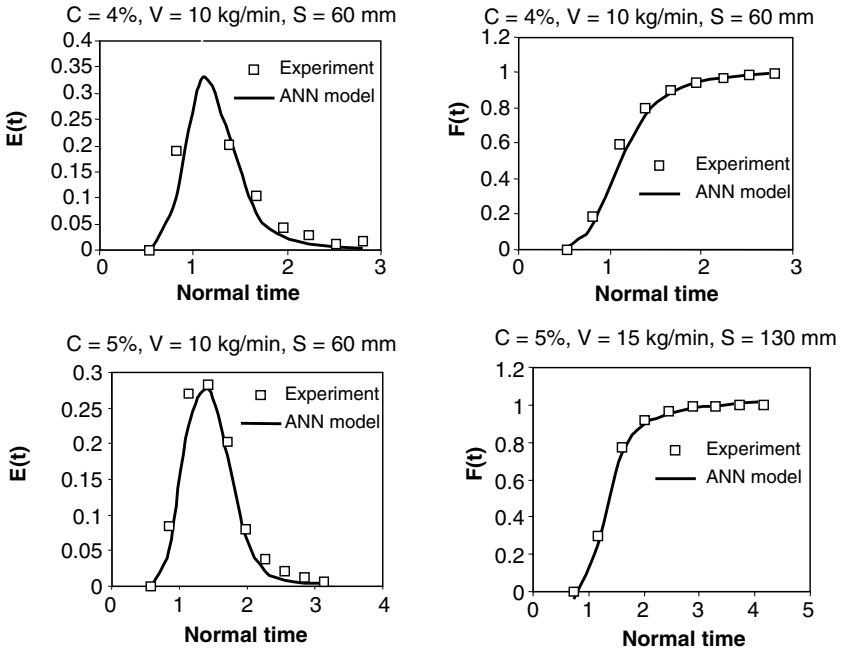

FIGURE 4.5 Comparison of ANN model predictions and experiments for *E* and *F* functions.

Genetic algorithms (GAs) are a combinatorial optimization technique, searching for an optimal value of a complex objective function by simulation of the biological evolutionary process, based on crossover and mutation, as in genetics. Chen and Ramaswamy[30] found that the combination of GA and ANN models can become an effective tool for optimization problems. This study might be the first report on application of ANN and GA for thermal processing optimization. The focuses of this study were on:

1. Developing ANN models for predicting process time (*PT*), average quality retention (*Qv*), surface cook value (*Fs*), equivalent unit energy consumption (*En*), temperature difference (*g*), and ratio of *F* value from heating to total desired *F* value (ρ) under constant retort temperature (CRT) processing conditions
2. Coupling ANN models and GA to search for the optimal quality retention and the corresponding retort temperature
3. Investigating the effects of main processing parameters on both optimal quality retention and retort temperature

Processing conditions as inputs for ANN models were selected as follows: retort temperature (*RT* = 110 to 140°C), thermal diffusivity (α = 1.1 to 2.14 × 10^{-7} m^2/sec), volume of can (*V* = 1.64 to 6.55 × 10^{-4} m^3), ratio of height to diameter

of can (R_{dh} = 0.2 to 1.8), total desired lethality value (F_o = 5 to 10 min) at the can center, and quality kinetic destruction parameters — decimal destruction time (D_q = 150 to 300 min) and their temperature dependence (z_q = 15 to 40°C). Six separate ANN models were developed for prediction of process time, average quality retention, surface cook value, equivalent energy consumption, final temperature difference at the can center, and lethality ratio, ρ (heating/total lethality), respectively. The data for training and testing ANN models were obtained from a finite difference computer simulation program. A second-order central composite design was used for constructing experimental data for training ANN models, while an orthogonal experimental design composed of six factors and three levels was used for the generalization of trained ANN models. The hybrid optimization method (shown in Figure 4.6) linking GAs with ANNs was employed for searching the optimal quality

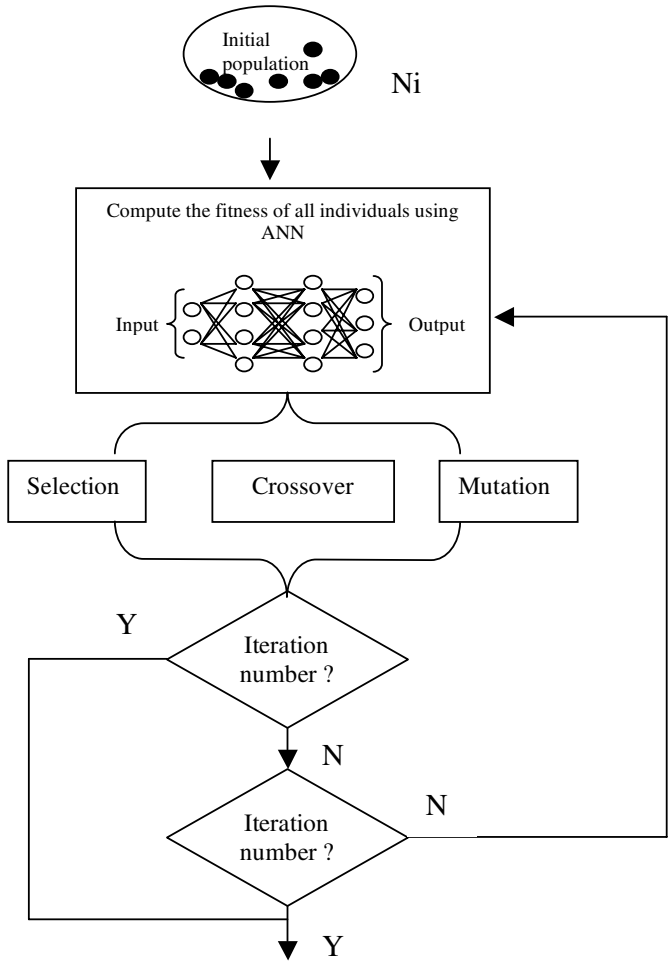

FIGURE 4.6 The procedure of the hybrid optimization method using GAs and ANNs.

retention and corresponding retort temperature, and for investigating the effects of main processing parameters on optimal results. ANN-based prediction models successfully described the various outputs of CRT thermal processing (correlation coefficients, $R^2 > 0.98$; relative errors, $Er \leq 3\%$). The coupled ANN-GA models, verified under several typical processing conditions, could be effectively used for optimization of CRT thermal processing. The main processing parameters and their interactions in the order of their importance with respect to the optimal quality retention and corresponding retort temperature were $V > z_q > F_o > R_{dh}$ and $z_q > F_o > R_{dh} > V$, respectively. The studies were later extended to variable retort temperature processes, demonstrating the excellent performance of ANN models.[30]

4.5.4 ANN Model-Based Multiple-Ramp Variable Retort (MRV) Temperature Control for Optimization of Thermal Processing

Variable retort temperature (VRT) thermal processing has been recognized as an innovative method to improve food product quality and save process times. The key to designing a VRT thermal process is to choose a reasonable (optimal) VRT profile for a given food product and package being thermally processed. The selection of optimal retort temperature profiles with a multistage ramp function involving multiple variables is complex and difficult to handle by conventional optimization methods.[33] The study consisted of three parts: (1) developing associated prediction models using ANN, (2) investigating the sensitivity of VRT parameters to processing results, and (3) searching for the optimal VRT profile using a hybrid optimization technique coupling ANN with GA.

For the first part, three separate ANN models were developed for predictions of process time, average quality retention, and surface cook value, respectively, each as a function of five input variables: ramp time, t, and four step temperatures, T1, T2, T3, and T4. ANN models were trained and tested by two data sets, respectively, which were generated by a computer simulation program of VRT thermal processing. The statistical results of the modeling performance for all ANN models had a correlation coefficient of >0.95 and an average relative error of <2.05%, indicating that these ANN models can be safely used for prediction purposes of VRT thermal processing with a multiple-ramp temperature profile.

In the second part, ANN models-based sensitivity analysis was used for investigation of effects of five MRV parameters on process time (*PT*), average quality retention (*Qv*), and surface cook value (*Fs*). For example, Figure 4.7 shows the effects of individual variables, including four step temperatures and ramp time on process outputs: *PT*, *Qv*, and *Fs* for the small size. As expected normally, the increase of step temperatures resulted in the decrease of process times (Figure 4.7a), but the decrease rate was dependent on the number of steps and temperature values. If the temperature was less than 119°C, T3 was the most sensitive to *PT*; if larger than 119°C, then T2 was the most sensitive factor to *PT*. The effects on the quality retention *Qv* were illustrated in Figure 4.7b. It showed that T1 and T4 had no effect on *Qv*, while effects of T2 and T3 were related to the temperature value.

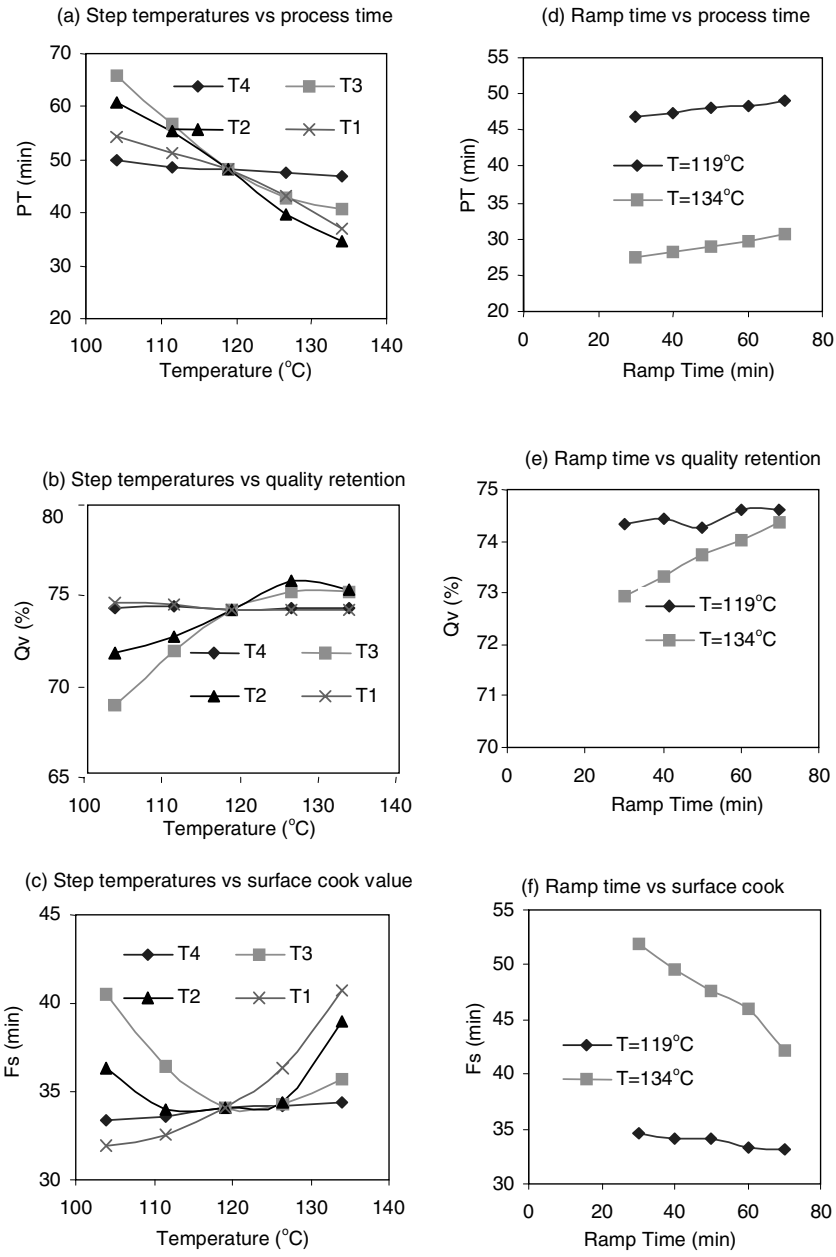

FIGURE 4.7 Effects of MRV parameters on process outputs for small size ($V = 1.64 * 10^{-4}\,m^3$).

Qv increased with the temperature value of T2 or T3 until the temperature reached around 127°C, and then decreased with the temperatures. The effects of step temperatures on the surface cook value *Fs* are presented in Figure 4.7c. It can be found that increasing temperatures T1 or T4 caused *Fs* to increase, especially for T4; and for T2 or T3, the best temperature was about 119°C, which had the minimum surface cook value. Effects of the ramp time on process outputs are shown in Figure 4.7d to f. Basically, the increase of ramp time made the process time and the quality retention increase and the surface cook value decrease. However, the sensitivity of ramp time was dependent on the base temperature.

Coupled ANN models and GA were then used for searching the optimal retort temperature profiles to meet the requirements of optimization objectives and constraint conditions. The typical optimal MRV profiles for the middle size ($4.92 * 10^{-4}$ m^3) achieved by the GA-ANN protocol are illustrated in Figure 4.8. It could be found that there were different specific MRV values for different optimization objectives and constraint conditions. By comparison of optimization objectives, it was indicated that the minimum *PT* used as the optimization objective needed much more ramp time than the minimum Fs as the optimization

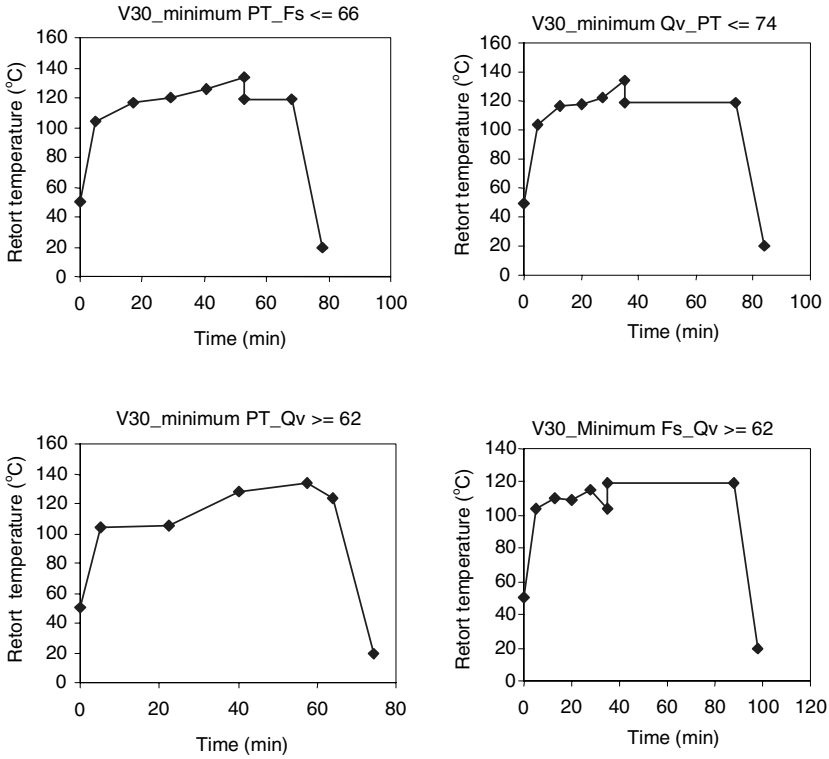

FIGURE 4.8 Optimal MRV profiles obtained by the GA-ANN method.

objective. For example, the ramp time was 70 min for the minimum *PT* with *Qv* 62%, while it was only 30 min for the minimum *Fs* with *PT* 74 or *Qv* 62%. From the step temperature point of view, the order of step temperatures was T4 > T3 > T2 > T1 if the *PT* or *Fs* was used as the constraint condition, while T4 was less than T3 if *Qv* was used as the constraint condition.

4.5.5 Analysis of Critical Control Points in Deviant Thermal Processes Using Artificial Neural Networks

The basic objective of thermal processing is to meet the safety requirements while trying to reduce quality degradation to a minimum. Theoretically, it is possible to design an optimal processing protocol for any food product, but in practice, it is difficult to obtain truly optimal results since considerable deviations exist in process parameters. In cases where deviations go beyond a certain critical level, there can be underprocessing or overprocessing. The former indicates that processed products cannot meet the sterility requirements for safety and consumption, while the latter means that quality destruction is more than optimal. Therefore, it is important to identify critical factors, to assess the effect of their deviations on the process calculations, and to establish control actions during thermal processing to avoid process deviations.

Thermal processing is a complex system, and standard processes are established based on achieving a target process lethality (*F* value) at a critical point, usually the package center. The required process time (*PT*) for a given product depends on the retort temperature (RT), product initial temperature (T_i), cooling water temperature (T_w), and several product-related properties, such as heating rate index (f_h), heating lag factor (j_h), and cooling lag factor (j_c). It is necessary to understand and estimate the influence of these process parameters and the deviations from their expected values on the required process time. Chen and Ramaswamy[33] developed ANN models for (1) evaluating the relative order of importance of different critical control variables with respect to process calculations, and (2) developing predictive models to compensate for their deviations. The critical variables studied were retort temperature, initial temperature, cooling water temperature, heating rate index, heating lag factor, and cooling lag factor. Their ranges of deviation from a set point were selected as –2 to 2°C for RT, –5 to 5°C for both T_w and T_i, –2 to 2 min for f_h, and –0.2 to 0.2 for both j_c and j_h. ANN models were developed and used for analysis of different critical variables with respect to their importance on the accumulated lethality, process time, cooling time (*CT*), and total time (*TT*) under the given processing conditions. By use of ANN models, the relative orders of importance of critical variables within the deviation ranges were as follows: for *F*, $RT > f_h > j_h > T_i \times T_w > T_i > T_i \times f_h > RT \times T_i > j_c > RT \times j_h$; for *PT*, $RT > f_h >> j_h > T_i > j_c > T_i \times T_w$; for *CT*, $j_c > T_w > f_h$; and for *TT*, $RT > f_h > j_h > j_c > T_w > T_i > T_i \times j_c > T_i \times T_w$. The accepted deviation ranges for various input variables under given control ranges were predicted by NN models, one of which is shown in Figure 4.9.

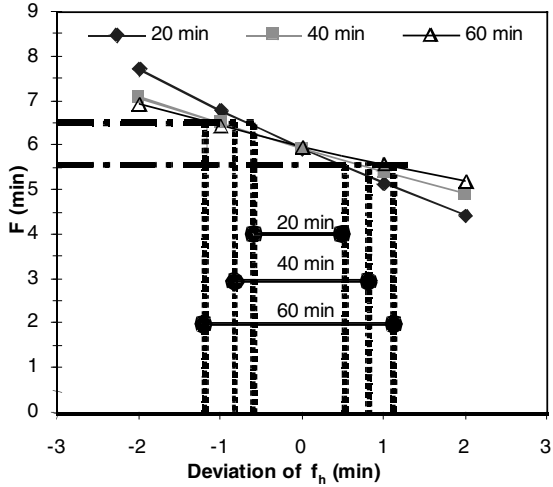

FIGURE 4.9 Acceptable deviation ranges predicted by ANN models for heating rate index, f_h.

Based on these graphs, it can be easily determined that when the desired F value was set at 6 ± 0.5 min, the maximum acceptable deviation ranges of different variables were ±0.3°C for RT; ±4°C for T_i; ±0.1 for j_h; ±0.8, ±1, and ±1.2 min for f_h at f_h = 20, 40, and 60 min, respectively; and ±0.4 for j_c. Neural network models were also used for analysis of the combination effect of multiple deviations on F, PT, and CT (shown in Figure 4.10). By use of this graph, the maximum changes in F and PT for different deviation combinations could be easily determined.

4.6 CONCLUSIONS

As confirmed by a variety of applications reported, the modeling capability of ANNs is not a question; they can be used for complex cases with multiple variables and nonlinear relationships usually too difficult for conventional methods. In food thermal processing, application of ANN is still relatively new to other academic areas. Although a few studies have been reported, as mentioned in this chapter, about ANN for modeling, optimization, and critical control points analysis of thermal processing, most of them are still on the hypothesis level, meaning that these results have not been used for industrial applications. Furthermore, the online use of neural networks in the thermal processing area is still blank. Therefore, there is more room for researchers to make efforts on application of neural networks in the thermal processing area.

It should be noted that ANNs are not without limitations. First of all, neural networks work like a black box; thus, ANN models cannot give clear internal relationships between input and output variables as provided by other models

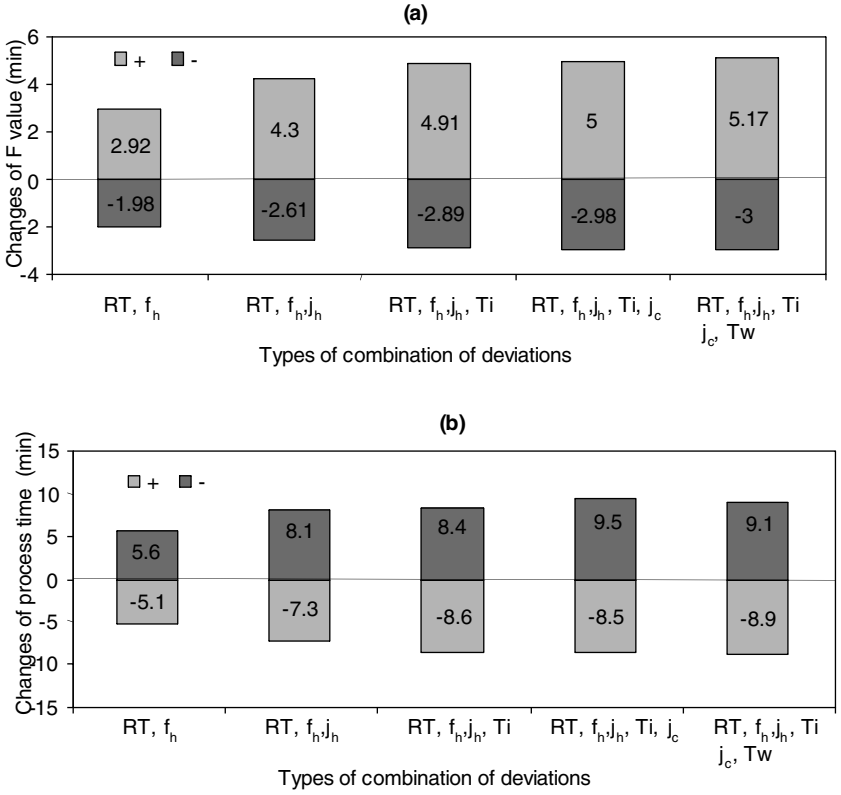

FIGURE 4.10 The comprehensive effects of multiple deviations predicted by ANN models: (a) lethality value, and (b) heating time.

based on conventional methods. Therefore, neural networks should be used as a tool for practical purposes rather than theoretical ones, focusing on developing and understanding the intrinsic relationships of various variables. For the practical application, the objective of developing ANN models is that they are to be used for different purposes such as optimization, online control, identification, etc. In order to achieve this goal, neural networks must be combined with other techniques, for instance, fuzzy logic, expert systems, and genetic algorithms or other search techniques. Therefore, the future trend for application of neural networks should be developing hybrid methods by using neural networks and other techniques that may have more potential for direct use for industrial purposes, instead of staying at the level that only confirms the feasibility of ANN modeling, as most current works have done. Second, the training ANN model needs enough data, which is the most important factor affecting the performance of ANN models. It is impossible to obtain an ANN model with a good performance using limited or bad distribution data. Thus, neural

networks are only suitable for problems with a large amount of experimental data, or those that can generate data using a separate computer simulator. In addition, like all other models, trained ANN models can only be used for predictions within the ranges of the variable being investigated. Otherwise, the precision of prediction results by ANN models might not be guaranteed.

NOMENCLATURE

Variables

CT	Cooling time, min
D	Decimal deduction time, min
Dq	Decimal destruction time for quality, min
En	Equivalent unit energy consumption, kJ/kg
Er	Relative average error, %
E	Time-specific particle concentration function or total square error
F	Accumulated lethality value, min, or cumulative particle concentration function
Fs	Surface cook value, min
F	Heating or cooling rate index, min
j	Heat or cooling lag factor
g	Final temperature difference between can center and retort, °C
h	Transfer coefficient, W/(m^2°C)
H	Height of the can, mm
PT	Process time or heating time, min
Qv	Average quality retention for whole can, %
R	Correlation coefficient or ratio of diameter to height of can
RT	Retort temperature, °C
T	Temperature, °C
T1–T4	Step temperature for MRV function, °C
U	Overall heat transfer, W/(m^2°C)
V	Volume, m^3
w	Weight (neural network)
y	Output value

Subscripts

c	Cooling
di	Desired output values
dh	Diameter to height
fp	Fluid to particle

h	Heating
i	Index, or initial
j	Index
m	Microorganism, or mean value
max	Maximum
min	Minimum
o	Desired value
q	Quality
w	Cooling water

Greek Symbols

α	Thermal diffusivity, m^2/sec
θ	Threshold value (neural network)
ρ	Density, kg/m^3, or lethality ratio
ε	Error

Abbreviations

ANN	Artificial neural network
CCP	Critical control point
CDT	Come-down time
CRT	Constant retort temperature
CUT	Come-up time
GA	Genetic algorithm
MRV	Multiple-ramp variable
RTD	Residence time distribution
VRT	Variable retort temperature

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5 Modeling Thermal Processing Using Computational Fluid Dynamics (CFD)

Xiao Dong Chen

CONTENTS

5.1 INTRODUCTION

In the food industry, thermal processing is referred to as the processes that heat, hold, and cool a product sequentially, which is required to be free of food-borne illness for a desired period. *Pasteurization* is a type of thermal processing that reduces the potential of contamination of a special pathogenic microorganism to

a predesigned extent. The product will still need to be refrigerated; otherwise, it will not be shelf stable. *Sterilization* is the process that leads to shelf-stable products in cans, soft containers, or bottles.[1] This process usually employs a much greater temperature than pasteurization.

5.2 BASIC THERMAL PROCESSING PARAMETERS

5.2.1 Decimal Reduction Time *D*

When you subject a living microorganism population, like *Escherichia coli*, to thermal processing at a constant temperature (T), its population will reduce. A typical plot of the microbial population over time (N vs. t) usually shows an exponential-like trend. A semilog plot of N vs. t may be correlated using a linear fit, yielding a straight line with a negative slope ($-D$):

$$D = \frac{t}{\log N_o - \log N} \tag{5.1}$$

D is called the *decimal reduction time*.

In other words, the microbial population reduction may be expressed as

$$\frac{N}{N_o} = 10^{-\frac{t}{D}} \tag{5.2}$$

Obviously, at different T, D would be different. The higher the temperature, the smaller the D value, and this means that the microorganisms are more vulnerable in a hotter environment.

Some typical values of D are given in Table 5.1.

A liquid is uniformly heated, held, and cooled through three steps, shown in Figure 5.1. The residual live population N_3 may be approximated with the following calculations:

$$N_1 = N_o \cdot 10^{-\frac{\Delta t_1}{D_1}} \tag{5.3}$$

TABLE 5.1
Typical Z and D_T Values[2]

Microorganism	Z (°C)	D_{121} (min)	Products
Bacillus stearothermophilus	10	4	Vegetables, milk
Bacillus subtilis	4.1–7.2	0.5–0.76	Milk products

Source: Fellows, P.J., *Food Processing Technology (Principles and Practice)*, Woodhead Publishing Series in Food Science and Technology, Abington, Cambridge, U.K., 1996. With permission.

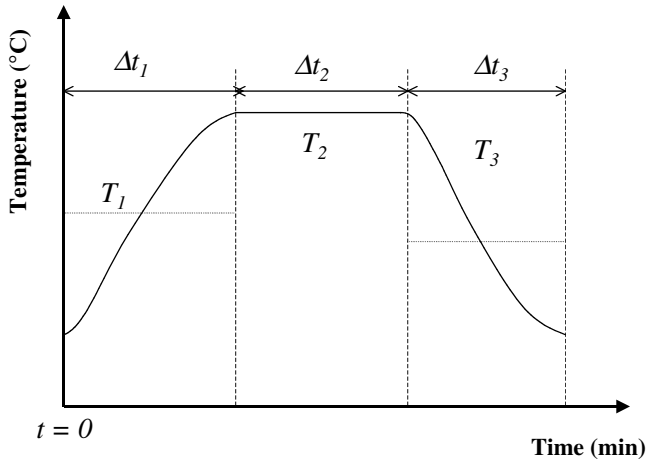


FIGURE 5.1 A typical heating, holding, and cooling curve of a fluid.

$$N_2 = N_1 \cdot 10^{-\frac{\Delta t_2}{\bar{D}_2}} \tag{5.4}$$

$$N_3 = N_2 \cdot 10^{-\frac{\Delta t_1}{\bar{D}_3}} \tag{5.5}$$

Therefore, combining the above three equations, one has

$$N_3 = N_o \cdot 10^{-\left(\frac{\Delta t_1}{\bar{D}_1} + \frac{\Delta t_2}{\bar{D}_2} + \frac{\Delta t_3}{\bar{D}_3}\right)} \tag{5.6}$$

where $\bar{D}_1$ is taken as the value when $T = T_1$, $\bar{D}_2$, is taken as the value when $T = T_2$, and $\bar{D}_3$ is taken as the value when $T = T_3$.

If the heating region and the cooling period can be approximated with more than one single step taking average T for each period, i.e., for the heating period, there are m steps, and for the cooling period, n steps,

$$N_3 = N_o \cdot 10^{-\left(\sum_{i=1}^{i=m} \frac{\Delta t_{1,i}}{\bar{D}_{1,i}} + \frac{\Delta t_2}{\bar{D}_2} + \sum_{j=1}^{j=n} \frac{\Delta t_{3,j}}{\bar{D}_{3,j}}\right)} \tag{5.7}$$

Different parts of the fluid being processed would experience different temperature–time histories; for each part, Equation 5.7 is needed to calculate the individual bacterial deactivation histories.

For example, if the fluid is thermally processed in a pipe (i.e., a tubular heat exchanger), the maximum (centerline velocity) is twice the average value at the laminar regime. For the turbulence regime, the maximum velocity is about 1.2 times

the average velocity. As such, the turbulence regime provides a more uniform mixing condition for thermal processing. The average residence time is the length of the pipe divided by the average velocity; thus, the microbes that travel at the maximum velocity would not be fully processed.

This is related to *aseptic processing*, where food is sterilized or pasteurized in a tubular, helical heat exchanger, scraped-surface heat exchanger, microwave, or ohmic heater. The aseptic process has significant quality advantages over classical thermal techniques, such as batch (canning) and semibatch operations. In general, flow modeling has to be used to ensure that food products meet the safety requirements. It determines the optimal lengths of the heating, holding, and cooling sections.

5.2.2 Thermal Resistance Constant *Z*

The *thermal resistance constant Z* is a parameter representing the microorganism's resistance to temperature rise:

$$Z = \frac{T_2 - T_1}{\log \dfrac{D_{T_1}}{D_{T_2}}} \tag{5.8}$$

5.2.3 Thermal Death Time *F*

The *thermal death time F* is the time required to cause a stated reduction in the population of microorganisms or spores. This time is expressed as a multiple of *D* values. A 99.99% reduction in microbial population is equivalent to 4*D*, for instance. Usually, *F* is expressed as F_T^z for a specific temperature *T* and a thermal resistance constant *z*.

5.2.4 Relationships between Chemical Kinetics and Thermal Processing Parameters

It is generally accepted that at a constant temperature, the microbial population or number concentration (microbe $\cdot$ m^{-3}) (*N*) reduces following the first-order reaction:

$$\frac{dN}{dt} = -k \cdot N \tag{5.9}$$

Therefore, the solution for this is

$$\ln \frac{N}{N_o} = -k \cdot t \tag{5.10}$$

Comparing Equation 5.10 with Equation 5.2, it is not difficult to arrive at

$$k = 2.303/D \tag{5.11}$$

During thermal processing, the microbial population is not uniformly distributed within the processing fluid, and also, the extent of the deactivation is different at different locations and different timing.

Equation 5.9 may also be directly expressed as

$$\frac{dc}{dt} = -k \cdot c \tag{5.12}$$

where c is the mass concentration of the live microbes ($c = m_{microbe} \cdot N$); $m_{microbe}$ is the mass of one microbe.

5.3 FUNDAMENTAL CONSERVATION EQUATIONS FOR CFD

The essential aspect of the *computational fluid dynamics* (CFD) approach is that regardless of the software being used, all need to solve the governing partial differential equations for continuity, momentum, energy, and mass balances.

For momentum transfer, the governing set of equations are the Navier–Stokes equations. The fluids of practical interest are usually considered to be noncompressible, except the cases when extreme high-pressure technology is applied. As such, only the governing equations for incompressible fluids for two typical coordinate systems are described in this section.[3]

5.3.1 Cartesian Coordinate System

Continuity

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \tag{5.13}$$

Momentum

$$\rho \cdot \left(\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} + w\frac{\partial u}{\partial z} \right) = \rho F_x - \frac{\partial p}{\partial x} + \mu \cdot \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) \tag{5.14}$$

$$\rho \cdot \left(\frac{\partial v}{\partial t} + u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y} + w\frac{\partial v}{\partial z} \right) = \rho F_y - \frac{\partial p}{\partial y} + \mu \cdot \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial z^2} \right) \tag{5.15}$$

$$\rho \cdot \left(\frac{\partial u}{\partial t} + u\frac{\partial w}{\partial x} + v\frac{\partial w}{\partial y} + w\frac{\partial w}{\partial z} \right) = \rho F_z - \frac{\partial p}{\partial z} + \mu \cdot \left(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} + \frac{\partial^2 w}{\partial z^2} \right) \tag{5.16}$$

Ignoring the viscous dissipation effect, the internal heat generation or dissipation is due to exothermic or endothermic reactions. The energy balance may be written as

$$\frac{\partial T}{\partial t}+u\frac{\partial T}{\partial x}+v\frac{\partial T}{\partial y}+w\frac{\partial T}{\partial z}=\frac{1}{\rho\cdot C_p}\cdot\left[\begin{array}{l}\dfrac{\partial}{\partial x}\left(k\cdot\dfrac{\partial T}{\partial x}\right)+\\ \dfrac{\partial}{\partial y}\left(k\cdot\dfrac{\partial T}{\partial y}\right)+\dfrac{\partial}{\partial z}\left(k\cdot\dfrac{\partial T}{\partial z}\right)\end{array}\right] \tag{5.17}$$

Here the thermal conductivity k can be temperature or concentration dependent.

The mass conservation for microbial species and nutrient species may be expressed as

$$\frac{\partial c}{\partial t}+u\frac{\partial c}{\partial x}+v\frac{\partial c}{\partial y}+w\frac{\partial c}{\partial z}=\frac{\partial}{\partial x}\left(D\cdot\frac{\partial c}{\partial x}\right)+\frac{\partial}{\partial y}\left(D\cdot\frac{\partial c}{\partial y}\right)+\frac{\partial}{\partial z}\left(D\cdot\frac{\partial c}{\partial z}\right)+\dot{m} \tag{5.18}$$

The mass diffusivity D can be a function of temperature and concentration, and $\dot{m}$ is determined by Equation 5.7:

$$\dot{m}=-k\cdot c \tag{5.19}$$

for either kind of species.

Equation 5.18 is valid only for the small microbes that are assumed to follow nicely the bulk fluid movement (relative velocity is zero).

When food particles are large enough, their movement must be traced using the Lagrange method (this aspect is not included in this chapter for simplicity).

5.3.2 Cylindrical Coordinate System

Continuity

$$\frac{\partial u_r}{\partial r}+\frac{1}{r}\cdot\frac{\partial u_\theta}{\partial\theta}+\frac{\partial u_z}{\partial z}+\frac{u_r}{r}=0 \tag{5.20}$$

Momentum

$$\begin{aligned}\rho\cdot\left(\frac{\partial u_r}{\partial t}+u_r\frac{\partial u_r}{\partial r}+\frac{u_\theta}{r}\cdot\frac{\partial u_r}{\partial\theta}+u_z\cdot\frac{\partial u_r}{\partial z}-\frac{{u_\theta}^2}{r}\right)&=\rho F_r-\frac{\partial p}{\partial r}\\ +\mu\cdot\left(\frac{\partial^2 u_r}{\partial r^2}+\frac{1}{r}\cdot\frac{\partial u_r}{\partial r}+\frac{1}{r^2}\cdot\frac{\partial^2 u_r}{\partial\theta^2}+\frac{\partial^2 u_r}{\partial z^2}-\frac{2}{r^2}\cdot\frac{\partial u_\theta}{\partial\theta}-\frac{u_r}{r^2}\right)&\end{aligned} \tag{5.21}$$

$$\rho\cdot\left(\frac{\partial u_\theta}{\partial t}+u_r\frac{\partial u_\theta}{\partial r}+\frac{u_\theta}{r}\cdot\frac{\partial u_\theta}{\partial\theta}+u_z\cdot\frac{\partial u_\theta}{\partial z}-\frac{u_r\cdot u_\theta}{r}\right)=\rho F_\theta-\frac{1}{r}\cdot\frac{\partial p}{\partial\theta}$$
$$+\mu\cdot\left(\frac{\partial^2 u_\theta}{\partial r^2}+\frac{1}{r}\cdot\frac{\partial u_\theta}{\partial r}+\frac{1}{r^2}\cdot\frac{\partial^2 u_\theta}{\partial\theta^2}+\frac{\partial^2 u_\theta}{\partial z^2}+\frac{2}{r^2}\cdot\frac{\partial u_r}{\partial\theta}-\frac{u_\theta}{r^2}\right) \quad (5.22)$$

$$\rho\cdot\left(\frac{\partial u_z}{\partial t}+u_r\frac{\partial u_z}{\partial r}+\frac{u_\theta}{r}\cdot\frac{\partial u_z}{\partial\theta}+u_z\cdot\frac{\partial u_z}{\partial z}\right)=\rho F_z-\frac{\partial p}{\partial z}$$
$$+\mu\cdot\left(\frac{\partial^2 u_z}{\partial r^2}+\frac{1}{r}\cdot\frac{\partial u_z}{\partial r}+\frac{1}{r^2}\cdot\frac{\partial^2 u_z}{\partial\theta^2}+\frac{\partial^2 u_z}{\partial z^2}\right) \quad (5.23)$$

Ignoring the viscous dissipation effect, the energy balance may be written as

$$\frac{\partial T}{\partial t}+u_r\frac{\partial T}{\partial r}+\frac{u_\theta}{r}\frac{\partial T}{\partial\theta}+u_z\frac{\partial T}{\partial z}=\frac{1}{\rho\cdot C_p}\cdot\left[\begin{array}{l}\frac{1}{r}\cdot\frac{\partial}{\partial r}\left(k\cdot r\cdot\frac{\partial T}{\partial r}\right)+\\ \frac{1}{r}\cdot\frac{\partial}{\partial\theta}\left(k\cdot\frac{1}{r}\cdot\frac{\partial T}{\partial\theta}\right)+\frac{\partial}{\partial z}\left(k\cdot\frac{\partial T}{\partial z}\right)\end{array}\right] \quad (5.24)$$

The mass conservation is given as

$$\frac{\partial c}{\partial t}+u_r\frac{\partial c}{\partial r}+\frac{u_\theta}{r}\frac{\partial c}{\partial\theta}+u_z\frac{\partial c}{\partial z}=\left[\begin{array}{l}\frac{1}{r}\cdot\frac{\partial}{\partial r}\left(D\cdot r\cdot\frac{\partial T}{\partial r}\right)+\\ \frac{1}{r}\cdot\frac{\partial}{\partial\theta}\left(D\cdot\frac{1}{r}\cdot\frac{\partial T}{\partial\theta}\right)+\frac{\partial}{\partial z}\left(D\cdot\frac{\partial T}{\partial z}\right)\end{array}\right]+\dot{m} \quad (5.25)$$

Body-fitted coordinate systems are also available in CFD packages, but the details are beyond the content of this text.[3]

5.4 BOUNDARY AND INITIAL CONDITIONS

5.4.1 Velocity Boundary Conditions

The solid-wall condition is that all the velocities at the wall (fluid–solid interface) are zero. The inlet and outlet of a system need to be specified with the velocity or mass flow rate values.

5.4.2 Thermal Boundary Conditions

Thermal boundary conditions are in general for one of the following situations: liquid–solid, liquid–liquid (nonimmiscible), or liquid–gas interfaces.

The boundary or interfacial temperature, being constant, may be specified, such as the cases when the convective heat transfer coefficient is very large or when the heat transfer coefficient is naturally large, e.g., condensation heat transfer in retort processing, which will be illustrated more later.

In general, the interfacial condition would be the conservation of the heat flux from one side (I) to the other (II). For instance, in a one-dimensional situation (e.g., the interface is perpendicular to the x direction), one can write the following:

$$-k_I \cdot \left.\frac{\partial T}{\partial x}\right|_I = -k_{II} \cdot \left.\frac{\partial T}{\partial x}\right|_{II} \tag{5.26}$$

To be more general, for the arbitrarily shaped interface, one needs to express the heat flux going through the interface at the direction perpendicular to the local interface.

In the cases when one side can be approximated using the *Nusselt* number approach (i.e., $Nu = h \cdot d/k$) to convection heat transfer, Equation 5.26 may be rewritten as[4]

$$-k_I \cdot \left.\frac{\partial T}{\partial x}\right|_I = h \cdot (T_s - T_\infty) \tag{5.27}$$

where T_s is the interface temperature, and T_∞ is the bulk temperature in region II.

If one side (II) is well insulated (for example, when an air bubble is considered to exist in a metal can, its insulation effect must be accounted for), Equation 5.26 gives

$$\left.\frac{\partial T}{\partial x}\right|_I = 0 \tag{5.28}$$

5.4.3 Mass Transfer Boundary Conditions

In general, the interfacial condition would be the conservation of the mass flux from one side (I) to the other (II). For instance, in a one-dimensional situation (e.g., the interface is perpendicular to the x direction), one can write the following:[4]

$$-D_I \cdot \left.\frac{\partial c}{\partial x}\right|_I = -D_{II} \cdot \left.\frac{\partial c}{\partial x}\right|_{II} \tag{5.29}$$

Note here that the partitioning effect is not considered for simplicity. To be more general, for the arbitrarily shaped interface, one needs to express the mass flux going through the interface at the direction perpendicular to the local interface.

In cases when one side can be approximated using the Sherwood number approach (i.e., $Sh = h_m \cdot d/D$) to convective mass transfer, Equation 5.29 may be written as

$$-D_I \cdot \left.\frac{\partial c}{\partial x}\right|_I = h_m \cdot (c_s - c_\infty) \tag{5.30}$$

where c_s is the interface concentration, and c_∞ is the bulk concentration in region II.

If one side (II) is impermeable, Equation 5.29 gives

$$\left.\frac{\partial c}{\partial x}\right|_I = 0 \tag{5.31}$$

The initial conditions inside a container, in Cartesian coordinate, for instance, are usually

$$u = v = w = 0, T = T_o, \quad \text{and} \quad c = c_o \tag{5.32}$$

It does, however, depend on whether the flow in-and-out system is considered. If there is flow in and out, then a fully developed flow is usually imposed before the heating or cooling starts.

5.5 SOLUTION METHODS

The methods of grid (or grid block) generation/formation and differential equation discretization for solving the sets of equations mentioned earlier have been described by many authors (e.g., the work by Patankar and Spalding[5]). Though the principles may be similar, the details are not given here, as they vary between CFD packages. In food process engineering research and design, existing commercially available CFD computer packages are commonly employed.

The most notable CFD packages to date are:

- PHOENICS (www.cham.co.uk)
- CFX (www-waterloo.ansys.com/cfx/)
- FLUENT (www.fluent.com/solutions/food/index)

FIDAP is one of the FLUENT series, specializing in optimizing the continuous sterilization process, e.g., the work by Jung and Fryer.[6] The FLUENT series has been used to simulate the beer bottle sterilization process, which is similar to that of the can (described in detail later).

The inputs of these computations include the geometrical data (size, shape, etc.) and physical and chemical properties.

5.6 WORKED EXAMPLES

The sterilization of the canned or pouched food liquid is a good example to investigate the interactions of the fluid movement, heat transfer, and species transfer using CFD.

The existence and whereabouts of the so-called *slowest-heating zone* (SHZ), or the *coldest zone* (CZ), where the temperature of the fluid is the lowest, and its reduction over sterilization time is one of the primary subjects. Due to the fluid movement, the *stagnation zone* (SZ) (usually within a *recirculation zone*) is also of primary interest, as the microbes or nutrient species would not be transported easily out of SZ. Therefore, the movement and size of CZ and the evolution and location of SZ, and interactions of the two are important subjects for CFD analysis to explore, e.g., the work by Datta and Teixeira[7,8] and Kumar et al.[9]

If the filled material in a can or pouch is basically solid, there would be no fluid movement. In this case, heat conduction and species diffusion within the solid matrix can be readily resolved according to classical theories and using relatively simple numerical procedures. Previous studies that used the conduction mode as the only heat transfer mechanism pointed to the CZ being the geometrical center. For a vertically placed cylindrical can in a retort device, CZ or the coldest point (CP) is located right at the center of the central axis.

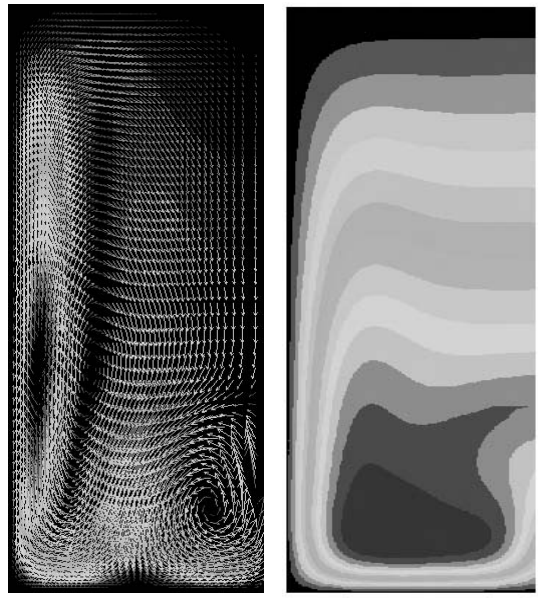
When the fluid flow is involved, CFD is required, under two- or three-dimensional situations. The process of can sterilization must involve CFD in order to locate the SZs and CZs. Furthermore, the species transfer involves fluid movement effect, which needs to be accounted for in CFD simulations. Though CFD is powerful in the ease of providing the details of the flow, temperature, and concentration fields, the interpretation of the simulation results and laboratory validations are all very important aspects of the CFD modeling exercises.

For either can sterilization or pouch sterilization processes, one must look up the recent series of important CFD and experimental studies carried out by Ghani[10] and Ghani et al.[11–26] In this series of work, the details of the fluid, heat, and mass transfer and their interactions have been demonstrated.

Here, the vertically placed cylindrical can (which is filled completely by a liquid) is considered as an example. In the early studies of Ghani and coworkers,[10,11] the main features of the fluid flow pattern and temperature distribution and their evolution during sterilization have been demonstrated. One typical result using CMC (sodium carboxymethyl cellulose) as a sample viscous fluid is shown in Figure 5.2. There are two circulation regions that can be identified (Figure 5.2a): one is near the side of the cylindrical section, and the other is located at the center region of the bottom surface.

The occurrences of these two regions result in the kind of temperature distribution shown in Figure 5.2b, which can be interpreted as shown in Figure 5.3 (X.D. Chen, unpublished analysis, 2004).

Figure 5.3a shows that when only the bottom plate is heated and the other parts of the container are colder, the circulation starts from the fluid rising from the bottom plate surface. Figure 5.3b shows that if the bottom plate is



(a) (b)

5.2 Velocity contours of a can filled with CMC after being heated by steam condensation for 1157 sec (the left side is the can side wall; the right side is the center axis of the can). (From Ghani, A.G., Thermal Sterilization of Canned Liquid Foods, Ph.D. thesis, Department of Chemical and Materials Engineering, The University of Auckland, New Zealand, 2002. With permission.)

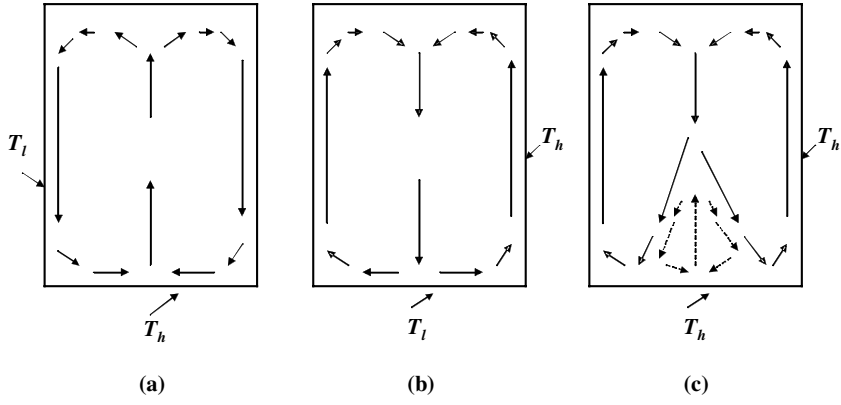


FIGURE 5.3 An interpretation of the flow pattern formation shown in Figure 5.2 (X.D. Chen, unpublished analysis, 2004).

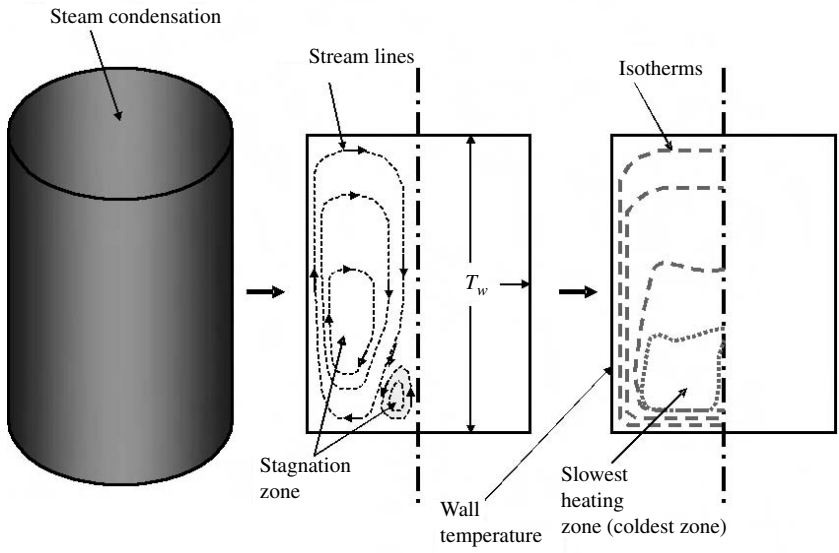


FIGURE 5.4 Schematic summary of the can sterilization process (fluid and temperature interactions) (X.D. Chen, unpublished analysis, 2004).

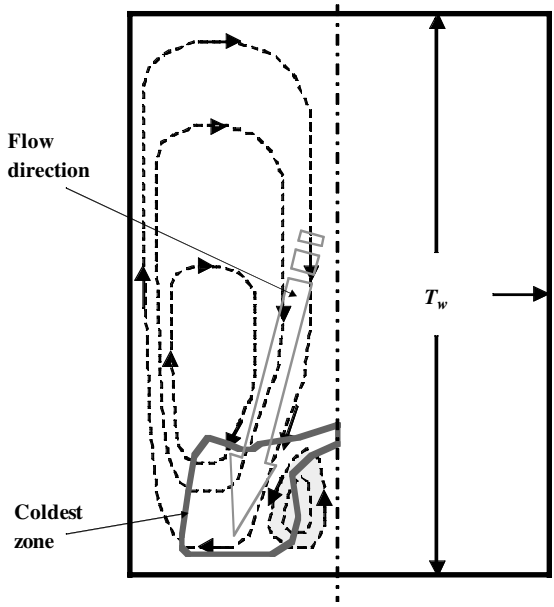


FIGURE 5.5 Illustration of the fluid flow direction and the formation of the coldest zone (X.D. Chen, unpublished results, 2004).

colder and the wall of the cylindrical section is heated (the top may also be heated), then the circulation should start from the hot side wall surface and move up to the top due to buoyancy effect, and then drop down to the lower region due to the gravity effect. As such, when all the sides are heated, including the bottom plate, there are at least two recirculation regions that compete against each other, forming the pattern shown in Figure 5.3c. For different physical properties of the fluid of concern, and the variation in the height-to-diameter ratio, the ratio of the size of the side region circulation to that of the bottom region should vary.

The above interpretation is schematically shown in Figure 5.3 and Figure 5.4. Figure 5.5 clearly shows how the velocity generated affects the location of the lowest temperature region (SHZ or CZ).

As is evident in Figure 5.4, the main fluid flow pathway corresponds nicely to the whereabout of the coldest zone. Figure 5.5 shows more explicitly such a phenomenon, while the effect of natural convection may be grossly viewed in a one-dimensional manner, i.e., a one-dimensional heat transfer affected by an overall downward fluid (at a velocity generated due to natural convection effect) (see Figure 5.6). This velocity is determined by the Grashof (*Gr*) number and Prandtl (*Pr*) number.[27]

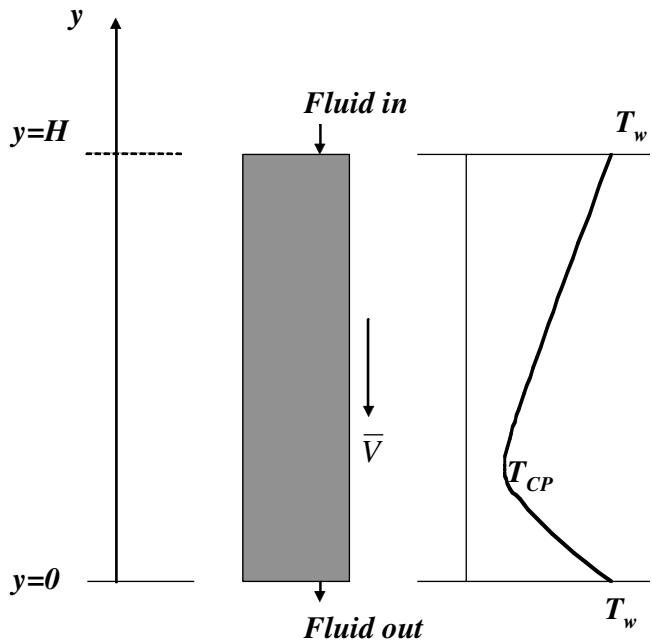


FIGURE 5.6 An equivalent one-dimensional system simulating the effect of natural convection on the development of SHZ or CZ (X.D. Chen, unpublished results, 2004).

A wide range of situations and geometries have been examined in the literature. Figure 5.7 shows an example of vertically placed can sterilization. The can sizes were 40.8 mm in radius and 111 mm in height. The basic equations used are the following. Note that a two-dimensional situation is considered due to the symmetrical nature.

Continuity

$$\frac{\partial u_r}{\partial r} + \frac{\partial u_z}{\partial z} + \frac{u_r}{r} = 0 \tag{5.20a}$$

Momentum

$$\rho \cdot \left(\frac{\partial u_r}{\partial t} + u_r \frac{\partial u_r}{\partial r} + u_z \cdot \frac{\partial u_r}{\partial z} \right) = -\frac{\partial p}{\partial r} + \mu \cdot \left(\frac{\partial^2 u_r}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial u_r}{\partial r} + \frac{\partial^2 u_r}{\partial z^2} - \frac{u_r}{r^2} \right) \tag{5.21a}$$

$$\rho \cdot \left(\frac{\partial u_z}{\partial t} + u_r \frac{\partial u_z}{\partial r} + u_z \cdot \frac{\partial u_z}{\partial z} \right) = \rho g - \frac{\partial p}{\partial z} + \mu \cdot \left(\frac{\partial^2 \boldsymbol{u}_z}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial u_z}{\partial r} + \frac{\partial^2 u_z}{\partial z^2} \right) \tag{5.23a}$$

Ignoring the viscous dissipation effect, the energy balance may be written as

$$\frac{\partial T}{\partial t} + u_r \frac{\partial T}{\partial r} + u_z \frac{\partial T}{\partial z} = \frac{1}{\rho \cdot C_p} \cdot \left[\frac{1}{r} \cdot \frac{\partial}{\partial r} \left(k \cdot r \cdot \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left(k \cdot \frac{\partial T}{\partial z} \right) \right] \tag{5.24a}$$

The mass conservation is given as

$$\frac{\partial c}{\partial t} + u_r \frac{\partial c}{\partial r} + u_z \frac{\partial c}{\partial z} = \left[\frac{1}{r} \cdot \frac{\partial}{\partial r} \left(D \cdot r \cdot \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left(D \cdot \frac{\partial T}{\partial z} \right) \right] + \dot{m} \tag{5.25a}$$

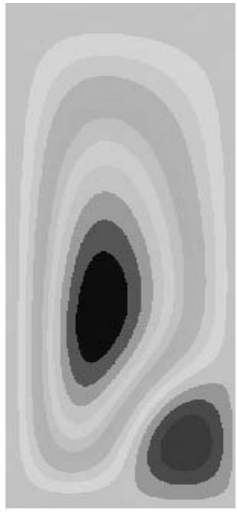
The Boussinesq approximation has been employed:[4,28,29]

$$\rho = \rho_{ref} \cdot \left[1 - \beta \cdot (T - T_{ref}) \right] \tag{5.33}$$

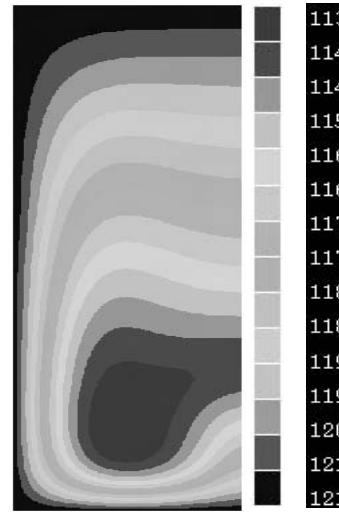
where *ref* denotes reference condition. β is the thermal expansion coefficient of the liquid. Equation 5.19 was used to calculate the deactivation rate.

5.7 CONCLUSIONS

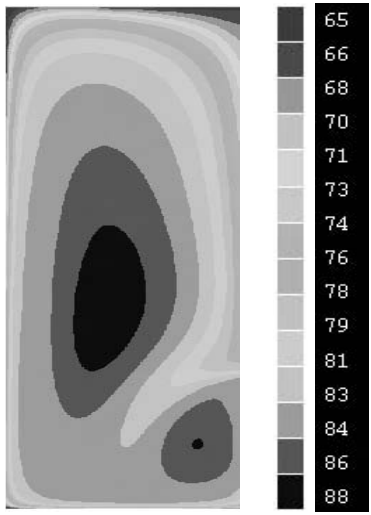
In this chapter, fundamental aspects of the mathematical modeling of the thermal processing of food fluids or suspensions are summarized. In food engineering research and design, a number of commercial software packages have been used. These software packages have been developed in the context of mechanical



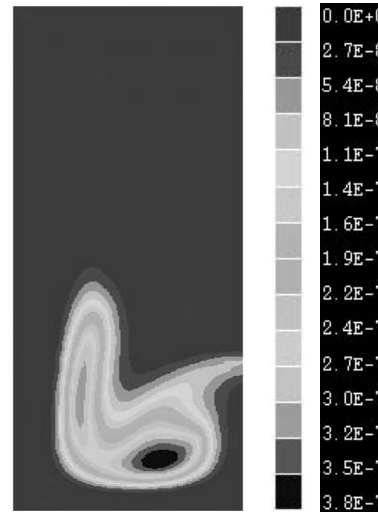
Streamline



Temperature



Remaining vitamin C



Bacteria deactivation

FIGURE 5.7 Temperature, bacteria deactivation, vitamin C destruction, and streamline profiles in a can filled with concentrated cherry juice (75˚Brix) and heated by condensing steam after 2450 sec. (Provided by A. Ghani, 2004.)

engineering, but have been applied to an ever-increasing list of industrial situations, including food and bioprocessing applications. In thermal processing, CFD packages can be used not only to analyze an existing process, but also to optimize the process and to explore scenarios of new, more effective operations. There is no question that food processing problems are complex and also, in most situations, involve transient, three-dimensional conditions. Analytical approximation and solutions may no longer be appropriate, and the CFD approach combined with chemical or biochemical kinetics equations is necessary. So far, only very limited thermal processing problems have been investigated using CFD, so there is a scope of further development that will no doubt be beneficial for the improvement and modernization of the current food industry to make it safer for consumers. Though powerful in many ways, in using the CFD approach, it is always necessary to be able to understand the underlined physics and chemistry in simple terms and indeed to conduct appropriate experiments to validate the calculations for the situations of interest.

NOMENCLATURE

A	Preexponential factor (sec^{-1})
c	Concentration ($mol \cdot m^{-3}$ or $kg \cdot m^{-3}$)
C_p	Specific heat capacity ($J \cdot kg^{-1} \cdot K^{-1}$)
d	Diameter or characteristic dimension (m)
D_T	Decimal reduction time at temperature T (min)
D	Diffusion coefficient ($m^2 \cdot sec^{-1}$)
E	Activation energy ($J \cdot mol^{-1}$)
F	Thermal death time (min)
Gr	Grashof number, $Gr = \dfrac{d^3 \rho^2 g \beta \cdot \Delta T}{\mu^2}$
g	Gravity acceleration ($m \cdot sec^{-2}$)
H	Height of the can (m)
h	Heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$)
k	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
Nu	Nusselt number, $Nu = \dfrac{h \cdot d}{k}$
p	Pressure ($N \cdot m^{-2}$ or Pa)
Pr	Prandtl number, $\mathrm{Pr} = \dfrac{C_p \cdot \mu}{k}$
r	Radius or radial coordinate (m)
R	Radius (m) or the universal gas constant ($J \cdot mol^{-1} \cdot K^{-1}$)
T	Temperature (°C)

u, v, w	Velocities at x, y, and z directions, respectively ($m \cdot sec^{-1}$)
u	Velocity in general ($m \cdot sec^{-1}$)
β	Thermal expansion coefficient (K^{-1})

Subscripts

r	Radial coordinate
ref	Reference
θ	Angular coordinate
z	z direction coordinate
w	Wall
h	High
l	Low

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Part II

Quality and Safety of Thermally Processed Foods

6 Thermal Processing of Meat Products

Harshavardhan Thippareddi and Marcos Sanchez

CONTENTS

6.1 INTRODUCTION

Thermal processing of meat probably started in prehistoric times, with the discovery that application of heat increases the palatability and extends the life of such treated meat. The benefits associated with the heating process include better flavor, palatability and texture, extended durability, and color modifications. These changes allowed meat processors to deliver a wide array of products with several degrees of flavors, colors, and textures, thus increasing the diversity of meat products in the market while satisfying consumer needs for convenience and value. Key advantages of heat processing include the extended shelf life of products, desirable organoleptic characteristics, enhanced economic value, and ensured food safety.

Additional methods have been developed to process meat products and control the growth of microorganisms. Despite development of nonthermal processing technologies, such as irradiation and high pressure processing, among others, heat continues to be the treatment of choice to enhance the characteristics of meat products, including safety and quality. In fact, heat treatments designed to achieve a specific lethality for food-borne pathogens are a critical control point in food processing and are fundamentally important to ensure the shelf life and microbiological safety of thermally processed foods.[1]

Through history, advances have been made on the development of techniques and technologies to prepare products with specific characteristics based on the raw materials used (meat species, animal part used, such as pork jowls, picnics, etc.), ingredients used (spices, smoke application, water addition, other functional ingredients, such as phosphates, nitrite, erythorbate, etc.), and processing techniques employed (fermentation/acidification, thermal process application, drying, refrigeration, etc.). While significant advances have been made in each of the categories in terms of understanding the behavior of muscles and muscle proteins, ingredients used in processing, and the processing technologies, meat processing, especially thermal processing of meat products, still remains an art form.

This chapter summarizes findings in the thermal processing of meat products, including beef, pork, and related animals. Poultry and seafood developments are covered elsewhere in this book.

6.2 TYPES OF THERMAL PROCESSING

Thermal treatments of meat products are highly diverse, influenced by the process temperature, relative humidity, and source of heat. The selection of the type of processing depends on the characteristics desired in the final product and the nature of the raw material. The amount of heat transferred into the meat product during thermal processing is dependent on the total cooking time, the heat transfer coefficient of the heating medium (rate of input of heat to the surface), and the cooking temperature.[2] Thermal processes can be classified into three basic groups; moist, dry, and microwave based.[3] However, treatments can vary significantly within categories, and combination treatments are usually applied to achieve desired characteristics of particular products.

6.2.1 Dry Thermal Processing

The source of heat in this category includes hot air in ovens, oil in fried products, and hot surfaces in pan-fried products. Hot air could reach up to 200°C, allowing significant heat transfer to the product. However, the rate of heat transfer during deep fat frying is greater because the oil medium allows a better heat transfer when heated to temperatures between 150 and 190°C.[2] Application of dry heat, however, is not recommended for nontender meat cuts because it may cause the product to be tough, thus reducing its palatability. As such, application of dry heat alone to meat products is rarely used in an industrial setting.

6.2.2 Moist Thermal Processing

The source of heat is usually hot liquid media, such as water or steam. Water heating could reach up to 100°C (boiling point), featuring significant heat transfer to the product. Moist treatments in closed environments allow chamber temperatures of 120 to 125°C, changing the characteristics of the product. High temperatures are observed in processes such as canning, retort cooking, and pressure cooking.[2] Cooking at higher temperatures causes gelatinization of collagen, therefore modifying the characteristic of collagen-rich meat products.[3] Steam cooking can reach only 100°C of heating; however, the heat transfer is better than hot water, because the latent heat from condensing steam aids in the heating of the product. In several of the thermally processed meat products, a combination of dry and moist (increased humidity) heating techniques is applied to retain product characteristics and prevent excessive loss of moisture from the product.

In typical meat processing applications, humidity is attained through evaporation of water by dripping onto electrical resistance heating coils or through steam. A typical processing schedule (Table 6.1) describes the thermal processing of the frankfurter and similar small-diameter casing sausages, including steps where moist heat is applied (humidity is raised) to condition the product surface, such as showering the product to create uniform surface conditions and to aid in uniform heat transfer. This will create a thin film of condensate on the cool product surfaces, attaining uniform product surface characteristics. In subsequent stages, dry heat is

TABLE 6.1
Typical Frankfurter Processing Schedule

Step Type	Step Time (min)	Dry Sensor (°C)	Wet Sensor (°C)	Relative Humidity (%)	Intake/Exhaust Dampers	Smoke
Condition	5	43	38	72	Auto	
Predry	5	50	0	—	Auto	
Smoke	30	50	0	—	Closed	On
Color set	10	65	0	—	Auto	
Cook	15	75	60	47	Auto	
Finish	To 71°C core	80	72	70	Auto	

Source: Courtesy of Robert Hanson, Alkar, Lodi, WI.

applied to aid in the development of specific product characteristics, such as moisture removal to a specific moisture:protein ratio, smoke incorporation, and color setting of the product. Typically, products are cooked to final endpoint temperatures in moist environments (high humidity) to aid in rapid heat transfer, reduce cooking times, and improve product temperature uniformity and shrink uniformity.

6.2.3 Microwave Processing

The application of microwave energy to heat foods was patented in 1945, while the first commercial ovens were introduced in 1955.[4] Microwave processing is based on the use of a portion of the electromagnetic spectrum. The frequencies commonly used for microwave heating are 915 and 2450 MHz, with wavelengths of 32.8 and 12.25 cm, respectively.[3] The final product temperatures attained depend on the energy input and usually are not higher than 100°C.[2] Most of the presently available appliances operate at 2450 MHz, which produces a single surface peak. Use of 915 MHz provides a more consistent product heating, as this frequency produces two peaks, one on the surface and one at the center. Use of microwaves in commercial meat processing is very limited and is exclusively used in the processing of ready-to-eat bacon.

Advantages of microwave heating include rapidity, wide degree of selectivity, ease of control, and lower energy usage.[3,4] On the contrary, there are limitations, which include limited capacity that depends on the quantity of the load, excessive steaming (produces sogginess in some products), focal heating in warmed areas of the product (affects uniformity), limitations in the containing materials of products (cannot utilize metal containers), and limited applicability with respect to browning.[3] Modifications or combinations with other treatments have been used to address these issues.

The effects of microwave processing on the destruction of microorganisms, especially pathogenic bacteria, have been studied extensively.[4–6] While destruction

of food-borne pathogens by microwaves is believed to be primarily due to thermal effects, research indicates that nonthermal effects can also cause inactivation of microorganisms. Doores[4] provides a more thorough treatise on the destruction of microorganisms by microwaves.

6.2.4 Combination Thermal Processing

Several commercial processes combine dry and moist thermal methodologies to achieve particular characteristics in meat products. For example, in the production of frankfurters, initial stages of cooking are characteristic of dry thermal processing, followed by steps where steam is injected to accelerate the cooking process. Other products may use dry heat to develop particular flavors, followed by a moist stage that finishes the cooking to a desired final temperature to destroy microorganisms.

Thermal processing equipment used for meat product manufacture can be broadly divided into two basic categories: batch and continuous. In *batch cooking systems*, products are loaded into the oven, cooked, and unloaded as a single batch (Figure 6.1). Components of a batch oven are depicted in Figure 6.2 and basically consist of heating and cooling systems, air circulation systems, temperature and humidity control systems, and dampers to ensure proper distribution of the heating/cooling medium or air within the oven when loaded (Figure 6.3). Most of the batch ovens have the capability to chill the product using chilled water or brine systems, and the product is subsequently moved to refrigerated rooms to further chill the products. Capacities of these ovens range widely from 150 to 25,000 kg,

FIGURE 6.1 Large-batch meat processing oven. (From Alkar-RapidPak, Inc. With permission.)

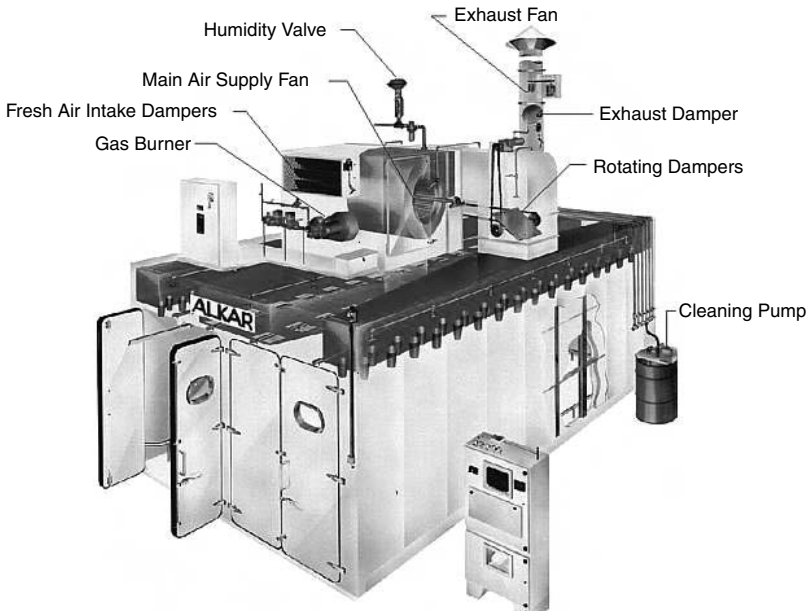

FIGURE 6.2 Typical components of a batch oven. (From Alkar-RapidPak, Inc. With permission.)

based on the production capacity required and type of product processed. In *continuous cooking systems*, the cooking and cooling functions are integrated into a single unit with multiple zones (Figure 6.4). The products are loaded onto conveying systems and are moved through either one or more cooking zones, and then through the cooling zone. The products are normally conveyed by chains, walking beams, or belt conveyors.

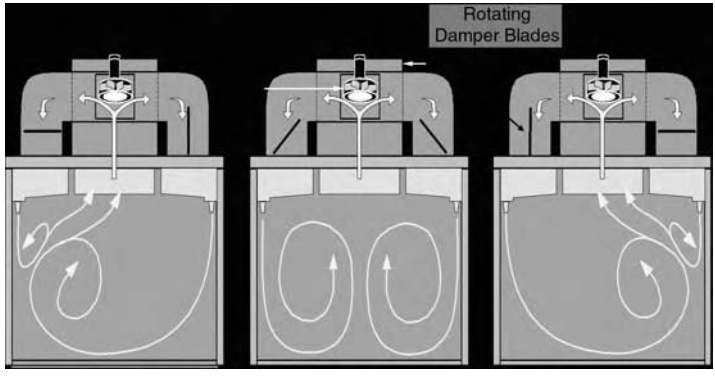

FIGURE 6.3 Oscillating airflow in a forced-air batch oven. (From Alkar-RapidPak, Inc. With permission.)

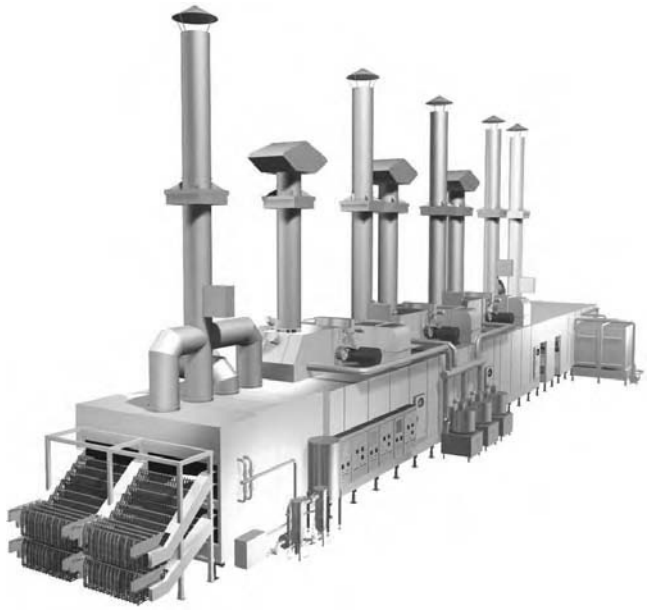

FIGURE 6.4 Straight-line chain conveyor — continuous frankfurter cook/chill. Linked sausages are looped onto sticks and then the sticks are manually placed on a dual-chain conveyor. The sticks span the gap between the two chains. (From Alkar-RapidPak, Inc. With permission.)

Continuous cooking equipment is commercially available and widely used to achieve higher yields, uniformity, enhanced safety, and longer shelf life of products.[3] The continuous ovens utilize different technologies to expose meat products to the heat. The four basic types are natural convection oven, forced-air convection oven, counterflow oven, and impingement oven. Natural convection ovens rely on exposure to a heat source with unforced air movement, very common in home appliances, but sparingly used in commercial operations. Forced-air convection ovens feature internal fans to accelerate the cooking rate and ensure uniformity of cooking. *Counterflow ovens* are characterized by a continuous conveyor that moves the cold product toward a heat source at the opposite end, accompanied by a counterflow air movement that accelerates the heat transfer process. Impingement ovens feature high air velocities from nozzles directed at the surface of the product that accelerate the cooking process (Figure 6.5).[3] The efficacy of continuous ovens has been studied extensively in microbiological challenge studies with meat and poultry products.[7–15]

6.3 EFFECTS OF THERMAL PROCESSING

With very few exceptions (dried meat, fermented sausage, rare parts of steaks, etc.), most meat products are rethermalized at a certain point before consumption by either the processor or the consumer.[2] Thermal processing imparts several

FIGURE 6.5 Air impingement steam cooking system. (From Alkar-RapidPak, Inc. With permission.)

characteristic properties to meat products that will not be possible otherwise. Some of the advantages include palatability, color development, tenderization, and added value to the finished product.[16] Due to the variability of processes, products, and regimes used in the industry, the effects caused by heat on meat are very diverse. However, the common effects in meat products are discussed below.[3]

6.3.1 Effects in Proteins

Meat muscles freed from adhering fat contain on average 21.5% nitrogenous material, the majority of which are proteins.[17] Thermal processing of meat products affects the structural characteristic of myofibrillar proteins and enzymes in the muscle. Several degrees of changes are observed, depending on the intensity of the heat treatment applied.

6.3.1.1 Denaturation

Thermal processing of meats causes coagulation of the proteins on the surface of the muscle, followed by protein denaturation that results in structural changes, thus affecting their solubility in the meat system. Proteins are usually unfolded from quaternary structures and lose their native conformation. Despite the denaturation of proteins during heating, these changes have little detrimental effect on the nutritional value of the meat, with the exception of overheated products that may be affected by the degradation of the amino acid lysine.[2] Initially, meat juices are solidified due to the denaturation and solubility changes in soluble proteins. Subsequently, changes in surface muscle fibers result in surface meat color changes. These changes are observed in cured as well as noncured products. Specific changes in meat proteins vary by the type of muscle fiber and temperature and are summarized in Table 6.2.

Structural changes are very important in comminuted products because during the formation of meat emulsions, fat is surrounded by proteins that are stabilized

TABLE 6.2
Classification of Some Processed, Ready-to-Eat (RTE) Meat and Poultry Products

Dried Products
Basturma, pastirma, basturmi, beef sticks, carne seca, dried beef, dry duck breast, meat/poultry jerky

Salt-Cured Products[a]
Cappicola, coppa, country ham, dry cured duck, parma ham, prosciutto, prosciutti

Fermented Products[b]
Alessandri (dry sausage), apenino (dry sausage), Arles or D'Arles (dry sausage), blockwurst (semidry sausage), cacciatore/cacciatora (dry sausage), cervelat, soft cervelat, chorizo, Lebanon bologna, pepperoni, salami, soft salami (Genoa, Italian, German, summer sausage, thuringer, soft thuringer)

Cooked or Otherwise Processed Whole or Comminuted Products
Meat: Berliner (cooked, smoked sausage), bologna, cooked bratwurst, Braunschweiger/liver sausage, breakfast link sausage or patties, brown-and-serve sausage, burritos, cheese smokies, cheesefurter, cheesewurst/cheddarwurst, chili, chorizo, cooked beef, cooked ham, cooked pork in BBQ sauce, cotto salami, Fleischkaese (cured, cooked sausage), frankfurters, gyros, meat loaf, meat salads, frozen meat soups, Nem-Chua (cooked, pickled ham with shredded pork skin), pasta with meat sauce, pastrami, pickled pig's feet in vinegar, pickled sausages/meat in vinegar, piroshki, pork barbecue, pork sausage patties, ravioli, roast beef, roast pork, souse, stews, white hots, wieners

Poultry (includes products containing any amount of poultry)
Chicken burritos, chicken BBQ, chicken bologna, chicken breast, chicken franks, cooked poultry, cooked poultry rolls, corn chowder with chicken, poultry loaf, poultry patties, poultry rolls, frozen poultry soups, turkey BBQ, turkey franks

Thermally Processed, Commercially Sterile Products
Canned spaghetti with meatballs, canned corned beef hash, canned ham, canned chicken salad, canned soups with meat or poultry

[a]Majority of these products do not undergo any thermal process.
[b]Most of these products originated in Europe, and as processed in Europe, they do not receive any heat treatment. However, the U.S. versions of many of these products receive a mild heat treatment.

by the heat treatment through coagulation (product binding), providing a homogeneous product. Additionally, the denaturation/coagulation and reduced moisture on the surface are responsible for the skin formation of some of these products.

6.3.1.2 Color Changes

Heat treatment of muscles causes color changes in the protein characterized by a change from red to brown or gray in noncured products and stabilizes the characteristic red/pink color in cured meats. Cured products do not change to brown or gray as nitrite reacts with the muscle pigments to produce a stable pink

color.[2,3] Overheating causes the formation of dark colors due to dehydration. The amine groups of the amino acids (lysine and alanine) that make up muscle proteins react with the available reducing sugars, such as glucose, and undergo a Maillard browning reaction.[18]

6.3.1.3 Improved Palatability

Cooking of meat to temperatures exceeding 70°C intensifies the flavor of meat and changes the blood-like or serumy taste of fresh meat to the pronounced cooked flavor and aroma.[3] Although flavor and aroma are dependent on the species, cooking method, spices used, meat aging, amount and kind of fat, as well as feeding regime, heat processing enhances these flavors, improving the product acceptability. Additionally, meat is made more tender, especially nonprime meat cuts, due to the softening of connective tissue.[2]

6.3.1.4 Inactivation of Proteolytic Enzymes

Normally, enzymatic activity is relatively slow compared with microbial degradation due to bacteria. However, it has been noticed that in irradiated products, usually free, or with reduced microbial levels, proteolytic changes occur, causing flavor (bitterness) and color changes in meat products, accompanied by the formation of tyrosine crystals.[3] A scalding process reaching 55 to 60°C may be sufficient to inactivate these enzymes and reduce this problem.

6.3.2 Effects in Fats

The fat content in meat is highly variable and dependent on the amount of fat removed from the muscle during preparation of the meat cut. On average, the fat contained in muscles freed from adhering fat is only 1.5%.[17]

6.3.2.1 Solubility

Thermal processing of meat products causes the fat to melt. While the melting temperatures generally are in the range of 37 to 40°C, the melting point of fats within each animal species depends on the feed type and the proportion of saturated:unsaturated fats in the animal feed. The released soluble fat escapes from the product mixture (muscle or comminuted product) at low temperatures unless held in an effective matrix. Therefore, in comminuted products, coagulation of the protein matrix is critical to retain the fat during thermal processing. Fatty tissues are heat tolerant up to 130 to 180°C; however, some adipose cells may burst in the process.[2]

6.3.2.2 Flavor Changes

The characteristic flavors of different meat species appear to reside mainly in the respective fats. Because of this, the older the animal, the stronger the flavor is due to changes in the oxidation levels of fats. Thermal processing triggers the development

of pleasant flavors and organoleptic enhancements in meat products. Juiciness is increased, allowing flavors from fat to be more readily perceived. The heating of fatty acids in the presence of air enhances oxidation, modifying flavor profiles of cooked products. Some meat components are degraded by hydrolysis, developing enhanced flavor compounds such as glutamic acid and its derivatives. Other flavors are produced by Maillard-type reactions on the surface of meat products (at 150°C).[2] Finally, the thermal process enhances the perception of other flavors associated with salt, spices, and curing agents added in the formulation.

6.3.2.3 Humidity Changes

Thermal processing causes free water in the muscle to be released and evaporated. There is a decrease in humidity levels in the surface of the product, causing drying that reduces the water activity. Being exposed to a lower water activity environment reduces bacterial growth of surviving and recontaminating bacteria.[3] The extent of water loss depends mainly on the product temperature, cooking time, and environmental conditions of humidity and temperature. There is a large increase in water loss in the temperature range of 50 to 60°C, reaching 80 to 100% of total loss by the time the temperature reaches 80°C.[2]

6.4 MEAT PRODUCTS

There are diverse types of meat products available on the market, and some of the categories of processed ready-to-eat meat and poultry products are shown in Table 6.3. Meat products can be broadly categorized into two basic groups: whole muscle meat products and comminuted and restructured meat products.

6.4.1 Whole Muscle Meat Products

Whole muscle meat products include raw meat cuts, ground beef, cooked beef, hams, and other derivatives prepared with whole meat muscles of animals.

6.4.2 Comminuted and Restructured Meat Products

Comminuted meat products include several categories, such as sausages, restructured hams, and other meat products formed from ground muscles. The U.S. Department of Agriculture–Food Safety and Inspection Service (USDA-FSIS) classifies sausages into several general categories, including fresh sausages, uncooked smoked sausages, cooked smoked sausages, cooked sausages, dry and semidry sausages, and luncheon meat, loaves, and jellied products.[3]

Fresh sausages are made fresh with uncured meat, generally cuts of fresh pork and sometimes beef. Taste, texture, tenderness, and color are related to the ratio of fat to muscle.[3] Raw materials include pork and beef trimmings. Pork products are required to be cooked thoroughly to eliminate the risk of trichinae parasites.

TABLE 6.3
Changes in Muscle Proteins during Cooking

Changes in Muscle Proteins	Temperature (°C)
Sarcoplasmic Proteins	
Loss of solubility and denaturation	40–60
Myofibrillar Proteins	
Denaturation	40–50
Coagulation	57–75
Unfolding of actomyosin	<70
Myosin, loss of solubility	45–50
Myosin, denaturation	53–65
Actin, loss of solubility	<80
Tropomyosin and troponin denaturation	30–70
Collagen	
Solubilization	60–70
Shrinkage	60–75
Conversion to gelatin	65
Fiber disintegration	60–80

Source: Adapted from Cross, H.R. et al., in *Muscle of Food*, Bechtel, P.J., Ed., Academic Press, Orlando, 1986, pp. 279–320.

Uncooked smoked sausages are similar to fresh sausages, except that they are smoked to give the product a different flavor and color. These products must also be cooked before eating to kill bacteria and parasites.

Cooked sausages include frankfurters, bologna, and other related semisolid comminuted products. Regulation in the U.S. dictates that they shall not contain more than 35% fat and no more than 10% added water. These sausages could be either smoked or nonsmoked.

Dry and semidry sausages are produced by fermentation due to either backslopping (natural) or addition of a lactic acid-producing culture.[3] Lactic acid production not only aids in preservation by lowering the pH and inhibiting the growth of bacteria, but also adds the characteristic flavor of fermented sausage.

The *luncheon meat*, *loaves*, *and jellied products* category is widely variable and includes diverse products with different standards of identity, composition, and processing.

6.5 MICROBIAL EFFECTS OF THERMAL PROCESSING

Thermal processing of meat products achieves the dual purpose of reducing the microorganisms that affect shelf life and improving safety of the resulting products by eliminating the food-borne pathogens. While interior animal tissue is

considered to be sterile, contamination with spoilage or pathogenic microorganisms occurs during slaughter, fabrication, and subsequent handling.

The effectiveness of microbial destruction during thermal processing is a function of time and temperature. Sterility is not a goal in thermal processing of most meat products. The majority of the products are processed to ensure safety, and some products, such as canned ham, are processed to achieve commercial sterility. Microbial spores can survive traditional thermal processes applied to meat products and can grow during cooling or under abusive storage conditions. Some of these spore-forming organisms include species that belong to the genera *Clostridium* and *Bacillus*. More extreme cooking regimes are applied during canning operations to eliminate not only vegetative cells, but also spores of pathogenic microorganisms.

Most spoilage and pathogenic microorganisms can grow rapidly in the temperature range between 10 and 63°C.[2,19,20] It is important to recognize that microorganisms are always present on fresh meat and the ingredients used during preparation, and that they are capable of growing in meat products. Therefore, thermal processes must be designed to eliminate food-borne pathogens and reduce the spoilage types as well.

6.5.1 Shelf Life: Destruction of Spoilage Microorganisms

Heat is applied to meat products to enhance organoleptic properties and to add value to the products. In addition, cooking also plays a major role in extending the shelf life of these products by the destruction of spoilage organisms. The storage life of most meat or meat products is the time required for the microbes to grow to sufficient numbers to cause adverse effects that will deter consumers from consuming the product. These effects include discoloration or formation of off-colors, odors, or physical effects, such as slime formation.

Recontamination of thermally processed products is especially critical, as the contaminating organisms can grow uninhibited by the absence of competing microflora. This is clearly evidenced in the case of *Listeria monocytogenes*, a pathogen that is capable of growth at refrigeration temperatures.

A survey conducted by the World Health Organization (WHO)[21] reported that approximately 25% of food-borne outbreaks could be attributed to recontamination of processed products. Additional factors include insufficient hygiene (1.6%), cross-contamination (3.6%), inadequate sanitation in processing or storage facilities (4.2%), contaminated equipment (5.7%), and contamination by personnel handling of the products (9.2%). Significant sources of recontamination include the environment (processing equipment, air in the processing rooms, and other nonproduct contact surfaces harboring microorganisms) and the personnel.

The growth of spoilage organisms in meat products causes the development of off-colors, odors, and flavors. Some contaminating microorganisms produce pigments that affect the color of meat, as is the case with green pigments produced by *Pseudomonas* spp. on the surface of meat products stored at refrigeration in aerobic conditions. In addition, these microorganisms can produce lipopolysaccharides, producing *slime* on product surfaces.

Gram-negative bacteria constitute the greatest spoilage potential for meat and meat products. When fresh meat is chill-stored aerobically, members of the genera *Pseudomonas*, *Acinetobacter*, *Psychrobacter*, and *Moraxella* display the fastest growth rates and hence the greatest spoilage potential.[22] On the other hand, species like *Shewanella* and *Enterobacteriaceae* require more favorable conditions than the organisms mentioned to produce spoilage metabolites.

Gram-positive organisms may constitute predominant microflora of fresh meat products and will directly influence the shelf life of meat products. The main groups of Gram-positive organisms include micrococci, followed by lactic acid bacteria and *Brochotrix thermosphacta*.[23] Gram-positive microflora include non-spore-forming pathogens *Staphylococcus aureus* and *L. monocytogenes*, as well as the spore formers *Clostridium* spp. and *Bacillus* spp. A comprehensive review of Gram-positive organisms present in meat products is provided by Holzapfel.[23]

Typical cooking processes employed for thermally processed meats achieve internal temperatures of 68°C (154°F), which would destroy the majority of non-spore-forming pathogens, *Salmonella* spp., *Escherichia coli* O157:H7, *S. aureus*, and others, including *Listeria*.[24] Thus, the majority of flora in processed products would represent microorganisms resulting from recontamination of the products.

In processed meats, growth of microorganisms may result in *souring* combined with other off-odors and off-flavors, discoloration, gas production, and the formation of polysaccharides in the form of slime. A typical example would be the greening of cured meats, caused by growth of thermotolerant organisms *Weissella viridescens*, *Enterococcus faecium*, or *Enterococcus faecalis* or contamination with *Carnobacterium viridans*, homo- and heterofermentative lactobacilli, or *Leuconostocs* subsequent to the heat processing.[25,26]

Nonetheless, it is important to recognize that some of the Gram-positive organisms in meat products are in fact used for meat fermentations to achieve other desirable changes in processed meat products.

6.5.2 Safety: Destruction of Pathogens

Food-borne illnesses can be classified as infections, where the consumer ingests foods containing live organisms mostly in large numbers, or intoxications, where the consumer ingests food containing preformed toxins. However, only food-borne pathogens of major importance are discussed briefly in this review due to their higher incidence and importance in meat products. Comprehensive reviews on these pathogens and their thermal destruction characteristics can be found in a treatise by the International Commission for Microbiological Specification of Foods (ICMSF).[20] Similarly, recent incidents of foot-and-mouth disease and bovine spongiform encephalopathy in cattle indictate that new safety issues will arise in the future.

The focus of this section will be on bacterial pathogens of significance in meat products and their destruction during thermal processing in combination with other methodologies. The pathogens of concern in meat products include *E. coli* O157:H7, *Salmonella* spp., *L. monocytogenes*, *S. aureus*, and *Clostridium* spp. (*C. perfringens* and *C. botulinum*).

6.5.2.1 *Escherichia coli* O157:H7

E. coli O157:H7 is considered a pathogen of significance in beef and ground beef products. Recently, *E. coli* O157:H7 and other enterohemorrhagic *E. coli* have emerged as prominent food-borne disease agents. Cattle are a reservoir of *E. coli* O157:H7, and the consumption of raw or undercooked beef has most often been associated with food-borne infections. Therefore, during the processing of meat products, thermal processes should be designed to eliminate this pathogen. Because this pathogen has similar growth and lethality characteristics as *Salmonella* spp., thermal processes developed for meat products target the elimination of *Salmonella* spp. rather than *E. coli* O157:H7. Similarly, pathogen modeling programs consider using *Salmonella* spp. as an indicator organism to model the survival/growth of this pathogen. USDA-FSIS based the lethality performance standards for processed products on this assumption.[27,28] *D* and *Z* values for *E. coli* O157:H7 had been determined in ground beef.[29]

6.5.2.2 *Salmonella* spp.

Salmonella spp. is widely distributed in nature and is a major cause of food-borne illness in the U.S., and >95% of the nontyphoidal *Salmonella* outbreaks are food-borne.[30] The growth rate of *Salmonella* spp. is substantially reduced at <15°C, while growth of most *Salmonella* spp. is prevented below 7°C. Maximal growth rates for *Salmonella* spp. are reported at 49.5°C.[19] The U.S. Department of Agriculture published lethality performance standards for certain processed meat and poultry products that prescribe *Salmonella* spp. reductions to be attained during processing.[27,28] These lethality standards require a 6.5 log destruction of *Salmonella* spp. during processing of prepared meat products, and a 7.0 log destruction of *Salmonella* spp. is required for products containing poultry meat.

6.5.2.3 *Listeria monocytogenes*

Listeria spp. is ubiquitous in nature. The organism is commonly found in the intestines of animals and humans without causing illness. It can survive for long periods of time in soil, leaf litter, sewage, silage dust, vegetation, and water. The organism has been isolated from a variety of products, including raw milk, cheese made from unpasteurized milk, soft cheese, meat and poultry and their products, cole slaw, and cabbage. *L. monocytogenes* grows under low-oxygen conditions at refrigeration temperatures and survives for long periods in the environment, on foods, in processing plants, and in household refrigerators. Although frequently present in raw foods of both plant and animal origin, it can also be present in cooked foods because of postprocessing contamination. Consumption of food contaminated with *L. monocytogenes* can cause listeriosis.

According to the U.S. Centers for Disease Control and Prevention (CDC), *L. monocytogenes* causes an estimated 2493 cases of listeriosis per year. Of these, 2298 persons are hospitalized and 499 persons die.[30] The case fatality rate is high across the whole population — 20 deaths per 100 cases of illness.

Epidemiologic surveillance data indicate that the case fatality rate varies by age, with a higher case fatality rate among newborns and the elderly.

L. monocytogenes can be in the food processing environment and can form biofilms on solid surfaces commonly found in food processing plants, including stainless steel and rubber under experimental conditions. *Listeria* can also survive adverse conditions on apparently smooth surfaces. Recently, several recalls of ready-to-eat (RTE) meat and poultry products have occurred because of adulteration with *L. monocytogenes*. Food-borne illnesses and deaths have been linked to some recalled products. It has generally been concluded that the adulteration occurred through cross-contamination from environmental sources following cooking.

6.5.2.4 *Clostridium perfringens*

C. perfringens is widely distributed in a variety of foods, particularly meat and poultry, and has been implicated in numerous food-borne disease outbreaks. The abilities of *C. perfringens* to form heat-resistant spores and grow at a very rapid rate at relatively high temperatures are the major contributing factors leading to food poisoning. The temperature range for growth of *C. perfringens*, 6 to 52.3°C is well documented.[20,31] A short generation time of 7.1 min in ground beef means that after the spores have germinated, rapid cooling of foods is critical.[1,32,33]

C. perfringens continues to be a concern to the food industry, particularly to the retail and food service industries, and has been implicated in several large outbreaks. The U.S. Centers for Disease Control and Prevention estimates more than 248,000 cases of food-borne illness due to *C. perfringens* annually in the U.S.[30]

Although *C. perfringens* vegetative cells do not survive the normal heat processing schedules employed in the meat industry, the spores can survive. Heat-activated spores can germinate and grow rapidly if these products are improperly chilled. Juneja and coworkers[1,32,33] reported $D_{58°C}$ values of 1.15 to 1.60 min for 10 strains of *C. perfringens* (vegetative cells) in a model beef gravy system, which are similar to the *D* values reported for vegetative food-borne pathogens such as *E. coli* O157:H7, *Salmonella* spp., and *L. monocytogenes*.[29,34] Lethality standards for *Salmonella* spp.[27,28] should be adequate to control normal incidence levels of *C. perfringens* vegetative cells in processed meat and poultry products.

In case thermal process deviations (heating or cooling) occur, spores of *C. perfringens*, if present in the raw meats utilized for processing of cooked products may be heat activated, germinate, and grow to hazardous levels during cooling or improper storage. The time/temperature guidelines for cooling cooked products specify that the maximum internal temperature should not remain between 54.4 and 26.7°C for more than 1.5 h, nor between 26.7 and 4.4°C for more than 5 h.[28] The U.S. Food and Drug Administration (FDA) Division of Retail Food Protection recognized that inadequate cooling was a major food safety problem and established a recommendation that all food should be cooled from 60 to 21°C in 2 h and from 21 to 5°C in 4 h.[35] Of importance is the use of organic acid antimicrobials such as lactates, diacetates, and citrates, which have been shown to act as bacteriostats to prevent outgrowth of activated spores.[36] A complete compilation

of studies determining the survival and growth of *C. perfringens* spores during thermal processing of meats is available.[37]

6.5.2.5 *Staphylococcus aureus*

S. aureus is ubiquitous and is common in the mucous membranes and skin of most warm-blooded animals, including food animals. *S. aureus* is an opportunistic pathogen, cannot compete well with other food spoilage bacteria, and can grow and cause illness in cooked foods that are cross-contaminated. Although staphylococci are readily destroyed by the temperatures normally used for processing of meat and poultry products, growth of the organisms to levels greater than 5.0 log CFU/g can result in production of extremely heat stable enterotoxins, which can survive even commercial sterilization processes. The organism is resistant to drying and may grow and produce enterotoxins in products having a_w as low as 0.85. It is very resistant to freezing and thawing and survives well in frozen meat products.[20]

The CDC estimates approximately 185,000 cases of staphylococcal illness annually and 100% of the outbreaks are food-borne.[30] Although *S. aureus* is not part of the lethality and stabilization performance standards for cooked ready-to-eat products, the ability of the organism to elaborate heat-stable toxins that can survive subsequent cooking contribute to its importance during thermal processing of meat products.

6.5.3 Destruction of Parasites

Trichinellosis is a parasitic disease caused by a roundworm of the *Trichinella* genus that infects carnivorous and omnivorous animals, including domestic swine and wild game (e.g., bears, cougars, and wild boars). While trichinellosis was traditionally attributed to pork and pork products, recent surveillance by the CDC indicates that wild game meat has emerged as the leading cause of the disease. While *Trichinella spiralis* is more commonly associated with swine, other species, *Trichinella nativa*, *Trichinella pseudospiralis*, and types *Trichinella* T-5 and *Trichinella* T-6 are associated with other wildlife.

Trichinellosis is acquired by ingesting meat containing cysts (encysted larvae) of *Trichinella*. After exposure to gastric acid and pepsin, the larvae are released from the cysts and invade the small bowel mucosa, where they develop into adult worms. After 1 week, the females release larvae that migrate to the striated muscles, where they encyst. Encystment is completed in 4 to 5 weeks and the encysted larvae may remain viable for several years. Ingestion of the encysted larvae perpetuates the cycle (Figure 6.6).

In the past, control measures for parasites were primarily postharvest treatments, such as cooking, freezing, curing, and irradiation. Commercial preparation of pork products by cooking requires that meat be heated to internal temperatures that have been shown to inactivate trichinae (Table 6.4). Similar requirements for *freezing* temperatures, times, and curing methods are prescribed in the Code of Federal Regulations Title 9, Chapter III, §318.10. Treatment of fresh pork with

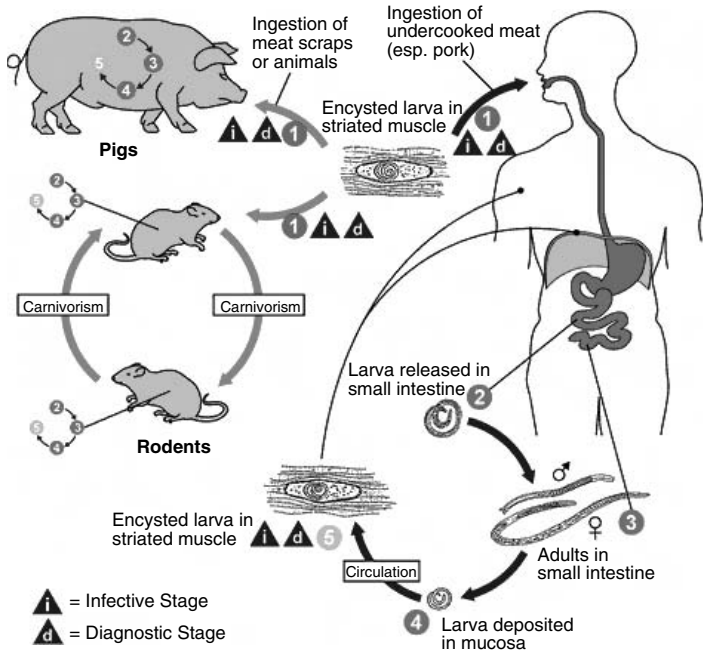

FIGURE 6.6 Life cycle of *Trichinella spiralis*.

TABLE 6.4
Time–Temperature Relationship for *Trichina* Kill (Minimum Internal Temperature) in Pork Products

Temperature		
°F	°C	Time
120	49.0	21 h
122	50.0	9.5 h
124	51.1	4.5 h
126	52.2	2.0 h
128	53.4	1.0 h
130	54.5	30 min
132	55.6	15 min
134	56.7	6 min
136	57.8	3 min
138	58.9	2 min
140	60.0	1 min
142	61.1	1 min
144	62.2	Instantaneously

TABLE 6.5
Number and Percentage of Trichinellosis Cases, by Type and Source of Implicated Meat Product in the U.S. between 1997 and 2001

Meat Type/Source No.	No. of Cases	Percentage (%)
Pork products	**22**	**31**
Commercial	12	17
Sausage	4	6
Chops	1	1
Ham	1	1
Pickled pigs feet	1	1
Sausage and chops	1	1
Sausage and smoked pork	2	3
Unspecified	2	3
Direct from farm	9	13
Hunted (wild boar)	1	1
Nonpork products	**30**	**42**
Bear meat	29	40
Cougar meat	1	1
Unknown	**20**	**28**
No information	15	21
Both pork and nonpork	5	7
Commercial pork chops, bacon, hamburger	1	1
Commercial pork roast, ham, bacon, moose/quail/pheasant meat	1	1
Commercial pork roast, hamburger	1	1
Commercial pork sausage, ham, hamburger	1	1
Commercial pork sausage, sliced beef	1	1
Total	**72**	**100**[a]

[a]Might not total 100% because of rounding.

Source: Centers for Disease Control and Prvention (CDC). *Surveillance Summaries,* July 25, 2003. MMWR 2003: 52 (no. 55–6).

0.3 kGy of Cs^{137} has been proven to render trichinae completely noninfective. Preharvest certification programs initiated and administered by pork producer groups have resulted in the gradual decline of the prevalence of this parasite in commercial pork products (Table 6.5).

Of the nine trichinellosis outbreaks in the years 1997 to 2001, five were associated with bear meat, two with home-raised swine, and two with commercial pork.[38] The prepared meats involved in the outbreaks include a bear jerky, roast, spaghetti dish, hamburgers, steaks, medium-rare barbecued bear meat, fried, barbecued, stewed, and uncooked pork, homemade pork sausage, and jerky and smoked pork. In view of the dramatic change in the epidemiology of trichinellosis, with the majority of the outbreaks from wild game and noncommercial swine operations, USDA-FSIS is proposing to eliminate the requirements from the meat regulations.

6.6 THERMAL PROCESSES COMMONLY APPLIED TO MEAT PRODUCTS

Because of the thermal resistance of some microorganisms, there are two categories of heat treatments based on the intensity of the process and the bacterial destruction achieved. In most cases, regulations prescribe that a thermal process must be designed to produce a significant reduction in the population of pathogenic organisms, such as in performance standards established by USDA-FSIS for thermally processed meat and poultry products.

6.6.1 Pasteurization

Pasteurization refers to the use of a relatively mild heat treatment and is widely accepted as an effective means of destroying all non-spore-forming pathogenic microorganisms and significantly reducing the number of natural spoilage microflora, thereby extending the shelf life of pasteurized products.[1] Meat products cooked to 70°C and held at that temperature for at least 2 min are generally considered as pasteurized, that is, free from active microbes, but may still contain spores, which can begin to grow again during cooling or storage at abusing temperatures.[2]

Sous vide (under vacuum) processing is characterized as a combination of mild thermal processing and vacuum packaging to preserve meat products. Mild heating destroys vegetative cells of bacteria while preserving the sensory characteristics of the product.[39] The thermal process usually reaches 70°C for 100 or 10 min at 90°C, followed by storage and handling at refrigeration temperatures.[2] Concerns associated with *sous vide* processing involve the microbiological safety of the product because psychrotrophic food-borne pathogens and spore-forming organisms, including *C. botulinum*, may have survived the mild heat treatment and may be capable of harming the consumer when improper storage or recooking methods are applied.[39] Several evaluations of the safety of a variety of *sous vide* products have been studied utilizing distinct microorganisms, including *C. botulinum* and *Bacillus* spp.[34,39–43] A survey study of commercially available *sous vide* products concluded that the health risks associated with these products is quite low as long as very low storage temperatures are maintained.[44]

6.6.2 Sterilization

High-heat processing or sterilization refers to the complete destruction of microorganisms, including spores.[1] Meat products are considered commercially sterile when spore-forming organisms are also destroyed by the heat treatment. To achieve this level of killing, the products are heated to at least 100°C for several hours, or to higher temperatures such as 120°C for several minutes.[2] To validate the process, the sterilization heating should eliminate spores from the most heat resistant organism, *Bacillus stearothermophilus*. Sterilized products can then be stored at nonrefrigerated temperatures while still remaining safe for consumption. Total sterility is not possible, and proper description of the products should be

"commercial sterilized," because these products may contain a low number of dormant bacterial spores.[1]

Thermal sterilization is usually associated with the canning process. Canning is considered a special cooking process because the heat applied is controlled to ensure long-term stability by inactivating all microorganisms that could cause spoilage or food poisoning.[2] The products are usually packaged in special containers such as cans, jars, bottles, flexible pouches, or sealed cartons. Eliminating the organisms contaminating the product with proper heating conditions is complemented by the lack of recontamination steps in the process if the integrity of the container is maintained. *C. botulinum* is a spore-forming heat-resistant organism that is capable of producing a highly dangerous toxin in food products. The canning process was developed to eliminate the risk of botulism in these products and minimize exposure to the toxin of this pathogen to consumers.

6.6.3 Postprocess Pasteurization

One of the most active areas in research is the development of postpackaging pasteurization of meat products (especially ready-to-eat) for the destruction of postprocessing-contaminating *L. monocytogenes*. The U.S. Department of Agriculture issued a regulation requiring ready-to-eat meat processors to address the *L. monocytogenes* problem by one of the following three approaches:[45]

1. Postlethality treatment of products AND antimicrobial agent/process
2. Postlethality treatment of products OR antimicrobial agent/process AND *Listeria* sanitation control program
3. *Listeria* sanitation control program that must meet requirements for specific products

Since postprocessing contamination of ready-to-eat meat products is mostly confined to the surface, pasteurization by steam and hot-water equipment has been studied extensively to determine its effects on the surface microbial contaminants. These treatments can result in a 7 log reduction of *L. monocytogenes* in inoculated vacuum-packaged fully cooked sliced chicken.[9–15] Treatments consist of exposing product at 90°C in a continuous steam cooker or hot-water cooker for 5 to 35 min.

Prepackage pasteurization and postpackage surface pasteurization studies in artificially inoculated samples resulted in a 1.25 to 3.5 log reduction with a treatment time of 60 to 120 sec at 118 to 204°C (245 to 400°F) air temperature.[7] Surface pasteurization was applied using a radiant oven. Prepackage pasteurization (60 sec) combined with postpackage submerged water pasteurization in several ready-to-eat products resulted in a 2 to 4.3 log reduction of *Listeria*.

Thermal surface pasteurization technologies that are in use employ either hot water or condensing steam to elevate the product surface temperatures that would be lethal to *L. monocytogenes*. These systems are commercially available within the U.S. and are marketed by Alkar (Lodi, WI) and Townsend (Des Moines, IA),

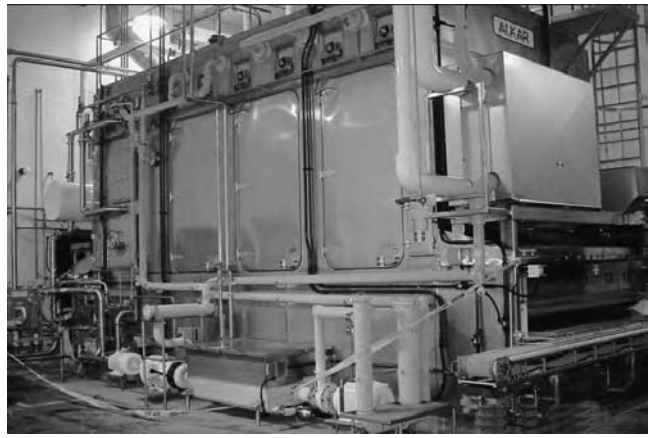

FIGURE 6.7 Schematic of a serpentine postprocess surface pasteurization system. (From Alkar-RapidPak, Inc. With permission.)

respectively. In some instances, the surface heating systems are integrated with cooling systems that would rapidly cool the product surfaces to minimize product quality deterioration with regards to purge, discoloration, and gel pockets on the surfaces of whole muscle products.

The Alkar serpentine system is a continuous surface pasteurization system, and different configurations are available to match product size, shape, and other considerations (Figure 6.7 and Figure 6.8). The Townsend system employs condensing steam to raise product surface temperatures to approximately 65 to 71°C within

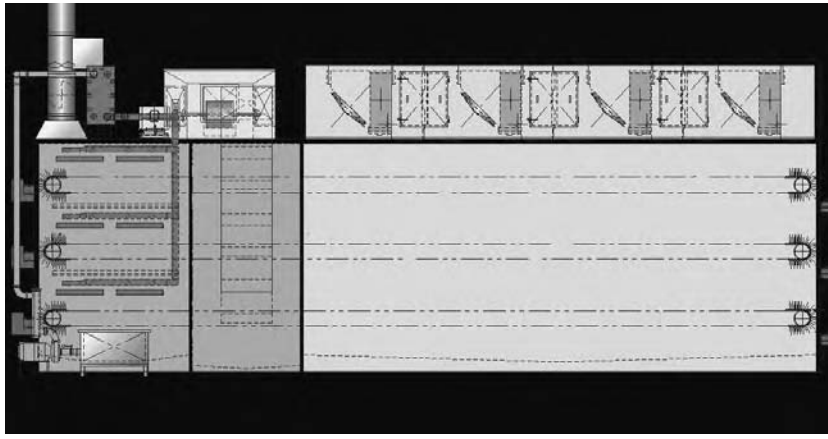

FIGURE 6.8 Serpentine postprocess pasteurization system. (From Alkar-RapidPak, Inc. With permission.)

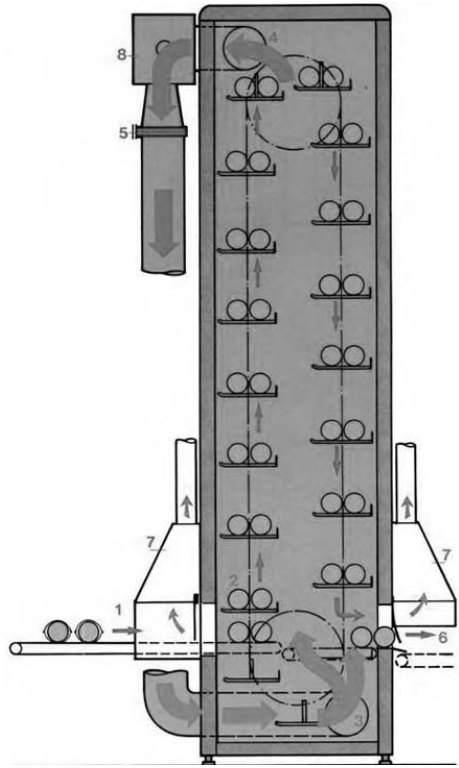

FIGURE 6.9 Schematic of a Townsend condensing steam postprocess surface pasteurization system. (From Townsend Engineering, Des Moines, IA. With permission.)

10 to 15 sec for a variety of whole muscle products, such as roast beef, hams, and turkey breast products of varying sizes (Figure 6.9 and Figure 6.10). Normal processing times required to achieve 2 to 4 log CFU/cm^2 reduction in surface *L. monocytogenes* range from 2 to 3 min in the condensing steam surface pasteurizing system.

Another postprocess pasteurization system that has been developed by Eastern Regional Research Center (Wyndmoor, PA) of USDA utilizes alternating steam and vacuum application to raise product surface temperatures to achieve lethality to *L. monocytogenes* and to achieve evaporative cooling to minimize product quality deterioration. The process has been validated to achieve 4 to 5 log CFU reductions in surface *L. monocytogenes* on small-diameter sausages like frankfurters and hot dogs. The process is being commercialized by Alkar (Lodi, WI).

Alternative technologies currently being studied include high hydrostatic pressure processing (HPP), among other nonthermal interventions. The technology minimizes organoleptic effects on the product due to extensive cooking. Although HPP was shown to inactivate pathogens without any thermal or chemical effects and at the same time preserve the quality of the product, the combination of mild heat and pressure has also been considered.[46]

FIGURE 6.10 Townsend condensing steam postprocess surface pasteurization system. (From Townsend Engineering, Des Moines, IA. With permission.)

6.7 THERMAL DESTRUCTION KINETICS OF MICROORGANISMS

Thermal processes are designed to provide characteristic properties to food products. However, the main target of these processes is to eliminate the risk of pathogens in the product to ensure safety to consumers. Therefore, the higher the initial microbial population in a product, the longer the processing/heating time or temperature required to achieve the same degree of microbial reduction.[1] Heat penetration in meat products occurs from the outside to the inside. Due to the high water content of meat, the conditions within the muscle fibers or comminuted particles are similar to the heating of water; therefore, they cannot reach temperatures above 100°C unless heated in a pressured environment.[2] The rate of heating depends on the thermal conductivity of the product and the surface temperature of the heating source.

TABLE 6.6
Typical Thermal Destruction Parameters for Common Food-Borne Pathogens

	Thermal Destruction Parameters	
Pathogen and Substrate	**$D_{60°C}$ (min)**	**Z (°C)**
L. monocytogenes		
Lean ground beef	2.07	5.17
Fat ground beef	3.29	6.33
E. coli O157:H7		
Lean ground beef	1.97	4.67
Fat ground beef	1.20	4.61
Salmonella spp.		
Lean ground beef	2.21	5.56
Fat ground beef	1.58	5.56
C. perfringens		
Lean ground beef	5.30	6.74

Since the objective is to eliminate the most heat resistant microorganisms in the product, it should be recognized that several factors influence the heat resistance of those microorganisms. Microbial factors include strain, source, and previous exposure to stress.[1,47] Intrinsic factors in the food matrix that influence heat sensitivity include media, fat content, pH, and water activity.[47] Sometimes, development of resistance to a given set of factors may cause cross-resistance to other affecting factors, such as heat.[48] A summary of the heat resistance of common foodborne pathogens is provided in Table 6.6.

Use of the terms "sterilization" and "pasteurization" in describing thermal processes applied to foods refers to the basic purpose of the treatment to destroy pathogenic microorganisms and those of spoilage types. The main difference lies in the application of the heat and the severity of the treatment. Pasteurization is the term most often applied to describe processes that are relatively mild, and to destroy vegetative pathogenic microorganisms in a food product. Sterilization is the term used to describe a more severe heat treatment, e.g., those given to low-acid canned foods that are designed to destroy virtually all microorganisms, regardless of heat resistance.

However, these severe heat treatments may result in products with unacceptable quality, and are often used in moderation to destroy microorganisms or spores of microorganisms of public health significance, such as *C. botulinum*, *C. perfringens*, and *B. cereus*. The implication is that these milder heat treatments may result in survival of the more heat resistant spore types, such as *B. stearothermophilus*, *B. subtilis*, and similar spore formers. Their growth in the food products during subsequent storage and distribution is restricted due to either product intrinsic characteristics, such as pH, a_w, etc., or the storage conditions, such as

lower temperatures, vacuum packaging, etc. Products produced using such milder heat treatments have been termed "commercially sterile," or the term "commercial sterility" is used to describe them.

Microbiologists and process engineers have extensively used thermal parameters such as *D*, *Z*, and *F* values to describe the thermal processes applied to foods since the description of the microbial survivor curves by Rahn.[49] Some of these parameters are defined here to provide a basic understanding:

D Value (decimal reduction time): The time required at temperature *T* to reduce a specific homogeneous microbial population by 90%. It is the negative reciprocal of the slope of the line fitted to the graph of the logarithm of the number of survivors vs. time. For the *D* value to be meaningful, the semilogarithmic survivor curve must approximate a straight line when using the general method for calculation of process lethality.

F Value (sterilization process equivalent time): Equivalent time in minutes of a heat process (integrated value under a lethal rate (*L* vs. *t*) curve). A measure of the microbial kill in or on the product, calculated using a specific value of *Z*.

L (lethal rate): The rate of microbial destruction at temperature *T* expressed in terms of the reference temperature, T^{ref}. The units of the lethal rates are minutes at T^{ref} per minute at *T*. Lethal rate can be calculated using the formula $L = 10^{(T-T^{ref})/Z}$.

Z Value (temperature coefficient of microbial destruction): The negative reciprocal of the slope of the thermal death time (TDT) or relative kill time (RKT) curves. The number of degrees of temperature change necessary to cause the *F*, *D*, or RKT value to change by a factor of 10, measured in degrees Fahrenheit or Celsius.

The food industry, especially the canning industry, has used the general method for calculation of process lethality and for design of microbial control processes since the 1920s. The initial process involved calculation of lethal ratios and relating these to the TDT charts for the process.[50] Ball and Olson[51] developed a form of the method and stated that the "actual thermal death time curve is employed having an *F* value of unity." A thorough discussion of the use of the general method is provided in Pflug.[50] Briefly, calculating the lethality of a process involves use of the following equation:

$$L_T = 10^{\left(\frac{\left(T-T^{ref}\right)}{Z}\right)} \tag{6.1}$$

where *L* is the lethal rate (min at T^{ref}/min at *T*), *T* is the product temperature at specific time, T^{ref} is the reference temperature, and *Z* is the *Z* value of the particular pathogen.

The *Z* value to be used in process lethality calculations should be carefully selected based on the temperature profile of the product in terms of the final

process temperatures. The selection of the Z value can have a significant impact on the calculated process lethality and should be conservatively chosen. Tables of lethal rates can be prepared for a range of product temperatures for a specific temperature and Z value.

To obtain the kill time at reference temperature, the sum of the lethal rates at each of the product temperatures (from product temperature history) is multiplied by the effective time (time between the measurements):

$$F_{T^{ref}} = \sum L_T x t_T \tag{6.2}$$

Thus, the process lethality (decimal reductions of pathogen) can be obtained by dividing $F_{T^{ref}}$ by the D value of the particular pathogen at T^{ref}. While this is a simplistic form of evaluating process lethality, caution should be observed when using this method in thermal process evaluations.

The general method for calculating process lethality has wide application in the canning industry and can be applied to thermal processes in enclosed systems, where the loss of moisture from the product (mass transfer) is minimal. An example for such a cooking system is moist cooking in smokehouses, where the humidity is high (wet and dry bulb temperatures are similar), such as cooking the product in bags in water or in high-humidity environments (steam cooking). Under these conditions, the predicted lethality will correlate well with the observed lethalities for vegetative food-borne pathogens.

Typical thermal destruction parameters for common food-borne pathogens are shown in Table 6.6. When dry heat is employed for thermal processing, such as in cooking hamburgers or cooking roast beef products, chicken thighs, or chicken breasts in a dry environment or environment with low humidity, the predicted lethalities will be greater than the observed lethalities. An example for this behavior is the work conducted by Goodfellow and Brown[52] on destruction of *Salmonella* on roast beef, which indicates that survivors could be observed on the surface-inoculated product using dry heat. Injection of steam either early or late in the cooking process resulted in complete destruction of surface-inoculated *Salmonella*. The authors[52] attributed the survival of the *Salmonella* during dry heating to dehydration of the microorganisms, resulting in increased resistance.

In some cases, predicted process lethalities for vegetative microorganisms do not agree with lethalities observed through microbial challenge studies. These anomalies can be explained by several factors that affect the microbial heat resistance. These factors can be categorized as those that pertain to the product and those that are related to the microbial cells. They have been recognized as early as the 1960s and include:

1. Product characteristics that affect microbial heat resistance
   a. Water activity (a_w)
   b. Fat content
   c. pH of the product

   d. Solutes or salts and other antimicrobial agents (NaCl, nitrates and nitrites, phosphates, lactates and other salts of organic acids, etc.)
   e. Packaging system employed (vacuum packaged vs. moderately aerobic conditions, such as meats' or sausages' moisture-permeable casing)
2. Microbial cell characteristics that affect heat resistance
   a. Species and strain of the organism
   b. Growth conditions of the organism (growth medium, temperature, etc.)
   c. Age of the population
   d. Concentration of the cells
   e. Method of preparation of the cells (centrifugation, washing, etc.)

The degree of variations in the heat resistance of microorganisms can be observed (Figure 6.11) for *L. monocytogenes*, summarized from various reports.[53] The destruction of microbial cells as described by the *D* value (first-order kinetics) assumes a log-linear relationship between the survivors and the heating time. However, deviations from the log-linear relationship have been observed and often are rationalized on the basis of some special property of the microorganism or its physiological state.[54] These deviations, termed shoulder or tailing regions on the survival curve, may be due to the clumps of microorganisms or the existence of a more heat resistant subpopulation (Figure 6.12).

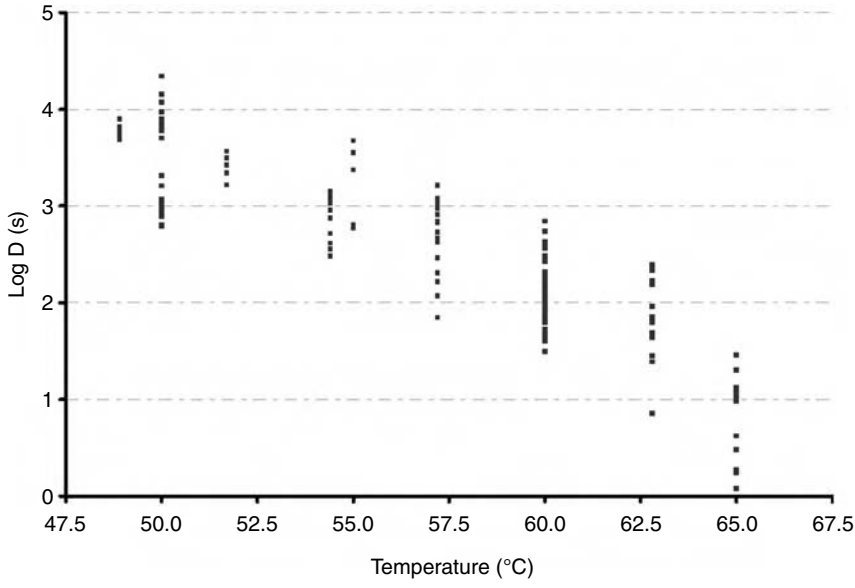

FIGURE 6.11 Heat resistance of *Listeria monocytogenes* in different substrates. (Adapted from Mackey, B.M. and Bratchel, N., *Lett. Appl. Microbiol.*, 9, 89–94, 1989.)

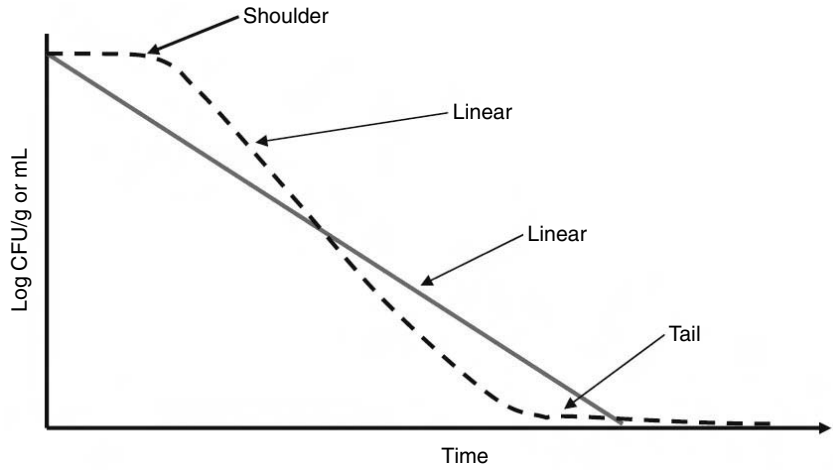

FIGURE 6.12 Graphic representation of shoulder and tailing in microbial populations during thermal treatments. (Courtesy of Dr. Vijay Juneja.)

In cases where extreme deviations from first-order kinetics are observed in thermal kinetics of microorganisms, it may be too simplistic to apply the general method of calculating the process lethality, and in most instances, it could be potentially hazardous. In such cases, it may be necessary to conduct microbial challenge studies (MCTs) and simulate natural conditions encountered during processing of a particular meat product. General guidelines for such challenge studies have been published and, in most cases, were developed for specific purposes, such as conduct of the MCTs for survival/destruction of *L. monocytogenes* on ready-to-eat meat products.[55]

In addition to these factors, process lethalities also depend on the processing schedules employed, e.g., the time when moist heat was introduced, the degree of dry heat vs. moist heat processing, product surface characteristics, initial moisture of the product, and degree or rate of moisture loss, among other factors.

6.8 PREDICTIVE MODELING OF THERMAL DESTRUCTION KINETICS OF VEGETATIVE PATHOGENS

Predictive modeling has gained popularity and wide acceptance from regulatory agencies as a tool to evaluate and predict the microbiological safety of food products. This probably is due to the regulatory shift from a prescribed command and control system to a hazard analysis and critical control point (HACCP)-based food safety approach.

TABLE 6.7
Models for Microbial Survival Curves

Model	Mathematical Formula
First-order kinetics	$N = N_0 e^{-kt}$ or $\log \frac{N}{N_0} = -\frac{L}{D}$
Chef	$\frac{N}{N_0} = F_1 e^{-k_1 t} + (1 - F_1) e^{-k_2 t}$
Kamau	For linear survival curves $\frac{N}{N_0} = \frac{2}{1 + e^{\beta t}}$ For biphasic survival curves $\log \frac{N}{N_0} = \log(1 + e^{-\beta t_{1/2}} - \log(1 + e^{-\beta t_{1/2}})$
Whiting and Buchanan	$\log \frac{N}{N_0} = \log\left(\frac{F_1(1 + e^{-\beta_1 t_L})}{1 + e^{\beta_1 (t - t_L)}}\right) + \frac{(1 - F_1)(1 + e^{-\beta_2 t_L})}{1 + e^{\beta_2 (t - t_L)}}$
Cole	$\log N = \alpha + \frac{\omega - \alpha}{1 + e^{4\sigma(\tau - \log t)/(\omega - \sigma)}}$
Gompertz	Modified Gompertz eqation $\log N = A - Ce^{-e^{-B(t-M)}}$ or $\log \frac{N}{N_0} = Ce^{-e^{BM}} - Ce^{-e^{-B(t-M)}}$
Membre	$\log N = (1 + \log N0) - e^{kt}$

Source: Adapted from Xiong, R. et al., *Food Microbiol.*, 16, 269–279, 1999.

Tremendous progress in predictive microbiology has been made in the past decade due to high-speed computers that can evaluate and develop mathematical descriptions of microbial growth, survival, and death. Predictive microbiology is an excellent tool in conducting microbiological risk assessments by evaluating the likely exposure of an individual to microorganisms in food.[56] The steps involved in development of sound predictive models involve planning, data collection and analysis, function fitting, and model validation.[57] Although initial

research involved use of empirical models, the modified Gompertz and square root model of Ratkowsky[58] have gained widespread use due to their ability to describe the data in the entire biokinetic range of growth for the microorganisms.

Models are normally developed under static conditions (growth rates and lag times are measured at a series of set temperatures, water activity values, and pH levels), and the results are combined to describe the effects of each factor or a combination of factors on population development.[57] Subsequently, the models are validated in foods under conditions that mimic situations encountered in normal practice, e.g., decreasing temperature, such as in cooling operations after heat treatments, or chilling of carcasses or fluctuating temperatures during distribution and storage of the food products.

While modeling of microbial growth presents some challenges for microbiologists and mathematicians, modeling of microbial thermal inactivation kinetics presents even greater challenges. Traditionally, thermal inactivation kinetics were modeled using first-order kinetics for simplicity and ease of use. However, deviations from first-order kinetics are frequently encountered in vegetative organisms, reflecting the inadequacy of the logarithmic death concept.[54]

The Gompertz model and its modified forms have been used to model asymmetrical sigmoidal shapes of microbial growth curves.[57,59] The modified Gompertz equations have been adapted to accurately describe the thermal destruction of food-borne pathogens, especially *L. monocytogenes* in liver sausage slurry.[60] Models that have been used in describing microbial survival curves are shown in Table 6.7.

These models, as developed and evaluated, can describe the destruction of vegetative cells at constant temperatures.[74] However, when processing meat and meat products, a continuously increasing temperature will be observed during heating, and conversely, a continuously declining temperature will be observed during cooling. Methods and models that integrate the destruction of the pathogens during the entire thermal process (including heating and cooling) need to be developed for effective use by the meat processing industry. Development of these models will greatly assist the processors in developing a safe thermal process for new products to be developed and in ensuring safe thermally processed meat products.

6.9 MICROBIAL SAFETY OF *SOUS VIDE* PRODUCTS

The need for prepared meals over the past 20 years due to changes in population demographics and changing lifestyles has resulted in availability of a greater variety of prepared products in the market. These products enjoy a greater market share these days, and have been made possible by processing and packaging advancements in foods, such as vacuum packaging.

While Chef Georges Pralus is credited with discovery of the *sous vide* food preparation method, a patent in 1971 assigned to W.R. Grace Company was instrumental in the growth of this technology.[42] The laminated plastic packaging material developed by W.R. Grace Company was able to withstand the extremes

of temperatures employed in cooking and cooling of foods and has made this technology a reality. The excellent sensory qualities of the products prepared using this technology have made them popular in most European countries. Subsequent realization of the food safety implications of such food products has resulted in extensive research efforts at minimizing the risk of food-borne pathogens in such products.

Due to the relatively mild thermal processes applied to the majority of these products, microbiological safety is the main concern, particularly nonproteolytic group II *C. botulinum*. Combinations of mild heat treatment and vacuum packaging may select for *C. botulinum* and increase the risk of botulism from these products. *Sous vide* products are generally formulated with little or no preservatives and do not possess any secondary barriers (pH, a_w, and NaCl) that can inhibit this pathogen either alone or in combination. Reliance on chill chain temperatures may not be adequate to control *C. botulinum* germination and outgrowth, considering the variability in temperatures observed.

Contamination of animal carcasses during slaughter is an unavoidable consequence, and if the spores of *C. botulinum* are present in the animal fecal material, contamination of the meat can result. Recent reports indicate contamination of approximately 73 and 5% prevalence of *C. botulinum* type B and type E spores, respectively, in feces of cattle in Sweden. The spore populations were higher in winter (4 spores/g) than in summer (1.5 spores/g).[61]

Research indicates that the hurdle concept would be the optimum approach to control nonproteolytic *C. botulinum* in *sous vide* products. Hyytia-Trees et al.[39] reported that *sous vide* products could be classified into safe and high-risk groups, based on the thermal process applied, NaCl content, and pH of the product (Table 6.8).

TABLE 6.8
Physical and Chemical Features of High-Risk and Safe *Sous Vide* Products

Physical or Chemical Feature	High-Risk[a] Products	Safe[b] Products
P value[c]	7.7 (0.0–22.9)	234.1 (118.9–349.2)
NaCl (% [wt/vol])	1.0 (0.2–1.9)	1.2 (1.0–1.3)
pH	5.8 (5.1–6.3)	5.3

[a]Samples strongly positive for *C. botulinum* or botulinum neurotoxin at both sampling times (products: pork cubes, beef roast, ground beef, and beef, pork, water, and vegetables).

[b]Samples negative for *C. botulinum* and botulinum neurotoxin at both sampling times (products: beef, vegetables, and water; and pork, vegetables, and water).

[c]*P* value = pasteurization value calculated using $T_{ref} = 82.2°C$, $Z = 16.5°C$, and $D_{82.2°C} = 32.3$ min.

Source: Adapted from Hyytia-Trees, E. et al., *Appl. Environ. Microbiol.*, 66, 223–229, 2000.

TABLE 6.9
Recommended Heat Treatments for *Sous Vide* Products

Source	Pasteurization Treatment (internal temperature)	Shelf Life (under refrigeration)	Target Organism
French regulations (Ministère de l'Agriculture 1974, 1988)	70°C for 40 min 70°C for 100 min 70°C for 1000 min	6 days 21 days 42 days	*E. faecalis*
DOH Guidelines (1989)	70°C for 2 min	5 days	*L. monocytogenes*
SVAC (1991)	80°C for 26 min or 90°C for 4.5 min	8 days	*C. botulinum* type E
ACMSF (1992)	90°C for 10 min	>10 days	*C. botulinum*
ECFF Botulinum Working Party (Gould, 1996)	70°C for 2 min 90°C for 10 min	Short shelf life Longer shelf life	*L. monocytogenes* *C. botulinum*

Note: DOH = Department of Health; SVAC = Sous Vide Advisory Committee; ACMSE = Advisory Committee on the Microbiological Safety of Food; ECFF = European Chilled Food Federation.

Source: Ghazala, S. and Trenholm, R., in Ghazala, S., Ed., *Sous Vide and Cook-Chill Processing for the Food Industry*, Aspen Publishers, Gaithersburg, MD, 1998.

In the U.K., the Advisory Committtee on Microbiological Safety of Food recommended a six log cycle (6-D) process, through use of thermal or combination processes for reduction of nonproteolytic *C. botulinum* (Table 6.9). Presently, regulatory performance standards are nonexistent for these types of food products in the U.S. Considering the botulism risk of these products, it may be prudent to evaluate the risks and incorporate necessary controls as performance standards. This is especially true when vegetable and other crop products are introduced into the *sous vide* product category, which were initially meat-based products. Development of performance standards for these types of products should be based on destruction of nonproteolytic *C. botulinum* spore populations during thermal processing, as well as control of germination and outgrowth during storage and distribution.

While very limited research is available on the control of germination and outgrowth of *C. botulinum* in these types of products, secondary inhibitors such as nitrites and, more popular in recent times, salts of organic acids such as lactic, citric, and acetic, hold promise. Citrate was more effective in delaying botulinal toxin production than propionate, acetate, and lactate on a molar basis in uncured turkey breast.[62] These authors[62] reported that inhibition of botulinal toxin production by monocarboxylic acid esters (pyruvic, lactic, acetic, and propionic) in uncured turkey was proportional to the dissociation constants (pK_a). However, citrate did not follow this pattern, showing greater inhibitory activity on a molar basis. The antibotulinal mechanism of citrate was attributed to chelation of metals and subsequent mineral depravation for germination and

growth.[63–65] The inhibitory action of organic acid esters has been attributed to lowering of the intracellular pH within the microbial cells, and alterations in cell membrane permeability, thus affecting substrate transport and inhibition of electron transport systems necessary for energy regeneration.[66] Similar mechanisms may be responsible for inhibition of *C. perfringens* outgrowth during abusive chilling rates of meat products followed in this study.

Houtsma et al.[67] reported inhibition of proteolytic *C. botulinum* growth and toxin production by sodium lactate in a peptone–yeast extract medium (pH 6.1). However, the inhibitory effect was gradually lowered as temperatures of incubation were increased.[67,68] Furthermore, sodium lactate alone or in combination with NaCl was shown to delay toxin production by proteolytic *C. botulinum* strains at 15 and 20°C at concentrations of 2 and 2.5%, respectively.[67] Complete inhibition of toxin production at 15, 20, and 30°C occurred at concentrations of 3, 4, and >4%, respectively. Maas et al.[69] proposed two possible mechanisms for delay of botulinal toxin production by lactates: (1) inhibition of a major anaerobic energy metabolism pathway essential for growth, and (2) inhibition of adenosine triphosphate (ATP) generation and subsequent lowering of lactate efflux from cells. In addition, the authors[69] reported that the delay in botulinal toxin production by sodium lactate was concentration dependent, resulting from inhibition of *C. botulinum* germination.

The USDA-FSIS[70] stabilization requirements for processed meat and poultry products were based on the prevention of germination and outgrowth of spore-forming bacteria that survive the normal heating regimes employed in the meat processing industry. The USDA-FSIS also stated that *C. perfringens* can be used alone in an inoculated pack (challenge) study to demonstrate that the cooling performance standard is met for both microorganisms, *C. perfringens* and *C. botulinum,* as the conditions of time/temperature that would limit the growth of *C. perfringens* to 1.0 $\log_{10}$ would also prevent multiplication of *C. botulinum*, which has much slower growth rates. It is evident from the literature that organic acid esters such as sodium or potassium salts of lactic, acetic, and citric acids are inhibitory to *C. botulinum* germination and outgrowth and botulinum toxin production.

Incorporation of these secondary inhibitors would enhance the microbiological safety of the *sous vide*–type meat products, especially with longer shelf life, as is the case in products produced in the U.S.

6.10 PERFORMANCE STANDARDS FOR THERMALLY PROCESSED MEATS

Through regulations and directives, the USDA-FSIS has mandated step-by-step processing measures to ensure the safety of the meat supply. Transition to an HACCP-based approach to ensure safety of the meat and poultry products has shifted the burden of designing and implementing manufacturing processes from the regulatory agencies to the meat and poultry industry. To achieve the food safety objectives of reducing food-borne illness, the USDA-FSIS has established *performance standards*

to be achieved in each of the product categories, based on quantitative risk assessments, with a degree-of-safety margin built into these standards.

Performance standards prescribe the objectives or levels of performance (such as pathogen reduction or standards for raw product) the establishments must achieve.[27] This allows the processors to develop and implement processing procedures customized to the nature and volume of production. Furthermore, the processors can still follow the previous requirements that are being disseminated as *safe harbors*.

The scientific validity of the performance standards has been questioned, and recent deliberations and publication of a report by the National Academy of Sciences[71] declared that the performance standards must be linked to a public health goal and must incorporate a measure of effectiveness in meeting the public health goal. The National Academy of Sciences defined performance standard as "the degree to which a step or combinations of steps in the production, processing, distribution and/or preparation of a food must operate to achieve the required level of control over a hazard."

Although these performance standards are prescribed within each country depending on the prevalence and severity of food-borne illness, global trade requires that science-based, verifiable standards be applied. The International Commission for Microbiological Specification of Foods (ICMSF) developed the concept of a food safety objective (FSO), on the lines of quality objectives in quality assurance and quality management standards.[72] FSOs are the maximum frequency or concentration of microorganisms or toxins of a microbiological hazard in a food at the time of consumption that provides the appropriate level of protection. FSOs are expressions of concentration of microorganisms or toxins at the moment of consumption, while the performance criteria or standards are concentrations at earlier stages of the food chain.[73]

Control measures should be applied during food production to achieve the defined FSO, and the outcomes of these measures are defined as performance criteria or standards (USDA-FSIS). The FSOs are often stated as public health goals, and to achieve this, performance standards or criteria should be established with consideration to the initial levels of the hazard and changes (either increase or reduction) occurring during production, processing, storage, preparation, and use of the product. The performance criterion should be less than or at least equal to the FSO and can be expressed as

$$H_o - R + I \geq \text{FSO} \tag{6.3}$$

where FSO is the food safety objective, H_o is the initial level of the hazard, R is the cumulative reduction of the hazard, and I is the cumulative increase of the hazard during processing, storage, and distribution of the product. These parameters are expressed as $\log_{10}$ units.

Examples of performance standards and criteria for lethality are shown in Table 6.10 for meat and poultry products in the U.S. In most cases, *Salmonella* spp. have been used as the pathogen of choice, with the intent that reductions in

TABLE 6.10
Proposed Performance Standards for Ready-to-Eat (RTE) and All Partially Heat-Treated Meat and Poultry Products

Product Category	Pathogen or Toxin	Requirement
Nonthermally Processed, Commercially Sterile Products		
(i) Lethality		
All meat products, other than poultry	*Salmonella* spp.	6.5 log reduction or 6.5-D process
Poultry products or meat products containing any amount of poultry	*Salmonella* spp.	7-D process
All fermented RTE meat and poultry products containing beef	*E. coli* O157:H7 (in addition to *Salmonella* spp. lethality)	5-D process
(ii) Stabilization		
All meat and poultry products	*C. botulinum*	No multiplication of toxigenic microorganisms or *C. botulinum*
	C. perfringens	<1.0 $\log_{10}$ multiplication of *C. perfringens*
(iii) General requirement		
All RTE meat and poultry products	Other pathogens, toxins, or toxic metabolites	Achieving performance standards for lethality and stabilization throughout product shelf life, under conditions of storage, distribution, and holding
(iv) Postlethality contamination		
All RTE meat and poultry products	*L. monocytogenes*	Either incorporating one or more controls in HACCP plan or testing food contact surfaces for *Listeria* spp.
Thermally Processed, Commercially Sterile Meat and Poultry Products		
All meat and poultry products	*C. botulinum* (depending on pH)	Eliminating (12-D process) or controlling *C. botulinum* and being packaged in a hermetically sealed container and the product commercially sterilized

Salmonella spp. will also achieve reductions in other pathogens of concern, *E. coli* O157:H7 and *L. monocytogenes*.

In addition to the lethality requirements, USDA-FSIS requires establishments to achieve a stabilization performance standard, for preventing the growth of spore-forming bacteria. These require that the cooling process of cooked meat products be sufficient to prevent multiplication of *C. botulinum* and no more than one log growth of *C. perfringens*. The sporeformers can survive the normal thermal processes applied to meat products, and thus can grow to hazardous levels during cooling, if the products are not cooled properly.

Thus, performance standards or criteria are an integral part of the thermal processing of meat and poultry products, and form the basis for designing the processing parameters. These processing systems should be customized on a case-by-case basis tailoring to the product characteristics.

6.11 CONCLUSIONS

With the consumer interest and demand for high-quality processed foods, food processors have sought new technologies to achieve food safety. These newer technologies include use of physical methods such as high hydrostatic pressure treatment, microwave processing, ultrasound, ohmic heating, and pulsed electric fields, in addition to the use of natural antimicrobial systems. Most of these technologies cannot be relied on to provide the degree of safety required to achieve the food safety objectives. Thus, these technologies are used in combination, and most often with heat or mild thermal treatments to achieve the performance standards of microbial pathogen reductions and to preserve the quality of the food. This technology, termed hurdle concept, has been used by manipulating the intrinsic properties of foods, such as water activity (a_w), pH, moisture, storage temperature, and preservatives.

Newer, milder technologies are increasingly being used in the food industry in combinations as hurdle technologies to deliver safe, high-quality food products. However, heat and thermal processing continue to be the basis for ensuring microbiological safety of meat and poultry products and are extensively used.

NOMENCLATURE

A	Lower asymptote, log CFU ml^{-1}
B	Relative death rate at M, (log CFU ml^{-1}) min^{-1}
$B(t)$	Lag time function, min
C	Difference in value of the upper and lower asymptotes, log CFU ml^{-1}
D	Decimal reduction time, min
$D_{\min}$	Minimum decimal reduction time, min
k	Death rate constant, log CFU ml^{-1} min^{-1}
$k_{\max}$	Maximum relative death rate, log CFU ml^{-1} min^{-1}

L_T	Lethal rate (min at T^{ref}/min at T)
M	Time at which the absolute death rate is maximal, min
N	Number of microorganisms, CFU ml^{-1}
N_0	Initial number of microorganisms, CFU^{-1}
N	Curvatural parameter
N_{min}	Minimum cell concentration, CFU/ml
q_B	Tailing ratio in the Baranyi model
q_G	Tailing ratio
t	Time, min
t_{lag}	Lag phase duration, min
(t)	Adjustment function or shoulder adjustment function
(t)	Tailing adjustment function
T	Product temperature at specific time, °C
T^{ref}	Reference temperature, °C
t_T	Time at a specific temperature (T), min
μ_{max}	Maximum exponential death rate, (log CFU ml^{-1}) min^{-1}
Z	Z value of the particular pathogen, °C

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7 Thermal Processing of Poultry Products

Paul L. Dawson, Sunil Mangalassary, and Brian W. Sheldon

CONTENTS

7.1 INTRODUCTION

Thermal processing of poultry meat and egg products serves several purposes, including elimination of pathogenic microorganisms, improvement of sensory properties (flavor, texture, appearance, etc.), stabilization of color in cured products, extraction of high-value components (fat rendering, lysozyme), and removal of undesirable components. Poultry products that are subjected to thermal processing include raw meat that is cooked, ready-to-eat (RTE) meats, liquid eggs, shell eggs, and rendered meat. On January 1, 2003, the Food Safety and Inspection Service (FSIS) of the U.S. Department of Agriculture revised the requirements for handling meat products under Title 9 of the U.S. Code of Federal Regulations. These regulations are specifically described in this chapter under the headings of cooked meat, canned meat, rendered products, and egg products. Comments on thermal processing of canned or retort pouch-type products that were made by representatives of the National Food Processors Association (NFPA) on May 10, 2001, at an FSIS public meeting on RTE performance standards are as follows:

> Following a food poisoning incident in 1971 in which the failure to properly apply a thermal process to a commercially canned product led to fatal consequences, the National Canners Association (now NFPA) petitioned the Food and Drug Administration (FDA) to promulgate new regulations to address the problem. Elements of this new program were designed to control the primary food safety hazards associated with canning operations — the survival of spores of *Clostridium botulinum* which could subsequently germinate and produce the deadly botulism toxin within the anaerobic environment of the sealed can. Consumption of even small amounts of this potent toxin, in the absence of prompt administration of antitoxin, can quickly lead to paralysis and death of any consumer, not just those who are immunocompromised or fall in some other special risk category.

Thermal processing is still the favored method to ensure microbiological safety of poultry products even though newer technologies such as irradiation, high-intensity electric fields, ultrahigh pressure, and high intensity light are finding niche applications in the food industry. Thermal processing will remain the dominant method used to impart safety, flavor, and value to poultry products. Consumer demand for convenience and food service needs has prompted the development of a myriad of cooked poultry products requiring a minimum amount of on-site preparation by the consumer or food service workers. This marketing shift has been accompanied by a shift in the regulatory approach to ensuring product safety. Inspection by governmental agencies, while still required, has given way to standards requiring the producer of the product to ensure and document the safety of its products. Regulations now require the processor to prove its product's safety. Since challenge studies (inoculation with a pathogen) in a commercial setting are not possible, research involving bacterial inactivation models has become prevalent. This chapter will summarize the applicable regulations and discuss the research pertaining to thermal processing of poultry meat and egg products.

7.2 MEATS

There are many factors that affect the thermal process used for treating food products. From a regulatory standpoint, the primary concern is product safety, which focuses on ensuring that all microbial pathogens are reduced to a level that renders the product safe. This translates into either a minimum log reduction in population or a zero tolerance for some target microorganisms. In general, bacteria survive better in meat products than in test solutions, buffered media, or growth media. Numerous studies have evaluated the relative heat resistance of target microorganisms as influenced by medium.[1–3] These studies are widespread since thermal inactivation is affected by many factors. Bacterial heat resistance is generally higher in meats than in buffered media or peptone water.[4–6] Some variables that influence the effectiveness of a heat inactivation process include pH,[2,3,7–9] fat content,[10] and water activity.[11,12]

Pasteurization using hot water or steam is employed as an effective method for reducing levels of pathogenic bacteria on the surface of poultry meat. Goksoy et al.[13] performed a series of experiments to determine the relationship between hot-water immersion temperature and residence time on the appearance of chicken skin and meat. The results showed that the changes caused to samples by heat treatment were initially textural rather than colorimetric, and thus could be identified visually but not instrumentally with a chroma meter. The visual examination revealed that there is no immersion heat treatment (below 90°C) capable of reducing thermotolerant microorganisms on poultry without causing adverse changes in the product. A device to surface pasteurize meat without producing a cooked appearance was built and tested.[14] The researchers[14] achieved a rapid heating by condensing pure, thermally saturated steam onto the meat surface in the absence of noncondensible gases, which could keep up with poultry slaughter line speeds.

7.2.1 Cooking of Poultry Meat

7.2.1.1 Current Research on Cooking Poultry Meat

Adequate thermal processing or cooking of meat products is one of the most important critical control points for eliminating pathogenic bacteria and viruses and preventing food-borne diseases. Cooking is a commonly employed critical control point in the *hazard analysis and critical control point* (HACCP) food safety program of meat processors and is one of the last control points applied to a food product before consumption.[15] The thermal inactivation of pathogenic organisms is expressed in terms of D and z values. The D value or thermal reduction time is defined as the time at a specified temperature required to reduce a population of organisms by 1 log cycle or 90%. The relationship between D value and temperature is defined in terms of the z value and is defined as the temperature change in degrees Celsius needed to bring about a 1 log cycle change in D value. The determination of D- and z values for a particular microorganism is useful in designing a thermal process that targets that specific microorganism.[16]

Due to the variety of factors affecting bacterial lethality, many researchers have attempted to model the effect of these multiple factors on process lethality (i.e., deriving D and z values for target microorganisms). *Salmonella* spp., *Listeria monocytogenes*, *Campylobacter jejuni*, and *Escherichia coli* O157:H7 are the four most common bacteria reported in the literature for which heat inactivation studies have been conducted. For example, Fain et al.[10] reported D values for *L. monocytogenes* in lean ground turkey of 81.3, 2.6, and 0.6 min at 51.7, 57.2, and 62.8°C, respectively. Veeramuthu et al.[17] published D values for *Salmonella* Seftenberg (211.35, 13.24, and 3.43 min) and *E. coli* O157:H7 (79.4, 5.47, and 1.69 min) in ground turkey processed at 55, 60, and 65°C, respectively. Moreover, Blankenship and Craven[4] recorded D values for *C. jejuni* in cooked chicken of 15.2 to 0.25 min when processed between 49 and 57°C. Murphy et al.[18,19] reported on the thermal inactivation kinetics for *Salmonella* spp. and *L. monocytogenes* in ground chicken. They found that the D value of a six-serotype mixture of *Salmonella* equaled the sum of the D values for each individual serotype.

Juneja et al.[20] discovered that the D values (at 55, 57.5, 60, 62.5, and 65°C) for a four-strain mixture of *E. coli* O157:H7 in lean ground chicken were lower than the D values obtained for a 90% lean ground beef product. In a subsequent study, Juneja et al.[21] generated survival curves (58 to 65°C) for an eight-serotype cocktail of *Salmonella* mixed in ground poultry samples containing varying levels of fat (1 to 12%). They found that for a given increase in fat level, ground chicken had higher D values than ground turkey. At the higher processing temperatures, the D values were longer for ground turkey than ground chicken. A general trend of increasing D value with fat level was found with chicken that was not found in turkey meat (Table 7.1).

Cooking methods can affect bacterial inactivation, as was demonstrated by Schnepf and Barbeau[22] with *Salmonella* Typhimurium-inoculated chicken cooked by either microwave, convection, or conventional ovens. Cooking method can also influence the degree of bacterial inactivation on the meat surface. For example, an air impingement oven (a popular commercial oven) having a high air velocity will dehydrate the meat surface faster than other methods, such as microwave and steam cooking. Thus, the inactivation of bacterial cells on poultry meat surfaces may in some instances be more impacted by oven relative humidity than by the water activity of the product. This observation was supported by Murphy et al.,[23] who discovered that the higher humidity environment in steam-injected ovens increased *Salmonella* spp. inactivation by >2 $\log_{10}$ cycles compared to a dry-air cooking method attaining the same endpoint temperature. Marks et al.[24] and Murphy et al.[25] demonstrated that water bath-based heating studies overpredicted *Salmonella* and *Listeria* spp. inactivation by as much as 5 $\log_{10}$ cycles compared to chicken breast patties heated in a dry-air convection oven.

Different approaches are used for the verification of thermal processing adequacy in meat products. Orta-Ramirez and Smith[15] categorized these into the following headings: thermocouples and thermometers, color determination, endpoint temperature indicators, enzymatic methods, immunoassays, physical methods, and time–temperature integrators. Thermal energy is an important factor in color

TABLE 7.1
***D* and *z* values for Selected Poultry Meat Products**

Organism	Product	Temperature (°C)	*D* Value (min)	*z* Value (°C)	Reference
S. aureus	Chicken a la king	60	5.37		140
L. monocytogenes	Minced chicken	70	—	6.7	120
	Ground turkey	51.7	81.3		10
		57.2	2.6		
		62.8	0.6		
	Turkey bologna	61	2.1	4.44	39
		65	0.27		
S. Seftenberg	Ground turkey	55	211.35		17
		60	13.24		
		65	3.43		
E. coli O157:H7	Ground turkey	55	79.4		
		60	5.47		
		65	1.69		
	Chicken	70	0.38–0.55		141
	Turkey bologna	55	4.83	13.9	41
		60	0.76		
		65	0.20		
		70	0.15		
S. Typhimurium	Chicken broth	55	4.16		37
	Turkey bologna	57	4.6	5.56	39
		60	1.4		

(*Continued*)

TABLE 7.1 (Continued)
***D* and *z* values for Selected Poultry Meat Products**

Organism	Product	Temperature (°C)	*D* Value (min)	*z* Value (°C)	Reference
Salmonella 8 serotype cocktail:	Chicken, 2% fat	58	7.38		21
S. Thompson	Chicken, 6.3% fat	58	7.33		
S. Enteriditis phage type 13A	Chicken, 9% fat	58	8.54		
S. Enteriditis phage type 4	Chicken, 12% fat	58	9.04		
S. Typhimurium	Chicken, 2% fat	60	4.83		
S. Hadar	Chicken, 6.3% fat	60	4.68		
S. Copenhagen	Chicken, 9% fat	60	5.40		
S. Motnevideo	Chicken, 12% fat	60	5.50		
S. Heidelberg	Chicken, 2% fat	62.5	1.14		
	Chicken, 6.3% fat	62.5	1.16		
	Chicken, 9% fat	62.5	1.16		
	Chicken, 12% fat	62.5	1.30		
	Chicken, 2% fat	65	0.41		
	Chicken, 6.3% fat	65	0.51		
	Chicken, 9% fat	65	0.53		
	Chicken, 12% fat	65	0.50		
	Turkey, 2% fat	58	7.50		
	Turkey, 6.3% fat	58	7.71		
	Turkey, 9% fat	58	6.91		
	Turkey, 12% fat	58	7.41		
	Turkey, 2% fat	60	4.56		
	Turkey, 6.3% fat	60	4.94		
	Turkey, 9% fat	60	5.13		
	Turkey, 12% fat	60	5.43		

	Turkey, 2% fat	62.5	1.53		
	Turkey, 6.3% fat	62.5	1.85		
	Turkey, 9% fat	62.5	1.45		
	Turkey, 12% fat	62.5	1.78		
	Turkey, 2% fat	65	0.59		
	Turkey, 6.3% fat	65	0.55		
	Turkey, 9% fat	65	0.57		
	Turkey, 12% fat	65	0.59		
C. jejuni	Turkey bologna	53	4.53	8.3	41
		55	3.20		
		60	0.64		
		62	0.42		

changes in heat processed meat and poultry products. Determination of color changes in meat or meat juice exudates has been suggested as a means of estimating endpoint temperature (EPT). Ang and Huang[26] found that the color of precooked chicken leg meat may provide a rapid estimation of the EPT to which the product has been heated, but it is limited by the packaging method and storage time, which significantly influenced the color values.

The catalytic activity, defined as the decomposition of H_2O_2 into H_2O and O_2, has been evaluated as a potential indicator of heat treatment endpoint for chicken patties. The catalytic activity test offered a simple and rapid procedure for estimating the EPT of processed chicken patties cooked to 73°C,[27] and a 3 to 4°C error in EPT prediction was observed. Bogin et al.[28] developed a biochemical method that could be performed under field conditions for verifying heat treatments for turkey breast meat. The activities of 12 enzymes and residual soluble proteins were examined following various heat treatments under different conditions. The enzymes aspartate aminotransferase, creatine kinase, malic dehydrogenase, isocitric dehydrogenase, and aldolase were shown to be valuable markers for the evaluation of heat treatment.

To predict heat penetration during thermal processing, heat transfer models have been widely used for meat products. Chen et al.[29] developed a two-dimensional axisymmetric finite element (FE) model to simulate coupled heat and mass transfer during convection cooking of regularly shaped chicken patties, under actual oven transient conditions. The predicted transient center temperature under various cooking conditions had an error of 3.8 to 5.7°C, compared to experimental data. The best prediction was obtained when both thermal conductivity and specific heat were modeled as state-dependent functions in the simulations.

7.2.1.2 Regulations for Cooking Poultry Meat

The U.S. Department of Agriculture–Food Safety and Inspection Service (USDA-FSIS) has implemented a 7 $\log_{10}$ reduction in population of *Salmonella* for fully and partially cooked poultry products.[30] The USDA-FSIS provided additional regulations in their "Guidelines for Cooked Poultry Rolls and Other Cooked Poultry Products," as published as part of the Draft Compliance Guidelines for Ready-to-Eat Meat and Poultry Products:

1. Cooked poultry rolls and other cooked poultry products should reach an internal temperature of at least 71.1°C (160°F) prior to being removed from the cooking medium. However, cured and smoked poultry rolls and other cured and smoked poultry should reach an internal temperature of at least 68.3°C (155°F) prior to being removed from cooking medium. In cooked ready-to-eat products where heat will be applied incidental to a subsequent processing procedure, the product may be removed from the media for subsequent processing provided that it is immediately fully cooked to a 71.1°C (160°F) internal temperature.
2. Establishments producing cooked poultry rolls and other cooked poultry products should have sufficient monitoring equipment, including

> recording devices, to ensure that the temperature (accuracy ensured within 0.56°C (1°F)) limits of these processes are being met. Data from the recording devices must be made available to USDA-FSIS program employees upon request.

These FSIS cooking guidelines also suggested new time–temperature combinations for cooking RTE poultry products having different fat levels. Two other examples of poultry meat cooking regulations are Canada and Illinois. Most states have cooking regulations or guidelines with similar terminology a those shown here.

The Canadian Food Inspection Agency, Bureau of Food Safety and Consumer Protection Retail Food, states the following in its information bulletins:

> Section B.22.026. No person shall sell poultry, poultry meat or poultry meat by-product that has been barbecued, roasted or broiled and is ready for consumption unless the cooked poultry, poultry meat or poultry meat by-product
>
> (a) at all times
>
> (i) has a temperature of 4.4°C (40°F) or lower, or 60°C (140°F) or higher, or
>
> (ii) has been stored at an ambient temperature of 4.4°C (40°F) or lower, or 60°C (140°F) or higher, and
>
> (b) carries on the principal display panel of the label a statement to the effect that the food must be stored at a temperature of 4.4°C (40°F) or lower, or 60°C (140°F) or higher.

The Illinois Department of Public Health requires that:

> Other foods, such as poultry; stuffed fish, meat or pasta; or stuffing containing fish, meat or poultry must be cooked to 73.9°C (165°F) or above for at least 15 seconds. Not cooking to the established temperatures could result in salmonella poisoning.

7.2.2 Ready-to-Eat Meat

7.2.2.1 Current Research on Ready-to-Eat Meat

The majority of recent recalls of meat and poultry products involve RTE products. Surface contamination of RTE meat with pathogenic organisms generally occurs during postprocess handling. To control this contamination, surface pasteurization thermal processes involving steam or hot water may be effectively applied either prior to packaging or as a postpackage pasteurization application.

A series of three papers from the same research group described the impact of in-package pasteurization of Vienna sausages on controlling spoilage microorganisms, primarily *lactic acid bacteria* (LAB).[31–33] Depending on the severity of the applied thermal treatment, LAB were reduced from 84.4% of the total bacterial population to between 52.9 and 74.6% of the total population for Vienna sausages

stored for 128 days at 8°C.[31] However, in-package pasteurization did not delay the rate of spoilage because of an increase in *Bacillus* spp. populations detected in the heat-treated sausages. Decimal reduction values (D values) of LAB (*Lactobacillus sake*, *Leuconostoc mesenteroides*, *Lactobacillus curvatus*) in packaged Vienna sausages ranged from 14.4 to 52.9 sec at 57, 60, and 63°C.[32] The combination of organic acid addition and in-package pasteurization or pasteurization alone extended the microbiological shelf life of Vienna sausages (i.e., reaching a 5×10^6 CFU/g total aerobic plate count) fourfold compared to nontreated samples.[33]

Several cooking thermal inactivation studies have been conducted for *Listeria* spp. and *Salmonella* spp. in chicken patties,[25,34,35] ground beef,[36] packaged ground chicken,[19] turkey, chicken, chicken broth,[37] *sous vide* beef mince and solid beef pieces,[38] and packaged low-fat (mixed species, including poultry) bologna.[39] A wide variety of heating temperatures were tested in these studies. Juneja et al.[37] reported a D value (55°C) for *S.* Typhimurium of 4.16 min in chicken broth, whereas McCormick et al.[39] reported D values of 278 (4.6 min) and 81 sec (1.4 min) for *S.* Typhimurium inoculated on the surface of individually packaged bologna slices cooked at 57 and 60°C, respectively. McCormick et al.[39] also reported D values for *L. monocytogenes* on packaged mixed species bologna of 124 (2.1 min) and 16.2 sec (0.27 min) at 61 and 65°C, respectively. When in-package pasteurization was combined with nisin-impregnated packaging films, *L. monocytogenes* inhibition during storage was enhanced.[40] Hughes et al.[41] found that *C. jejuni* D values for in-package pasteurized turkey bologna were 272.0, 192.1, 38.4, and 25.2 sec at 53, 55, 60, and 62°C, respectively. These researchers also reported *E. coli* O157:H7 D values for in-package pasteurized turkey bologna of 289.5, 45.8, 15.8, and 9.1 sec at 55, 60, 65, and 70°C, respectively. Selected D and z values for poultry meat products are shown in Table 7.1.

Murphy and Berrang[42] discovered that postprocess pasteurization of fully cooked vacuum-packaged chicken breast strips with hot water or steam at 88°C for 10 to 35 min significantly lowered the *Listeria innocua* populations. Muriana et al.[43] reported a 2 to 4 log reduction of *L. monocytogenes* populations in RTE deli-style vacuum-packaged whole or formed turkey, ham, and roast beef following a post-package pasteurization process at 90.6 to 96.1°C (195 to 205°F) for 10 min. Murphy et al.[44] examined the effect of packaging film thickness on thermal inactivation of *Salmonella* spp. and *L. innocua* in cooked chicken breast meat. Their findings indicated that increasing film thicknesses reduced heating rates and reduced the level of inactivation of the test organisms. In a subsequent publication, Murphy et al.[45] suggested a model to use in predicting the amount of heating time required to achieve a 7 $\log_{10}$ reduction in *Salmonella* spp. or *L. innocua* populations for different thicknesses of fully cooked, vacuum-packaged chicken breast meat products pasteurized in a hot-water cooker at 90°C.

The same research group[45] also evaluated a postcook in-package pasteurization process against *L. monocytogenes* inoculated on a fully cooked turkey breast meat product. The effectiveness of the heat treatment was affected by product surface roughness. About 50 min of heating time was needed to achieve a 7 $\log_{10}$ CFU/cm^2 reduction on products having a convoluted surface roughness of up to 15 mm in depth.

Gande and Muriana[46] recorded a 1.25 to 3.5 log reduction in *L. monocytogenes* populations following a prepackaging surface pasteurization treatment (60 to 120 sec at 246.1 to 398.9°C) of a fully cooked meat product removed from its primary packaging wrap. When the turkey bologna was subjected to both a pre- (60 sec) and postpackaging (45 or 60 sec) pasteurization process, they detected a 2.7 to 4.3 log reduction in *L. monocytogenes* populations. These relatively low log reductions for the time used for surface pasteurization can be explained by the relatively large meat mass compared to individual slices. The effect of thickness on heat penetration is well documented, but the effect of sample thickness on surface heating rate is less well documented. Mangalassary et al.[47] found that thicker and higher fat turkey bologna samples had slower surface heating rates than thinner and lower fat samples. For example, at 80°C the in-package pasteurization times for a 5 log reduction of *L. monocytogenes* on the surface of turkey bologna were 0.72, 4.56, and 7.12 min for 4-, 12-, and 20-mm-thick samples.[47] The rates of surface heating for 4-, 12-, and 20-mm-thick bologna in the package are shown in Figure 7.1.

7.2.2.2 Regulations for Packaged Ready-to-Eat Poultry Meat

The U.S. regulations governing the thermal processing of ready-to-eat meats have evolved from a specific endpoint temperature requirement to a lethality requirement. This evolution roughly follows the move from a USDA inspection-based meat and poultry processing system to a food processing-derived HACCP-based program. Thus responsibility for documenting the safety of food products has shifted from the government to the processor. The 1999 USDA-FSIS ruling (CFR 381.150) specified a lethality of heat treatment for ready-to-eat whole muscle poultry meat of 7.0 $\log_{10}$

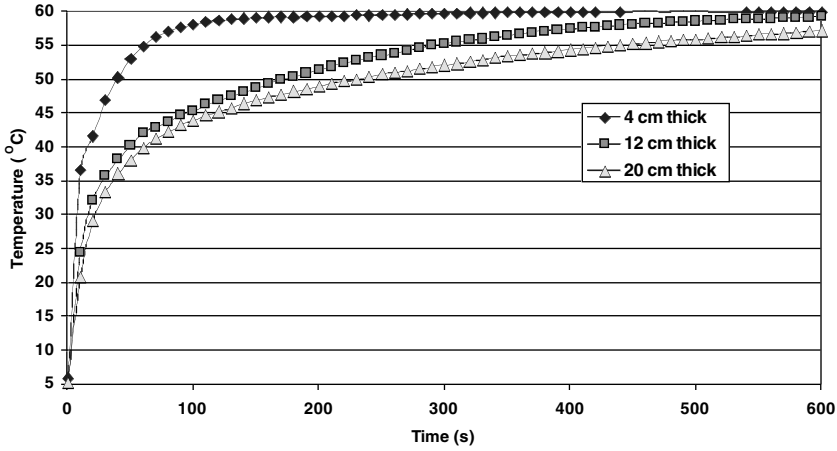

FIGURE 7.1 Meat thickness effect on surface heating rate in a 60°C water bath for in-package pasteurized bologna.

cycles for *Salmonella* spp. Processors are therefore required to validate their thermal process for each product using a "scientifically supportable means."

RTE meat and poultry products are products that have been processed so that they may be safely consumed without further preparation by the consumer (i.e., without cooking or application of some other lethality treatment to destroy pathogens) (66FR 39:12590). On February 27, 2001, FSIS published a proposed rule titled "Performance Standards for the Production of Processed Meat and Poultry Products" (66FR 12590). The proposed regulations include lethality and stabilization performance standards and *Listeria* testing requirements.

Except for thermally processed, commercially sterile products, the performance standards for lethality for all RTE poultry products require a 7.0 $\log_{10}$ reduction of *Salmonella* throughout the finished product. Moreover, except for thermally processed, commercially sterile products, the performance standards require no growth of *Clostridium botulinum* and no more than 1 $\log_{10}$ growth of *Clostridium perfringens* throughout the RTE meat and poultry product. For poultry products, an endpoint cooking temperature necessary to achieve a 7.0 $\log_{10}$ reduction of *Salmonella* is recommended.

Postprocessing lethality treatments, such as steam pasteurization, hot-water pasteurization, and radiant heating, have been developed to prevent or eliminate postprocessing contamination by *L. monocytogenes*. The postprocessing lethality treatment that reduces or eliminates the pathogen must be included in the establishment's HACCP plan. The interim final rule for the control of *L. monocytogenes* in RTE meat and poultry products includes three alternative approaches that establishments can choose in applying a postprocess lethality treatment:

1. Employ both a postprocess lethality treatment and a growth inhibitor to control *Listeria* on RTE products. Establishments opting for this alternative will be subject to FSIS verification activity that focuses on the efficacy of the postprocess lethality treatment. Sanitation programs are important, but are generally designed into the degree of lethality required for safety as delivered by the postprocess lethality treatment.
2. Employ either a postprocess lethality treatment or a growth inhibitor to control *Listeria* on RTE products. Establishments opting for this alternative will be subject to more frequent FSIS verification activities than those for the alternative (1).
3. Employ sanitation measures only. Establishments opting for this alternative will be targeted with the most frequent level of FSIS verification activity. Within this alternative, FSIS will place increased scrutiny on operations that produce hot dogs and deli meats. In a 2001 risk ranking, FSIS and the Food and Drug Administration identified these products as posing a relatively high risk for illness and death.

Currently there are no regulations governing the surface pasteurization of cooked meat products. A process would need to be established for each product based on the desired level of pathogen destruction at the product surface.[48]

7.2.3 Canned and Retorted Poultry Meat

7.2.3.1 Current Research on Canned and Retorted Poultry Meat

Thermally processed, commercially sterile meat and poultry products are commonly referred to as canned products, although the containers can be flexible, such as pouches, or semirigid, as in lunch bowls.[49] The incoming quality of raw materials (refrigerated chicken legs and breasts) used for the manufacture of canned chicken products and the outgoing quality of the finished products were evaluated by Turek et al.[50] Analysis of the canned products showed complete sterility and good physicochemical properties.

Lyon et al.,[51] studied the texture profiles of canned, boned chicken meat from birds treated under different processing regimes. They concluded that textural fibrousness and cohesiveness of mass associated with shortening, aging chilling times, and subsequent cooking of chicken meat may be an asset for products that undergo further heat treatment, such as retorting.

Vacuum-canned, commercial, mechanically deboned chicken meat was initially challenged by Thayer et al.[52] with either *C. botulinum* spores or *Salmonella* Enteritidis irradiated at 0, 1.5, and 3.0 KGy, and then stored at 5°C for 0, 2, and 4 weeks. None of the samples stored at 5°C developed botulinum toxin. However, when the samples were temperature abused at 28°C, they became toxic within 18 h and demonstrated obvious signs of spoilage, such as can swelling and putrid odors.

Studies were carried out by Rywotycki[53] to determine the effect of seasonal variations in the temperature of the cooling water used, water consumption, and the cooling time of pasteurized turkey meat cuts canned in containers of different sizes and shapes, ranging from 0.455 to 1.365 kg. Season markedly influenced cooling water temperature and hence the amount of water required for cooling; temperatures were the highest in the summer and the lowest in the winter. Season also had a marked effect on the shelf life of the canned product; bacterial counts were lower in cans produced in winter months than those produced in the summer, with no significant differences noted between products manufactured in the autumn or spring.

Sauvaget and Auffret[54] described the benefits of adding citric acid to canned chicken, turkey, and rabbit for maintaining the integrity and firmness of muscles, bones, and cartilage during the canning process. Zhang et al.[55] compared three different types of thermocouples and receptacle designs with regard to their effect on the observed heat penetration rate of a conduction-based heat treatment of chicken gravy packaged in small-diameter containers (202×204 and 211×300 cans). Their results indicated that stainless steel receptacles and needle-type thermocouples inserted into 202×204 cans significantly increased the apparent heat penetration rates.

7.2.3.2 Regulations for Commercially Sterile Products

A canned meat/poultry product is defined by the USDA as a "product having a water activity of 0.85 or higher and receives a thermal process either before or after being packed in a hermetically sealed container." The USDA further

defines commercially sterile as a "condition achieved by application of heat, sufficient alone or in combination with other treatments and/or treatments to render the product free of microorganisms capable of growing in the product at non-refrigerated conditions (over 10°C) at which the product is intended to be held during distribution and storage." Subpart X, Sections 381.300 to 381.311 of the Code of Federal Regulations stipulate the thermal processing requirements for canned poultry products. For a low-acid food receiving a thermal or other bactericidal process, that process must be validated to achieve a probability of 10^{-9} that there are *C. botulinum* spores in the container capable of growing or a 12 $\log_{10}$ reduction of *C. botulinum*, assuming an initial load of 1000 spores per container.

7.2.4 Rendering

7.2.4.1 Current Research on Rendered Poultry

The demand for poultry meat has increased considerably in recent years. The change in consumer preference for portioned or further processed poultry has resulted in increasing amounts of *by-products* and underutilized products. Skin and subcutaneous fat together account for about 19% of carcass weight.[56,57]

The basic purpose of *rendering* is to produce stable products of commercial value, free from disease-bearing organisms, from raw materials that are often unsuitable or unfit for human consumption. Rendering involves two basic processes of first separating the fat and then drying the residue. The most common method used to extract fat from the tissue is heating.[58] Different types of thermal processing are involved in rendering of poultry fat.

Piette et al.[59] inoculated one set of finely homogenized chicken skin samples with *Acinobacter* sp., *Bronchothrix thermosphacta*, *Candida tropicalis*, *Debaromyces hansenii*, *Enterobacter agglomerans*, *Enterococcus faecalis*, a *Lactobacillus* spp. or *Pseudomonas fluorescens*, while the control samples were not inoculated. Both samples were heated to 80 or 50°C to extract fat. Extraction of fat at 80°C resulted in nearly complete inactivation of the indigenous and inoculated microflora, resulting in microbiological counts in the rendered fat of generally below detection level. Conversely, large number of organisms (3.69 to 7.28 $\log_{10}$ CFU/g) survived the 50°C extraction process.

A second study was undertaken by the same researchers[60] to determine the influence of extraction temperature on the recovery of fat from chicken skin. A maximum amount of fat (89.6% of the initial fat) was recovered from homogenized skin heated to 80°, whereas the 50°C rendering temperature resulted in the lowest fat recovery (51.5% of skin fat content).

Sheu and Chen[61] studied the yield and quality characteristics of edible broiler skin fat obtained from five rendering methods: microwave rendering, conventional oven rendering, water cooking, griddle rendering, and deep-fat frying. Microwave rendering produced the highest fat yields (47.5%), followed by deep-fat frying (33.4%), conventional oven baking (31.6%), griddle rendering (25.8%), and water cooking (24.8%). The moisture content of the rendered skin fat was the highest

for the water cooking process (1.43%) and the lowest for the conventional oven baked process (0.19%). No significant differences in free fatty acid contents were observed among the rendering methods.

7.2.4.2 Regulations for Rendered Poultry Meat

Chapter III, Part 315 of the U.S. Food Safety and Inspection Service, Department of Agriculture, describes rendering or other disposal of carcasses and parts passed for cooking. Section 315.1 addresses carcasses and parts passed for cooking, rendering into lard or tallow:

> Carcasses and parts passed for cooking may be rendered into lard in accordance with Sec. 319.702 of this subchapter or rendered into tallow, provided such rendering is done in the following manner:
>
> (a) When closed rendering equipment is used, the lower opening, except when permanently connected with a blowline, shall first be sealed securely by a Program employee; then the carcasses or parts shall be placed in such equipment in his presence, after which the upper opening shall be securely sealed by such employee. When the product passed for cooking in the tank does not consist of a carcass or whole primal part, the requirements for sealing shall be at the discretion of the circuit supervisor. Such carcasses and parts shall be cooked for a time sufficient to render them effectually into lard or tallow, provided all parts of the products are heated to a temperature not lower than 76.7°C (170°F) for a period of not less than 30 minutes.
>
> (b) At establishments not equipped with closed rendering equipment for rendering carcasses and parts passed for cooking into lard and tallow, such carcasses or parts may be rendered in open kettles under the direct supervision of a Program employee. Such rendering shall be done during regular hours of work and in compliance with the requirements as to temperature and time specified in paragraph (a) of this section.

Part 315, "Rendering or Other Disposal of Carcasses and Parts Passed for Cooking," describes carcasses and parts passed for cooking and their utilization for food purposes after cooking:

> Carcasses and parts passed for cooking may be used for the preparation of meat food products, provided all such carcasses or parts are heated to a temperature not lower than 76.7°C (170°F) for a period of not less than 30 minutes either before being used in or during the preparation of finished product.

7.3 EGG PRODUCTS

As foods of animal origin, eggs may be contaminated with a variety of potentially pathogenic microorganisms. Understanding and controlling the microbiological composition of eggs are issues of importance in terms of both ensuring product

safety and providing acceptable refrigerated shelf life. Because many *egg products* provide nearly ideal growth media for a wide variety of bacterial pathogens, tolerances for viable microorganisms in finished products are quite small.

Over the last century, the growth of the egg products industry has been linked to advances in egg processing, packaging, and distribution technologies. At the expense of grade A shell eggs, a variety of processed egg products have emerged as growing segments of the total egg market.[62] Refrigerated liquid egg products include liquid whole egg (LWE), scrambled egg mixes (i.e., whole egg plus nonfat dried-milk solids and vegetable oil), egg white (albumen), egg yolk, and various blends of yolk and white.[62] Some nonegg ingredients that are sometimes added to preserve or improve the physical characteristics and functional performance of egg products include carbohydrates (e.g., corn syrup, sucrose), hydrocolloids (e.g., gums, starches), salt, and citric acid.[62] In a conventional egg processing facility, the sequence of operations for producing liquid egg involves sorting to remove leakers and inedibles, movement of eggs through an egg washer, rinsing in a solution containing 100 to 200 ppm available chlorine, mechanical egg breaking, collection (either as whole egg or separated albumen and yolk), homogenization (either before or after heat treatment), pasteurization, cooling, packaging, quality assuarance testing, and distribution (either frozen or refrigerated). Details of these procedures are provided by Stadelman and Cotterill.[63]

Among the advantages cited for the use of refrigerated liquid egg over shell eggs or frozen egg blends are consistent quality, convenience, storage space savings, elimination of freezing costs, and labor savings at the point of use. Because such products are thermally processed (pasteurized) before packaging and distribution, they offer improved shelf stability and microbiological safety relative to fresh shell eggs.[62]

7.3.1 Development and Purpose of Egg Pasteurization

7.3.1.1 Historical Background

The storage stability and safety of refrigerated egg products are closely linked to the microbiological quality of the final packaged product at the time when it enters the distribution chain. The primary means of ensuring the microbiological safety of liquid egg products is the use of appropriate egg pasteurization processes. The term "pasteurization" refers to the heat treatment of foods at temperatures below those needed for complete sterilization.[64] As a result of product pasteurization, some microorganisms are inactivated, some may be attenuated (i.e., sublethally injured), while bacterial spores may be stimulated to germinate.[64] In the current regulatory context, minimum pasteurization processes have been designed to destroy certain target microbial pathogens in specific foods. Enhanced microbial shelf stability is an additional benefit of pasteurization, provided that the spoilage organisms present in the raw product are relatively heat sensitive or are prevented from multiplying through the use of controlled refrigeration, freezing, or other preservation technologies.

Pasteurization of liquid egg products was first used commercially in the U.S. in 1938, primarily as a means of extending the shelf life of frozen liquid egg products.[65] A small, gradual increase in the numbers of companies using thermal treatments for liquid eggs occurred in the 1940s and 1950s. Brant et al.[66] reviewed the early literature on batch pasteurization of liquid eggs. At present, most egg processors in the U.S. utilize continuous egg pasteurization processes. Regulations promulgated by the USDA and the FDA regarding the incidence of *Salmonella* in processed egg products made liquid pasteurization virtually mandatory in 1966.[63] The Egg Products Inspection Act of 1970 brought egg pasteurization requirements in the U.S. under more uniform regulatory control.[67]

7.3.1.2 Egg Pasteurization and *Salmonella* Safety

Current USDA regulations stipulate that liquid, frozen, and dried whole egg, yolk, and whites be pasteurized or otherwise treated to inactivate all viable salmonellae.[64] It is important to note that *Salmonella* is the only bacterial pathogen specifically addressed within the context of these regulations.[68] A limiting factor in the development of egg pasteurization processes is the fact that the time and temperatures that inactivate salmonellae in egg products are at or near those that adversely affect the physical and functional properties of the egg proteins.[67] USDA-mandated egg pasteurization specifications, listed in the Code of Federal Regulations (Title 7, Section 59.570), require that every particle of egg be held for at least a specified time and temperature to "assure complete pasteurization" (Subsection b) and to produce "a *Salmonella*-negative product" (Subsection c).[69]

The pasteurization requirements prescribed by the USDA vary according to the egg product due to the susceptibility of certain egg fractions (e.g., unsupplemented egg white) to heat-induced protein denaturation. Current minimum time–temperature combinations for the average particle range from 6.2 min at 55.6°C (for unsupplemented albumen) to 3.5 min at 63.3°C (for salt whole egg, sugar yolk, or salt yolk).[69] The liquid egg pasteurization requirements of a number of Asian and European countries and the U.K. were summarized by the International Commission on Microbiological Specifications for Foods[67]; for liquid whole egg, these processes range from 2.8 min at 61.7°C (Northern Ireland) to 9 min at 65.2°C (Germany). The predicted microbial lethality of such processes is prescribed only for *Salmonella* spp. In the U.S., a 3.5-min holding time at 60°C is said to yield a 9 log cycle (9-D) reduction in the viable *Salmonella* population (where 1-D results in a 90% reduction in the target population) in the average particle of LWE. Under laminar flow conditions, a 9-D process for inactivation of salmonellae would be equivalent to only a 4.5-D process within the fastest-moving particle of egg. The time–temperature combinations prescribed in 1966 for other liquid egg products (Table 7.2) were reportedly designed to provide "approximately equal pasteurization effectiveness."[68]

In recent years, a renewed interest has emerged to more accurately define the microbiological safety of current USDA-mandated pasteurization processes.

TABLE 7.2
Requirements for the Conventional Pasteurization of Liquid Egg Products in the U.S.

Liquid Egg Product	Minimum Temperature (°C)	Minimum Time (min)
Albumen (without use of chemicals)	56.7	3.5
	55.6	6.2
Whole egg	60.0	3.5
Whole egg blends (less than 2% added nonegg ingredients)	61.1	3.5
	60.0	6.2
Fortified whole egg and blends (24–38% egg solids, 2–12% added nonegg ingredients)	62.2	3.5
	61.1	6.2
Salted whole egg (2% or more salt added)	63.3	3.5
	62.2	6.2
Sugared whole egg (2–12% sugar added)	61.1	3.5
	60.0	6.2
Plain yolk	61.1	3.5
	60.0	6.2
Sugared yolk (2% or more sugar added)	63.3	3.5
	62.2	6.2
Salted yolk (2–12% salt added)	63.3	3.5
	62.2	6.2

Source: Egg Pasteurization Manual, ARS 74–78, Agricultural Research Service, U.S. Department of Agriculture, 1969.

Although the implementation of uniform egg pasteurization requirements for liquid egg products has clearly improved consumer food safety, experimental results included in the findings of Schuman and Sheldon[70] and Palumbo et al.[71] indicate that the relative microbial lethality of various liquid egg pasteurization processes does differ relative to that predicted for *Salmonella* spp. in liquid whole egg. This issue represents an active area of microbiological egg safety research and an ongoing issue of regulatory policy debate.

7.3.1.3 Egg Pasteurization and Shelf-Life Extension

In addition to providing a margin of *Salmonella* safety, a secondary benefit of liquid egg pasteurization is the extension of the refrigerated shelf life of the product. As noted previously, such conventional pasteurization processes do not render the product sterile. Vegetative and spore-forming microorganisms that survive pasteurization may cause liquid egg spoilage during storage, handling, and distribution. Furthermore, microbial contaminants capable of spoiling liquid egg may be introduced into the product during postpasteurization handling.[72]

Pasteurized liquid whole egg and whole egg blends currently constitute the majority of the liquid egg products produced in the U.S.[73] The shelf life of conventionally pasteurized liquid whole egg is relatively short, ranging from 12 days at 2°C to 5 days at 9°C.[74] Because of such shelf-stability limitations, liquid egg processors have relied upon either rapid (<14 days) transport, using requirements for refrigerated liquid whole eggs, or frozen storage and distribution of the pasteurized packaged product.[72] While extending shelf life, the process of freezing and thawing whole egg products yields several undesirable physicochemical changes, including gelation of the yolk proteins, phase separation, color changes, and increased viscosity.[75] The functional properties of whole egg products may also be diminished as a result of frozen storage.[76,77]

7.3.1.4 Ultrapasteurized, Aseptically Packaged Liquid Whole Egg

In 1987, Ball and coworkers[72] documented the development of ultrapasteurization processes (i.e., heating at >60°C for <3.5 min), which, when coupled with *aseptic processing* and packaging, yielded LWE with a shelf life of 3 to 6 months at 4°C.[72] At present, commercially ultrapasteurized LWE has a code-dated shelf life of 10 weeks at 4°C.[78] The extended shelf life of this nonsterile product is dependent on (1) the use of raw LWE of excellent initial microbiological quality, (2) unique high-temperature short-time thermal treatments, (3) packaging of the product using an aseptic filler within a sterile zone, and (4) maintenance of proper refrigeration temperatures (1 to 4°C) throughout distribution and retail storage. In 1994, 175 to 200 million pounds of extended-shelf-life LWE were produced using this ultrapasteurization and aseptic packaging technology.[78] Ultrapasteurized LWE products offer a number of advantages over both frozen liquid eggs and shell eggs, including consistent product quality, convenience, portion control, storage space savings, and economy (in terms of time and labor savings and the elimination of the need for frozen distribution).[78]

Relative to conventionally pasteurized LWE, the ultrapasteurized product offers enhanced microbiological shelf stability (at 1 to 4°C) and a greater assurance of *Salmonella* safety. In addition, achieving a predicted 9-D inactivation of the bacterial pathogen *L. monocytogenes* was one of the design criteria used by Ball and coworkers in the development of egg ultrapasteurization processes.[79] While conventional liquid whole egg pasteurization represents only a 2.1- to 2.7-D process with respect to *L. monocytogenes* inactivation,[80] the egg ultrapasteurization processes of Ball and coworkers were demonstrated to provide process lethalities against *Listeria* of at least 6.7 to >7.3 log cycles.[81]

7.3.1.5 Extended-Shelf-Life Liquid Egg Substitutes

Liquid egg substitutes represent another category of extended-shelf-life liquid egg products. These products were developed nearly 20 years ago to simulate the features of LWE, yet with little or none of the cholesterol or fat normally present in yolk or whole egg. Egg substitutes consist primarily of liquid egg white plus

a variety of nonegg ingredients (e.g., nonfat dried milk, vegetable oils, emulsifiers, stabilizers, gums, artificial color, vitamins, minerals) that mimic to an extent the appearance, flavor, and texture of LWE.[62] These products are pasteurized and filled into a variety of retail packages, generally in a nonaseptic manner. The finished product has a pH of 6.4 to 8.0 and a code-dated refrigerated shelf life of 8 to 12 weeks at 1 to 4°C.[82]

7.3.1.6 In-Shell Pasteurized Eggs

Because of the increased concern over the egg-associated food-borne pathogen *S.* Enteritidis (SE), research efforts have focused on developing an *in-shell pasteurization* process for producing pathogen-free shell eggs that can be used as is or in products receiving little or no additional heating prior to consumption. During the 1940s and 1950s, the thermal treatment of eggs to prevent embryonic growth in fertile eggs, to reduce the incidence of spoilage during long-term storage, and to maintain internal quality received considerable research attention. Stadelman[83] presents a concise review of that research with particular attention directed toward the practice of *thermostabilization*, a patented process[84] whereby shell eggs are placed in heated water or oil to extend storage life and prevent spoilage and deterioration of egg shell quality. Hou et al.[85] documented the feasibility of combining water bath and hot-air oven processing to reduce viable SE populations within inoculated intact shell eggs. In a related study, Schuman et al.[86] evaluated the effects of water immersion heat treatments on the inactivation of SE within intact shell eggs. Six pooled strains of SE (ca. 3×10^8 CFU, inoculated near the center of the yolk) were completely inactivated within 50 to 57.5 min at a water bath temperature of 58°C and within 65 to 75 min at 57°C (an 8.4- to 8.5-D process per egg). Haugh unit values and albumen whip times increased during heating, although yolk index and albumen pH values were unaffected. The authors[86] concluded that broken-out whole egg or yolk from immersion-heated shell eggs could provide *Salmonella*-free ingredients for the preparation of a variety of minimally cooked foods of interest to consumers and food service operators.

7.3.2 General Egg Safety Considerations

Foods of animal origin, including dairy products, meat, poultry, and eggs, have long been recognized as the primary source of many of the bacteria responsible for food-borne infections and intoxications.[87,88] Based on the published literature, a list of currently recognized bacterial pathogens with a reasonable likelihood of occurrence in blended raw egg products could include *Salmonella* spp., *Staphylococcus aureus*, *Bacillus cereus*, *L. monocytogenes*, *Aeromonas hydrophila*, *Yersinia enterocolitica*, and *Campylobacter* spp. Between 1973 and 1987, eggs (unspecified product types) were linked to only 1% of all outbreaks and 1% of all cases with known vehicles.[89] The proportion of salmonellosis outbreaks associated with eggs increased from none (in 1973–75) to 1% (1976–78), 4% (1979–81), 3% (1982–84), and 8% (1985–87). In a more recent review of international food-borne disease

surveillance statistics, Todd[90] reported that contaminated meat products were linked to more outbreaks of food-borne disease (i.e., 16%) in the U.S. than all other food product categories. Of the 22 countries surveyed, France and Spain were the only two nations to report that eggs and egg products were the vehicles most frequently involved in outbreaks of food-borne illness.

7.3.2.1 *Salmonella*

Of the above-listed pathogens, *Salmonella* species have the greatest historical association with contaminated eggs and egg products. The bacterial pathogens *L. monocytogenes* and *A. hydrophila* pose particular concerns if present in chilled liquid egg products due to their ability to multiply in foods at proper refrigerated storage temperatures (i.e., 5°C). Over the last decade, the egg-associated serotype *S.* Enteritidis has emerged as one of the leading causes of food-borne salmonellosis in the U.S., Canada, the U.K., France, Spain, and other nations.[90] In the U.S., the number of cases of salmonellosis caused by *S.* Enteritidis increased slowly but steadily between 1976 and 1987. Since 1988, the isolation rate for *S.* Enteritidis from clinical cases of salmonellosis has risen sharply, possibly as a result of this serotype becoming more invasive in egg-laying flocks.[91] Since 1990, the number of salmonellosis cases caused by *S.* Enteritidis have exceeded those attributed to all other serovars, including *S.* Typhimurium.[92] Epidemiological studies indicate that grade A shell eggs are a major source of *S.* Enteritidis infections in humans.[93] Between January 1985 and May 1987, 35 food-borne *S.* Enteritidis outbreaks of known cause were reported to the CDC; of these, 27 outbreaks (77%) were epidemiologically linked to the consumption of foods that contained eggs or eggs alone, either inadequately cooked or eaten raw in such foods as hollandaise sauce, homemade eggnog, or Caesar salad dressing.[93] Between 1985 and 1991, a total of 380 *S.* Enteritidis outbreaks were reported in the U.S., involving 13,056 cases and 50 deaths. Grade A shell eggs were implicated in 82% of the outbreaks.[94]

Without question, the implementation of the Egg Products Inspection Act of 1970 and its accompanying liquid egg pasteurization requirements has dramatically reduced the incidence of egg-associated salmonellosis in the U.S.[95] The use of pasteurized liquid egg products (rather than shell eggs) for the preparation of a variety of egg dishes is viewed as the major means for preventing salmonellosis outbreaks, especially in food service settings and nursing homes.[69] When pasteurized liquid egg products are properly packaged, stored, and handled by food preparers, egg-associated risks of salmonellosis may be significantly reduced. To date, no salmonellosis outbreaks in the U.S., England, or Wales have been associated with foods containing pasteurized liquid egg.[96]

7.3.2.1.1 Thermal Resistance of Salmonella in Eggs and Egg Products

Because liquid egg pasteurization processes were designed to ensure inactivation of *Salmonella,* numerous investigators have sought to define the thermal inactivation kinetics of this important pathogen.[67,96] The conventional pasteurization process for

LWE (i.e., 3.5 min at 60°C for the average particle) was based on the assumption that typical strains of *Salmonella* have a D value at 60°C of approximately 0.4 min in blended whole egg.[68] Despite differences in *Salmonella* serovars/strains and in the experimental procedures used, this assumption has proven to be reasonably accurate, based on kinetic data from a variety of research laboratories.

Representative decimal reduction time data for *Salmonella* Oranienburg and *S.* Typhimurium in various whole egg, yolk, and egg white products are presented in Table 7.2.[67] The predicted D value for *S.* Oranienburg in LWE (pH 7.0) at 60°C is 0.3 min when extrapolated from the decimal reduction time curve of Cotterill et al.[97] Humphrey et al.[98] reported D values of 0.20 and 0.26 min for two *S.* Typhimurium strains heated in LWE at 60°C. As presented in Table 7.3, *S.* Oranienburg and *S.* Typhimurium were more heat resistant in plain yolk than in LWE (pH 7. 0); in contrast, these strains were more heat sensitive in unsupplemented albumen (pH 9.2 to 9.5) than in whole egg. Similar heat resistance trends were documented by Humphrey et al.,[98] who evaluated the heat resistance of three *S.* Enteritidis isolates and two *S.* Typhimurium isolates. D values for the five isolates ranged from 0.20 to 0.44 min in LWE heated at 60°C.[98] In a similar study of 17 strains of *S.* Enteritidis (primarily phage type 8), Shah and coworkers[95] reported that D values at 60°C ranged from 0.20 to 0.52 min in LWE (mean = 0.32 min). Even with a D value of 0.52 min (the highest value reported in the study), conventional pasteurization of LWE at 60°C for 3.5 min would provide a predicted lethality of 6.7 log cycles. Baker[99] used a continuously stirred three-neck flask to assess the thermal resistance of nine strains of *S.* Enteritidis in raw LWE. D values at 60°C ranged from 0.31 to 0.69 min (mean = 0.42 min). When using a plate pasteurizer, Michalski et al.[100] reported a greater than 9-D reduction in *S.* Enteritidis in whole egg at 60.0°C for 3.5 min. They attributed the greater kill to better mixing due to turbulent flow in the right-angle turns in the holding tube of the plate pasteurizer. Based on the above decimal reduction time data, a 3.5-min process at 60°C would yield a 5.1 to 11.3 log reduction in the viable *S.* Enteritidis population in LWE.

The published thermal resistance data for *Salmonella* spp. heated in liquid egg white or liquid yolk have varied more widely according to the strains tested, the investigator, and the laboratory methods used. For example, Humphrey et al.[98] reported a D value of 1.0 min for *S.* Typhimurium heated at 55°C in albumen. Using a different strain, Garibaldi et al.[101] obtained data that yielded a predicted D value of only 0.58 min at 55°C. Palumbo et al.[102] determined survival of a six-strain mixture of *S.* Enteritidis, *S.* Typhimurium, and *S.* Senftenberg (not 775W) in egg white using a submerged vial technique. As reported in previous studies,[103] these researchers also reported that *Salmonella* is much more heat resistant at low albumen pH. Log reductions using a 3.5-min holding time at 56.6°C were 0.97 at pH 7.8, 1.64 at pH 8.2, 2.20 at pH 8.8, and 4.24 at pH 9.3. Michalski et al.[100] reported a 7.5 D value for a five-strain cocktail of *S.* Enteritidis in egg white (pH 9.0, 100-µl capillary tubes). In liquid egg yolk, the D values at 60°C reported by Humphrey et al.[98] (D = 0.8 min) and Garibaldi et al.[104] (D = 0.4 min) also differed substantially for different strains of *S.* Typhimurium. Palumbo and

TABLE 7.3
Thermal Resistance of *Salmonella* spp. in Various Liquid Egg Products

Test Organism	Product	D Value (min) at °C							z Value (°C)	Reference
		50	52	54	56	58	60	62		
S. Oranienberg	Whole egg, pH 7.0	—	—	4	1.7	—	—	—	4.5	97
	Whole egg + 10% sucrose	—	—	25	10	3.5	—	—	4.3	
	Whole egg + 10% salt	—	—	30	12	6	3	—	7.0	
S. Typhmurium	Whole egg, pH 5.5	—	—	17	5.5	—	—	—	4.2	143
	Whole egg + sorbic acid, 100 ppm	—	—	14	4.5	—	—	—	4.1	
	Whole egg + – propiolactone, 100 ppm	—	—	11	4.5	—	—	—	4.5	
	Whole egg + benzoic acid, 500 ppm	—	—	6.5	2.2	—	—	—	4.1	
S. Typhmurium	Egg yolk	—	—	9.5	3	1.3	0.4	—	4.4	104
	Egg yolk + 10% sucrose	—	—	75	25	10	4	—	4.8	
	Egg yolk + 10% salt	—	—	110	45	17	6	2	4.6	
S. Tphimurium	Egg white, pH 9.2	10	3.5	1	—	—	—	—	4.2	104
	Egg white, pH 9.2, + 10% sucrose	20	7	2.5	0.8	—	—	—	4.3	
	Egg white, pH 7.3, + aluminum salt	—	22	6.5	2.5	—	—	—	4.2	
Mix of 3 strains	Egg white, pH 9.5	9	3.5	1.1	—	—	—	—	4.8	144
	Egg white, pH 9.5, + 0.5% polyphosphate	1.1	0.6	0.3	—	—	—	—	4.6	

coworkers[71] reported D values at 60°C of 0.55 to 0.75 min for six *Salmonella* spp. heated in unsupplemented liquid yolk. The D values for 10% sugared yolk at 63.3°C was 0.72 min, while 10% salted yolk had an observed D value of 11.50 min at 63.3°C. Generally, *Salmonella* spp. are more heat resistant in yolk, but yolk is less sensitive to higher temperatures, as it affects functional properties. However, the addition of salt and sugar apparently further increases the heat resistance of these organisms in yolk products, especially salted yolk at 10 and 20%.[71,104] In contrast, Michalski et al.[100] observed an 8-D reduction in 10% salted yolk at 63.3°C and a 1-D reduction in egg yolk containing both 5% salt and 5% sugar using capillary tubes. These noted differences in heat resistance may be partially explained by the use of capillary tubes, which largely eliminate the come-up time and the effect of viscosity.[105]

In summary, the thermal resistance data discussed above indicate that conventional pasteurization processes for liquid yolk, liquid albumen (pH 9.2), and LWE are predicted to provide minimum process lethalities for *Salmonella* spp. of 7.75, 6.2, and 5.1 log cycles, respectively. It should be noted that differences in the experimental methodologies used in assessing the thermal resistance of salmonellae (and other pathogens) in liquid egg may impact the accuracy of the D values reported. In addition to the major factors affecting the wet-heat inactivation of microorganisms (e.g., proximate composition of the heating menstruum, moisture content, pH, inoculum concentration, growth conditions, etc.), the geometry of the heating vessel (e.g., test tubes, reaction vials, capillary tubes, or flasks) and its headspace volume and orientation within the heating bath may bias the resultant batch kinetic data.[106–108] The analysis of subsamples drawn from a single large heated vessel appears to be particularly unreliable. For example, Dabbah et al.[109] reported exceptionally high D values (i.e., >6.0 min at 60°C) when *Salmonella* spp. were heated in LWE in a 300-ml stirred glass flask. While there remains no general consensus on the best experimental methodology for bacterial thermal resistance testing, the advantages of using small (i.e., very low volume capillary tubes), sealed and fully immersed heating vessels have been documented.[70,107,110]

Several investigators have evaluated the efficacy of simulated domestic or food service cooking methods as means to inactivate *S.* Enteritidis in grade A shell eggs. Saeed and Koons[111] asked persons who identified themselves as regular egg consumers to cook sets of 11 eggs by each of three methods. As expected, the individuals varied considerably in the times used to cook the product to their preferred degree of doneness. When the contents of shell eggs contained 10^1 to 10^3 CFU per ml, viable salmonellae were detected in 24% of fried eggs, 15% of scrambled eggs, and 10% of omelets tested. Baker[99] reported that endpoint internal temperatures of 74°C for scrambled eggs and 61 to 70°C for fried eggs were necessary to ensure the inactivation of *S.* Enteritidis. With respect to hard-cooked egg preparation, Licciardello et al.[112] and Baker et al.[113] demonstrated that when shell eggs were internally inoculated with 10^8 to 10^9 *Salmonella* cells, the pathogen was effectively inactivated when the eggs were placed directly into boiling water for a minimum of 7 to 8 min. While the above procedures provide valuable guidance for the safe preparation of fully cooked egg dishes, there is a need for

the egg industry to provide refrigerated shell eggs with a greater assurance of microbiological safety to retail consumers and the food service industry. Shell egg safety improvements of this kind would be particularly valuable if they would permit the safe preparation of a variety of foods (e.g., soft-boiled eggs, soft-poached eggs, sunny-side fried eggs, gourmet sauces, salad dressings, custards, etc.) that call for the use of fresh shell eggs as ingredients.

7.3.2.2 *Listeria* and *Aeromonas*

Over the last 10 to 15 years, both *L. monocytogenes* and *A. hydrophila* have been identified as emerging food-associated pathogens. Common features of concern to public health agencies and food processors include the psychrotrophic nature of these pathogens, their wide distribution in nature and raw agricultural commodities, their ability to persist in moist low-nutrient niches in processing plants, the special techniques required to identify low numbers of each pathogen amidst a diverse background microflora, and the fact that the infectious dose levels for *L. monocytogenes* and *A. hydrophila* are currently unknown.[114,115] *L. monocytogenes* is relatively resistant to environmental extremes (e.g., low pH, high sodium chloride levels, reduced water activity, low nutrient density, freeze–thaw cycling) and is among the most heat resistant vegetative bacterial pathogens of concern in foods.[114] Although there have been no documented cases of listeriosis linked to the consumption of eggs or egg products, *L. monocytogenes* has been associated with laying hens, raw and cooked poultry meat products, and commercially blended raw liquid whole egg. Of the 23 avian species in which listeriosis has been documented, chickens have remained the most common avian host for nearly 60 years.[116] Interest in risks associated with poultry-borne listeriae has increased as a result of several cases of human listeriosis in the U.S. and the U.K. that were linked to consumption of turkey frankfurters and ready-to-eat, cook-chill chicken.[116]

In the first published survey of its kind, Leasor and Foegeding[117] reported that *Listeria* spp. were isolated from 15 of 42 (36%) previously frozen samples of raw, commercially broken LWE obtained from 6 of 11 (54%) commercial egg processors located throughout the U.S. Of the 15 *Listeria*-positive samples, 15 contained *L. innocua* and 2 samples contained *L. monocytogenes.* In a survey of the largest egg processing plant in Northern Ireland, Moore and Madden[118] isolated *Listeria* spp. from 125 of 173 (72%) in-line filters used to remove shell debris from raw blended LWE. The only species isolated were again *L. innocua* (62%) and *L. monocytogenes* (37.8%). Additional LWE samples (approximately 140 ml each) were collected just prior to the pasteurizer on nine consecutive days, and the highest concentration of *Listeria* spp. obtained was approximately 40 listeriae per ml of liquid egg.

The results of a large, unpublished U.S. national survey conducted by the USDA (Agricultural Marketing Service, Poultry Division, Egg Products Inspection Branch) in 1992 demonstrated that 32.8% of all raw liquid egg products (n = 1555) and 2.9% of all conventionally pasteurized liquid egg products (n = 1292) tested positive for the presence of *Listeria* spp. In the same survey, LWE products

containing citric acid showed *Listeria* spp. incidence rates of 40.0% (for 90 samples of raw LWE) and 3.2% (for 95 samples of conventionally pasteurized LWE). *Listeria* spp. were also isolated from 42 of 98 (42%) environmental processing plant swab samples collected during the USDA national survey. In a survey of two egg washing facilities in southeastern Ontario, Laird et al.[119] isolated *L. innocua* in egg wash water (pH 10.2 to 11.8) and certain environmental samples (i.e., preloaders, sewer drains, and floors). In summary, the above surveys indicate that *L. monocytogenes* and *L. innocua* occur in commercially processed raw liquid egg products at relatively high incidence rates, yet at fairly low concentrations (estimated at <100 CFU per ml). Nonetheless, the refrigerated storage life of extended-shelf-life liquid egg products permits ample time for this pathogen to multiply to high cell populations if present (as a thermal process survivor or a postprocess contaminant) in the finished, packaged product.

7.3.2.2.1 Thermal Resistance of Listeria in Eggs and Egg Products

The thermal resistance of *L. monocytogenes* in a variety of foods and microbiological media has been reviewed by Mackey and Bratchell[120] and Farber and Peterkin.[114] The literature to date supports the contention that *L. monocytogenes* is among the most heat resistant non-spore-forming pathogens associated with foods, with a calculated Z_D value range (in most foods and broths) of 6.7 to 6.9°C.[120] In the aftermath of the 1983 milk-associated listeriosis outbreak in Massachusetts, the adequacy of fluid milk pasteurization processes to inactivate *L. monocytogenes* was the subject of numerous publications. In a summary of this research, Mackey and Bratchell[120] predicted that high-temperature short-time pasteurization conditions (71.7°C for 15 sec) and vat pasteurization conditions (63°C for 30 min) would achieve 5.2- and 39-D reductions in the viable *Listeria* populations, respectively. These results are noteworthy in that a similar 5-D lethality standard for *L. monocytogenes* could be considered in the context of evaluating desirable or achievable pathogen-reducing requirements for continuously pasteurized (conventional) liquid egg products.

In 1990, Foegeding and Leasor[80] published a study in which D values were determined for five strains of *L. monocytogenes* in sterile raw LWE. The experimental units consisted of 0.05-ml samples of inoculated LWE within sealed glass capillary tubes that were heated by immersion in a preheated water or oil bath. D values for strain F5069, the most heat resistant isolate tested, averaged 22.6, 7.1, 1.4, and 0.20 min at 51, 55.5, 60, and 66°C, respectively.[80] For the five strains evaluated, minimum conventional pasteurization conditions for LWE (60°C for 3.5 min) were predicted to represent 2.1- to 2.7-D processes with respect to *L. monocytogenes*. In a subsequent study, Foegeding and Stanley[81] determined thermal death times (F values) for *L. monocytogenes* F5069 in raw LWE using the immersed sealed capillary tube procedure (0.05 ml of liquid egg per tube). This *Listeria* strain was eliminated from inoculated samples (5.0×10^6 to 2.0×10^7 CFU/tube) after 16, 8, 4.5, 1.6, and 0.6 min at 62, 64, 66, 69, and 72°C, respectively.

Bartlett and Hawke[121] evaluated the heat resistance of *L. monocytogenes* strains Scott A (a clinical isolate) and HAL 975E1 (an egg isolate) in the following five liquid egg products: liquid whole egg (LWE), 10% NaCl whole egg (LWEN), 10% sucrose whole egg (LWES), 10% NaCl egg yolk (EYN), and 10% sucrose egg yolk (EYS). The presence of salt decreased the water activity (a_w) of the products to a greater extent than sucrose; all water activity values were >0.91 except for salt yolk (a_w = 0.867). Survivor curves were constructed and D values calculated based on data from a 0.2-ml submerged sealed test tube procedure. The relative heat resistance of *L. monocytogenes* in the five products was as follows: heat resistance in salted egg yolk > salted liquid whole egg >> sucrose egg yolk ≥ sucrose liquid whole egg ≥ liquid whole egg. These thermal resistance trends were very similar to those reported by Cotterill et al.[97] for *S.* Oranienburg in liquid egg products. Based on current U.S. conventional egg pasteurization requirements, Bartlett and Hawke[121] predicted that process lethalities against *L. monocytogenes* Scott A would range from 0.2 log cycle (for salt egg yolk) to 1.8 log cycles (for sucrose LWE). Similar thermal resistance trends were reported by Palumbo et al.,[71] who determined D values for six pooled strains of *Salmonella* spp. and for five pooled strains of *L. monocytogenes* inoculated in plain liquid egg yolk (EY) and in various EY products containing added salt or added sucrose. Both pathogens were more heat resistant in EY + 10% NaCl than in EY + 10% sucrose or in plain EY. Based on D values derived by using a submerged capped test tube procedure, the lethality of USDA-mandated conventional egg pasteurization processes was estimated to range from 0.3 log cycle (in EY + 10% NaC1) to 6.1 log cycles (in plain EY) for *Salmonella* spp., and from 0.2 log cycle (in EY + 10% NaCl) to 3.3 log cycles (in EY + 10% sucrose) for *L. monocytogenes*.[71]

In summary, the above four publications indicate that the margin of safety provided by conventional pasteurization requirements for LWE, plain yolk, and products containing added sucrose is not large, especially if *L. monocytogenes* is present in the raw bulk tank at levels of >100 CFU/ml. In NaCl-supplemented LWE or yolk, conventional pasteurization would be inadequate to inactivate even 10 CFU/ml of *L. monocytogenes.* These findings take on additional significance in light of a recent USDA document that details the criteria for approval to produce and market liquid egg products with an extended shelf life (i.e., >4 weeks at 4.4°C).[122] In order to gain regulatory approval to produce such products, companies must pasteurize the product at 60°C for 3.5 min. If alternative thermal processes are used, the company must provide laboratory data demonstrating that the thermal process yields a 7 log reduction in the viable *L. monocytogenes* population. As noted previously, the data of Foegeding and Leasor[80] and Bartlett and Hawke[121] clearly demonstrate that a 3.5-min process at 60°C represents only a 1.7- to 2.7-D *Listeria* inactivation process. Thus, the proposed 7-D lethality requirement appears to be unduly harsh and may not permit production of liquid egg products of acceptable organoleptic and functional quality. At the time of this review, no studies documenting the thermal resistance of *Listeria* spp. in liquid egg white or in liquid egg substitutes were available in the published scientific literature.

Two research groups have evaluated the survival potential of *L. monocytogenes* in eggs heated under simulated food service or domestic conditions. Using inoculated shell eggs (containing >5 × 10^5 CFU/g of egg contents), Urbach and Shabinski[123] reported that viable listeriae were isolated from fried eggs cooked in a manner that coagulated the white yet left a soft yolk. In a more detailed study, Brackett and Beuchat[124] reported that frying inoculated whole eggs sunny-side up until the albumen was partially coagulated reduced both low (10^2 CFU/g) and high (10^5 CFU/g) *L. innocua* by only 0.4 log CFU/g. In contrast, cooking one or three scrambled eggs on a skillet to an endpoint internal temperature of 70 to 73°C reduced the lower inoculum by >1.8 log cycles, and the higher inoculum by 3.0 log cycles. The authors[124] concluded that although it is unlikely that large numbers of listeriae would survive such cooking procedures unless present at >10 CFU/g, it would be prudent for persons who might be especially susceptible to listeriosis to consume only thoroughly cooked eggs.

The significance of *A. hydrophila* as a potential food-borne pathogen has been the subject of publications by Buchanan and Palumbo,[125] Morgan and Wood,[126] and Abeyta et al.[127] Aeromonads have been isolated from a wide variety of refrigerated foods of animal origin, including finfish, shellfish, raw milk, whipped cream, butter, veal, beef, lamb, pork, and poultry products.[128] Poultry products from which *A. hydrophila* have been isolated include raw chicken (unspecified cut) and chicken liver,[129] chicken thigh meat,[130] and fresh broiler carcasses.[131] *Aeromonas* spp. have also long been recognized as potential spoilage organisms in checked or cracked shell eggs.[132]

Although published data on the incidence of *Aeromonas* spp. in raw or pasteurized LWE produced in the U.S. are currently unavailable, the pathogen has been isolated from commercially broken raw LWE in Japan[133] and Australia.[134] In the Australian study, MacKenzie and Skerman[134] reported that *A. hydrophila* was the fourth most predominant strain present in samples of spoiled LWE, and aeromonads were isolated with higher frequency when liquid egg was stored at 4 or 10°C, compared to 20 or 25°C. Kraft and coworkers[135] characterized the microflora present in fresh raw LWE obtained from two Iowa egg-breaking plants. The five most prevalent bacterial genera (of 148 total isolates) were *Pseudomonas* (47.3%), *Arthrobacter* (18.2%), *Aeromonas* (17.6%), *Escherichia* (8.8%), and *Micrococcus* (2.7%).

7.3.2.2.2 Thermal Resistance of Aeromonas in Eggs and Egg Products

The documented growth potential of *A. hydrophila* in LWE at 6.7°C (slight temperature abuse) underscores the importance of ensuring the adequacy of egg pasteurization/ultrapasteurization processes with respect to *Aeromonas* inactivation. To date, only two published studies have addressed the heat resistance of *A. hydrophila* (human clinical isolate) in an egg product. Nishikawa et al.[136] reported that a 4-min process at 55°C was sufficient to inactivate the pathogen (initially inoculated at 10^8 CFU/ml) in raw liquid egg yolk heated in capped test tubes dipped in a preheated water bath. The authors[136] also demonstrated that *A. hydrophila* was

substantially less heat resistant than a clinical isolate of *S.* Typhimurium when heated in liquid yolk. Because the study was conducted at only one water bath temperature (55°C, without correction for come-up times), neither D nor z_D values were reported. In the second study, Schuman et al.[105] sought to kinetically characterize the heat resistance of *A. hydrophila* in raw liquid whole egg using an immersed sealed capillary tube procedure. Decimal reduction times of four individual strains of *A. hydrophila* at 48, 51, 54, 57, and 60°C were found to range from 3.62 to 9.43 min (at 48°C) to 0.026 to 0.040 min (at 60°C). Both egg processing plant isolates were more heat resistant than the ATCC strains. The z_D values were 5.02 to 5.59°C, similar to those for other non-spore-forming bacteria. Although this study indicated that *A. hydrophila* is substantially less heat resistant than *Salmonella* liquid whole egg, it is important for egg processors to take measures to prevent postpasteurization contamination of liquid egg products by *Aeromonas* spp. and other psychrotrophic pathogens, including *L. monocytogenes*. At the time of this review, no other reports on the thermal resistance of *Aeromonas* spp. in other liquid egg products or in shell eggs cooked under simulated food service conditions were available in the published scientific literature.

Although several investigators have attempted to kinetically characterize the thermal inactivation of *A. hydrophila* in model buffer systems and in skim milk,[137,138] each study yielded nonlinear (tailing) survivor curves, which complicated analysis of the thermal destruction data. The previous studies yielded diphasic (tailing) inactivation curves, in which surviving populations of 10^2 to 10^5 CFU/ml of solution were detected long after the initial linear phase of inactivation. For purposes of calculating D values, these authors[138] disregarded the tailing portions of the survivor curves, while noting the potential significance of microbial subpopulations of apparently greater heat resistance than the rest of the inoculum. Using a buffered peptone system, Stecchini et al.[139] reported that the inactivation of *A. hydrophila* in 9-ml capped test tubes was a nonlinear process, best described mathematically by a complex hyperbolic function.

7.4 CONCLUSIONS

Application of heat continues to be the most efficient method for preserving food. Current issues facing producers of poultry products and food processors in general include the persistence of *L. monocytogenes* in RTE products, antibiotic-resistant bacteria, and handling of animal coproducts. The USDA has issued regulations to address the *Listeria* problem in RTE meats, as described in this chapter. The use of antibiotics in animal production is also being addressed by both poultry companies and governing bodies worldwide by reducing or eliminating their use. Between 40 and 50% of a carcass is not destined for human consumption and thus must be handled and recycled if possible. Poultry meat from this nonedible portion is often used as an animal feed component. Concern over the bacterial levels in these products reentering the food cycle through the feed has been debated. The survival of *Salmonella* in poultry meat and bone meal has been shown to be well below levels found in foods for human consumption. The high temperatures and times

used in the rendering process virtually eliminate most vegetative bacterial cells. Other issues, such as mad cow disease, that have not yet affected the poultry industry may affect the handling of these coproducts in the future.

Thermal processing remains the best and most reliable process used to render products safe for consumption by humans and use as animal feed. The fact that the microorganisms can only develop limited resistance to heat, and that this resistance is lost without continued exposure, as well as the relatively low cost have kept thermal processing the chosen method.

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8 Thermal Processing of Fishery Products

Isabel Medina Méndez and José Manuel Gallardo Abuín

CONTENTS

8.1 INTRODUCTION

Heating is the treatment mostly applied in the fish canning industry and is also used in a wide variety of processes, such as cooking, pasteurization, and sterilization of marine products. Each type of process has specific objectives and provokes different chemical and sensorial changes. Sterilization of canned fish is aimed to avoid bacteriological and microbiological contamination, but the

chemical effects affecting color and flavor can be also significant. Industrial treatments usually employed in foodstuffs can mainly modify proteins and lipids and induce interactions among components. Marine lipids with high amounts of polyunsaturated fatty acids are very prone to suffer modifications by heat. The degree, rate, and nature of these reactions depend on the type of product, quality of raw material, and thermal processing employed.

The objective of this chapter is to review the effects that thermal processes have on the quality of seafood. Information on the general principles governing the heat transfer, evaluation, and determination of heat penetration data is not emphasized here.

8.2 MAIN OPERATIONS IN FISH THERMAL PROCESSING

Precooking is relatively severe heat treatment before sterilization. Fish is usually cooked with steam at 100 to 102°C. The main objectives of fish precooking are:

- To prevent its loss during retorting due to partial dehydration of fish muscle
- To remove lipids to avoid off-flavor
- To coagulate the protein
- To produce more palatable food
- To improve the digestibility and to eliminate the meat from the shell in shellfish

The time of precooking depends on the fish species, size, quality of the raw material, and temperature along the backbone. A consequence of thorough cooking is the destruction or reduction of vegetative cells of pathogens that may have been introduced in the process before cooking.

Pasteurization is a mild or moderate treatment, usually performed on fishery products placed into a hermetically sealed container. This process is used to extend the refrigerated shelf life of different seafood.

The purposes of pasteurization are:

- To improve the safety of the product during an extended refrigerated shelf life, which involves eliminating the spores of *Clostridium botulinum* type E and nonproteolytic B and F, which are the types of *C. botulinum* most commonly found in fish
- To eliminate or reduce other target pathogens (e.g., *Listeria monocytogenes*, *Vibrio vulnificus*)

For pasteurization processes that target nonproteolytic *C. botulinum*, generally a reduction of six orders of magnitude in the level of pathogens is suitable. This is called a 6-D process. Examples of properly pasteurized products are blue crabmeat pasteurized to a cumulative lethality of $F_{85°C}$ ($F_{185°F}$) = 31 min, z = 9°C

(16°F) and *surimi*-based products pasteurized at an internal temperature of 90°C (194°F) for at least 10 min. The control of later refrigeration is critical for the safety of these products.

Sous vide is a French term that means "under vacuum." *Sous vide* involves the cooking of fish inside a hermetically sealed vacuum package. *Sous vide* technology or cooking under vacuum defines those foods that are cooked in stable containers and stored in refrigeration. Because these products are processed at low temperatures (65 to 95°C), the sensorial and nutritional characteristics are maximized in comparison with the sterilized products. The final product is not sterile and its shelf life depends on the applied thermal treatment and storage temperature. Because the pasteurization does not produce the commercial sterility, the final fish product requires refrigerated storage. There are not many studies on the effect of *sous vide* pasteurization on the quality of seafood, and more research is necessary.

8.2.1 Thermal Processing for Canned Fishery Products

The heat treatment applied in sterilization of canned fish manufacture is aimed to eliminate pathogenic microorganisms, together with others that cause spoilage during storage. The bacteria vary in their resistance to moist heat, and some can form resistant spores. Among the spore-forming microorganisms, *C. botulinum* types A and B is the most heat resistant, constituting a potential health hazard. For low-acid products with pH values greater than 4.5, such as canned fish, the anaerobic conditions are ideal for growth and toxin production by *C. botulinum*. Therefore, its destruction is the critical parameter used in heat processing. It has been established that the minimum thermal process sufficient for safety should achieve 12 decimal reductions in the population of *C. botulinum* spores; this is known as a 12-D process. For such heat processes, the probability of *C. botulinum* spore survival is 10^{-12}, or one in a million million. This probability of survival is commercially acceptable and does not represent a significant health risk. When the thermal process is sufficient to fulfill the criteria of safety and prevention of nonpathogenic spoilage under normal conditions of storage, the product is "commercially sterile." Figure 8.1 and Figure 8.2 show the calculation of z values and F for the canning of mussels performed at our pilot plant.

There are infinite numbers of time–temperature combinations that can produce commercial sterility, but it is important to establish a combination that provides a final product that retains quality attributes. For this reason, the optimization of thermal processes for nutrition and quality retention is necessary. In this chapter we have summarized the main aspects affecting seafood components subjected to thermal stress.

8.3 PROXIMATE COMPOSITION OF FISH MUSCLE

The muscle of fish contains a series of chemical constituents as proteins, lipids, minerals, and vitamins. Around 60 chemical elements are present in fish muscle: 75% is oxygen, 10% hydrogen, 9.5% carbon, 3% nitrogen, 1.5% calcium, and other traces of elements.

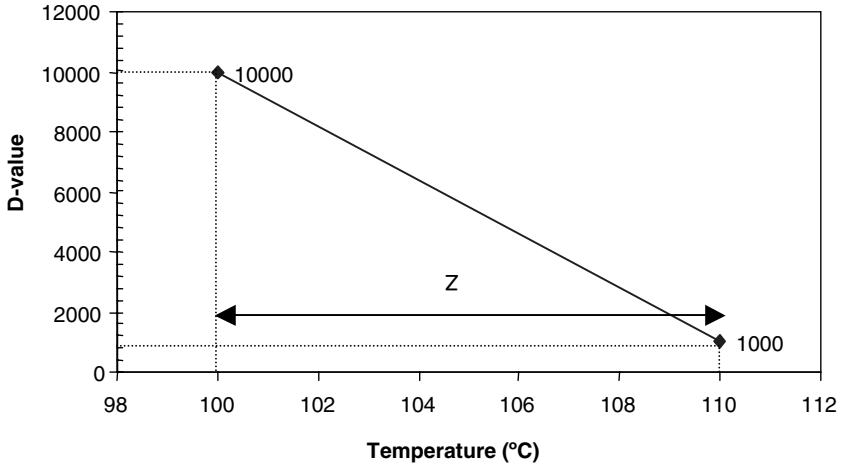

FIGURE 8.1 Curve of decimal reduction time, D value, and z value.

The main obstacle to establish the chemical composition in marine species is the high seasonal variability, especially in their lipid concentration. Intrinsic factors affecting these variations are genetic, morphological, and physiologic, but there are also exogenous factors, such as those derived from life conditions, feeding, and geographical area. The fat or lipid content in fish is highly variable in fish species due to all the above-mentioned aspects. Because of fat variations

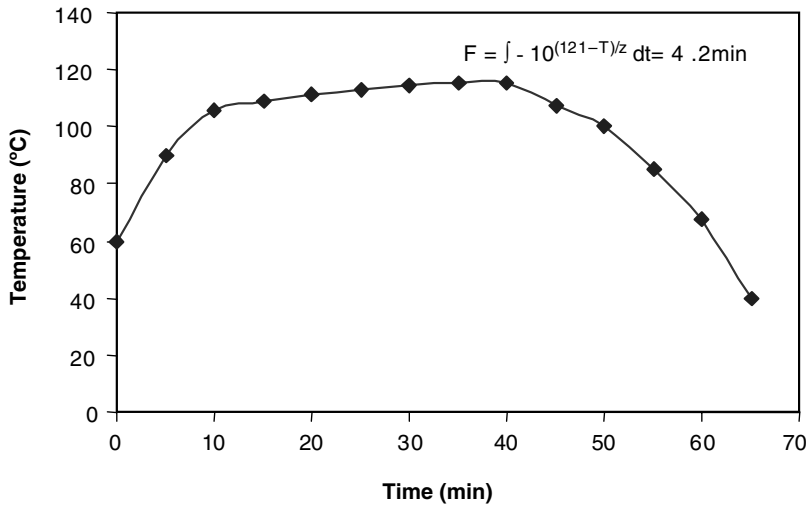

FIGURE 8.2 Curve time/temperature during sterilization of canned mussels.

and their influence on quality and flavor, fish can be classified into three categories according to their fat content: lean, with a fat content of up to 2%; medium fatty, with a fat content between 2 and 5%; and fatty, with a fat content exceeding 5%.

The effect of cooking and sterilization on the proximate composition of albacore was reported by Gallardo et al.[1] During cooking of tuna fish, the moisture falls about 10%, the protein increases about 9%, and the fat about 61%. The water losses result in a higher fat content in cooked tuna than in raw fish. After sterilization, the moisture loss is about 14% and the protein content increased to about 24%. Ruiz-Roso et al.[2] reported an important moisture loss after precooking of sardines. Other authors have also reported the effects of different cooking methods on the proximate composition of different species.[3–6]

Fish flesh is a source of macrominerals and trace elements. Fish contains an important amount of potassium (around 300 mg/100 g), phosphorous (around 200 mg/100 g), magnesium (about 25 mg/100 g), and calcium (about 15 mg/100 g). Fish contributes through consumption of trace elements such as iron, zinc, copper, and other elements, such as iodine, selenium, manganese, copper, cadmium, lead, vanadium, cobalt, and boron, which are important for human health. The effect of heat treatments on the elements was reported by Ackurt.[7] Gall et al.[4] and Steiner-Asiedu et al.[8] found little or no effect on the minerals after thermal processing. However, Gokoglu et al.[6] reported a considerable effect on the *mineral* content due to cooking.

There is no doubt that these elements have an important function in the human body, and that fish is a valuable source of them; however, fish accumulates substantial concentrations of heavy metals, such as cadmium, mercury, lead, copper, and zinc, as a result of agricultural and industrial activities. As a consequence of their toxicity, the concentration of heavy metals in fish flesh can be essential. During cooking by baking and steam blanching, a reduction in the heavy metal concentrations related to the loss of water and uncoagulated proteins has been reported by Atta et al.[9] The reduction depends on the medium of cooking, temperature, and time.

Struvite is a crystal of magnesium ammonium phosphate ($MgNH_4PO_4 \cdot 6H_2O$) that is found in canned products such as shrimp, crab, tuna, salmon, and other seafoods. Struvite crystals are formed by the union of the mineral constituents to fish meat during sterilization. The formation of struvite in canned tuna is related to pH and is more likely to occur in fish having pH values of >6.0. Struvite is not harmful, and it dissolves in dilute acid, such as vinegar or lemon.

8.4 VITAMINS

Fish is a source of vitamins, whose concentration depends on species, anatomical part of the fish, and age. Most vitamins are degraded to some extent during heating. The fat-soluble vitamins (vitamins A, D, E, and K) are more stable than the water-soluble vitamins (B1, B2, B6, C, niacin, folic acid, and pantothenic acid). During canning vitamin B1 (thiamine) and vitamin C are destroyed substantially.[10] Thiamine is the most thermolabile B vitamin, and its losses during precooking and after conventional sterilization were about 42 and 90%, respectively. The losses after

TABLE 8.1
Kinetic Parameters for Thiamine and Surface L Value Thermal Degradation

Parameter	Thiamine	Surface L Value
D_{ref} (min)	90.5 ± 2.1	1468 ± 112
Z (°C)	31.4 ± 0.6	44.0 ± 3.6
$S(y)^2$	3683×10^{-4}	$12{,}417\times10^{-4}$
Predicted vs. observed correlation	$y = 0.968x + 1.71$	$y = 0.962x + 2.7$
R^2	0.988	0.908

Note: L value = luminosity, universal chromatic scale; D_{ref} and Z = kinetic parameters; $s(y)^2$ = variance of the regression; R^2 = correlation coefficient between observed and predicted values.

Source: Courtesy of Banga, J.R. et al., *Z. Lebensm. Unters. Forsch.*, 197, 127–131, 1993. With permission.

sterilization at high-vacuum flame are about 68%. Niacin and riboflavin showed higher heat stability than thiamine, and the retention in canned albacore was about 60 to 70%, respectively.

Many kinetic data are available for thiamine in vegetables, milk, and meat, but there are few kinetic studies in fish. The kinetics of thermal degradation of thiamine was determined by Banga et al.[11] in canned tuna using an unsteady-state experimental procedure. The values calculated by these authors for D and z were 90.5 min (at 121.1°C) and 31.4°C, respectively (Table 8.1). The D value is in agreement with that reported by Suparno et al.[12] for the destruction of thiamine in trout, but the z value is higher. The kinetic model permits the simulation and optimization of the process and provides the maximum retention of nutrient.

8.5 SENSORY CHARACTERISTICS

The effect of thermal processing on sensory quality in marine products is difficult to predict because of intra- and interspecific variability of fish species and factors such as appearance, odor, color, flavor, and texture.

The color of canned tuna is an important quality attribute. Myoglobin is a monomeric globular hemoprotein with a molecular weight of 18 kDa, and it is localized in the red muscle fiber. Three forms of myoglobin contribute to the color of muscle: the reduced or deoxymyoglobin, which is purple-red; the red oxymyoglobin, associated with a high-quality product; and the metmyoglobin, which is brown and is responsible for discoloration of meat during storage. Cooking favors the formation of metmyoglobin because the oxidation is accelerated by the action of temperature. In general, fish myoglobins, especially in tuna fish, are sensitive to autooxidation, and this autooxidation increases during thermal processing.

The thermal denaturation mid-point of tuna myoglobin is 85°C. This denaturation can produce a color change denominated *greening*, associated with cooking of albacore, yellowfin, skipjacks, and other tuna species. The formation of the green pigment was studied in model systems by Grosjean et al.[13] This pigment was found in a system composed of tuna myoglobin, trimethylamine oxide (TMAO), and cysteine heated in phosphate buffer. The presence of a cysteine side chain in the fish protein allows the reaction of the sulfhydryl group with an oxidant as TMAO and the free cysteine. Some works have reported the relationships between trimethylamine and trimethylamine oxide and the myoglobin concentration of tuna muscle for predicting tuna greening.[14–17]

Another important discoloration is *blueing*, which has been detected in king crab, blue crab, and Dungeness crab.[18–20] The blue discoloration is generally associated with the heat processing, and an important review was reported by Boon.[21] The blueing occurs in pasteurized and canned crabmeat. It is developed during the heat treatment, and its effect increases during storage. It has been related to the presence of copper and iron. A significant correlation between copper concentration and discoloration intensity was found in Dungeness canned crab by Elliot and Harvey[20] and Babbit et al.[22]

The oxidation of phenolic compounds, such as tyrosine, to produce *melanin* is the other cause of discoloration.[23] Tyrosinases and phenooxidases present in the live crab initiate the oxidation of phenols to melanins. The posterior nonenzymatic oxidation and polymerization of these intermediate phenolics in canned crabmeat may proceed to form colored chromophores, mainly in the presence of metals. According to Babbit et al.,[22] the holding time of live crab before cooking and the times of cooking have a significant effect on the extent of the blueing of crab. The cooking at 100°C for 30 min of fresh crab was ideal for inactivating the polyphenoloxidases and preventing blueing, but not the cooking for 15 min. However, cooking at 100°C for 30 min does not prevent blueing when the raw material is not fresh.

According to Lund,[24] changes in the sensory quality by thermal processing are closely related to chemical reactions, which usually have a temperature dependence that can be described by a z value of 33°C. That temperature dependence of sensory quality changes during thermal processing was determined by Ohlsson[25] in fish, meat, and vegetable products. The experimentally determined z values ranged from 13 to 34°C, with an average value of 23°C. The average z value obtained by Ohlsson is in fair agreement with the z value for thiamine degradation (26.7°C).

Kinetics of thermal degradation of surface color in canned tuna was reported by Banga et al.[11] The z value found by these authors was $z = 44$°C, which is much higher than that found by Ohlsson[25] in fish ($z = 25$ºC). The minimal sugar content of tuna can explain this difference.

8.6 PROTEINS

The muscle of fish mainly consists of myofibrillar proteins, 65 to 75% of the total muscle proteins. They are contractile proteins as myosin and actin and regulatory proteins as tropomyosin and troponin, and other minor proteins. Other proteins of

fish muscle are sarcoplasmic proteins or water-soluble proteins, which account for 20 to 30% of the total proteins. They are mostly enzymes and are involved in postmortem biochemical changes. Fish flesh also contains about 3% connective tissue proteins, which are related to the texture of fish fillets.

According to Johnston,[26] the resulting variation in muscle cellularity and the associated changes in the connective tissue matrix are thought to be important determinants of fish flesh characteristics. Muscle cellularity is the major determinant of texture.[27,28] It has been suggested that variations in the quality of fillet along fish are due to variations in the size distributions of the muscle fibers and to the collagen present. Differences in the texture of fish muscle have also been related to the lipid and water content.[29] The lipid and water content reduced the structural factors of the muscle, lowering its mechanical strength. Kanoh et al.[30] found that the dark muscle of yellowfin tuna, whose fiber diameter is more inferior than the ordinary muscle, has a firmer texture than the ordinary muscle, and proposed that the fiber size is important for the tenderness of fish meat. The differences in toughness changes during thermal processing have a high correlation with fiber sizes and ultrastructures of the two types of fish muscle.

The contribution of muscle fibers to firmness was studied in cooked muscle of five fish species using optical and scanning electron micrography by Hatae et al.[27] These authors propose that when muscle is cooked, the sarcoplasmic protein is released from the contracting muscle fiber and is coagulated in the interstitial spaces.

In general during fish heating, sarcoplasmic and myofibrillar proteins are coagulated and denaturated. The extent of these changes depends on the temperature and time and affects the yields and final quality of the fishery product. In heat denaturation of flesh proteins, H-bonds, which are involved in the secondary and tertiary structures of proteins, are broken, resulting in an unfolding of the native configuration. During the early stages of cooking (30 to 50°C), there is an unfolding of peptide chains and a partial denaturation of sarcoplasmic proteins, which results in toughness and decreased water-holding capacity. When the temperature increases (50 to 70°), stable cross-linkages are formed with denaturation and coagulation of proteins.

Thermal processing is important to reduce heat-labile pathogens and to obtain a palatable product; by this reason, it is necessary to establish accurately the conditions of fish cooking. Several studies have been carried out to determine the *endpoint* temperature in meat products, but the studies on marine products are limited. For the control of heating temperature in fishery products, two methods based on the thermal denaturation of fish proteins have been proposed. Doesburg and Papendfor[31] used the coagulation test to determine the degree of heating of muscle, and Chan et al.[32] measured the amounts of sarcoplasmic and myofibrillar proteins extractable from fish muscle heated to temperatures of up to 100°C. Isoelectric focusing (IEF) of sarcoplasmic proteins was used for determining temperature in cooked fish and smoked fish because of the presence of parvalbumins, which are heat-stable proteins.[33] The changes in the protein patterns of parvalbumins may reflect the degree of the heating. The suitability of these methods was investigated in fish-heated extracts, heated minced fish muscle, and smoked

herring and mackerel by Rehbein.[34] According to this author, herring heated at 55 or 60°C could be differentiated by IEF from herring that was smoked at 65 to 70°C. Different protein patterns were also obtained by IEF for mackerel smoked at 55, 60, 65, or 70°C. From these results, it can be inferred that IEF or coagulation test can be used for determining temperatures of fish heating of up to 65°C.

The coagulation method was used for determining the endpoint temperature of heated blue marlin meat in the range of 1 to 67°C.[35] From the analysis of proteins by sodium dodecyl sulfate–polyacrilamide gel electrophoresis (SDS-PAGE) and by studying the enzymatic activity, lactate dehydrogenase was found to be responsible for coagulation at 67°C. The assessing of the endpoint temperature of heated fish and shellfish using the coagulation method was also reported by Uddin et al[36] The coagulation test could determine the endpoint temperature of shellfish meats between 60 and 67°C, and the results were confirmed by SDS-PAGE and enzyme activity determination. A thermostable protein with a molecular weight of 35 kDa was detected in heated shellfish meats up to 108°C. This protein was found to be a tropomyosin subunit in the scallop adductor muscle. According to the results obtained from these authors, tropomyosin could be used as an indicator of the endpoint temperature. However, the applicability of the enzyme activities can have great difficulties because they depend on the physiological condition of the fish.

Differential scanning calorimetry (DSC) can also be used to investigate the thermal stability of proteins and to estimate the cooking temperature of the seafood products. The thermal stability of fish myosin of different species in the range of 20 to 80°C by DSC was reported by Ogawa et al.[37] The denaturation process was different depending on the species. The DSC curves of myosin of sardine, stone flounder, sea bram, and carp had two peaks; trout, bigeye tuna, and yellow tail showed three peaks; and horse mackerel only one peak.

The thermal denaturation of hake myofibrillar proteins using DSC was studied by Beas et al.[38] Two endothermic transitions with T_{max} values at 46.5 and 75.3°C and a shoulder at 51°C were obtained by these authors. Martens and Vold[39] reported similar transitions for cod muscle. The DSC of the exudative sarcoplasmic fraction of the whole muscle showed three peaks at 45.2, 59, and 75.5°C and contributed to denaturation peaks.

The protein denaturation during fish precooking implies texture and binding changes, which allow for a better differentiation between red and white muscle and an easier separation of muscle from bone. The most labile proteins are the sarcoplasmic proteins and myosin, and their denaturation is sufficient to ensure textural changes needed. The effects of the thermal protein denaturation and moisture loss in skipjack tuna during steam cooking were reported by Bell et al.[40] The DSC thermogram showed that the first peak at 52°C corresponds to myosin denaturation, the second peak at 59°C to collagen, and the third peak at 68°C to actin. During the precooking of skipjack, the structural muscle proteins decrease in dimension upon reaching their thermal denaturation temperatures and shrinkage of the muscle fibrils and tissue occurs.

Sulfhydryl groups and disulfide bonds are important in maintaining structure and functions of native proteins. At temperatures above 90°C the oxidation of

sulfhydryl groups (SH) occurs and leads to the formation of covalent S–S bonds. The effect of heating on the –SH groups and S–S bonds was studied by Opstevedt et al.[41] in Alaska Pollock and Pacific mackerel (Table 8.2). Heating for 20 min at temperatures ranging from 40 to 115°C showed a linear decrease in the –SH groups and an increase in the content of S–S disulfide bonds at temperatures from 50 to 115°C.

Heating at 115°C causes a loss in cystine plus cysteine.[42,43] The loss of cysteine plus cystine produces H_2S. The release of H_2S during seafood sterilization is a problem because of the corrosion of tins and discoloration of cans, and it provokes an offensive off-flavor when the can is opened. The production of H_2S indicates the destruction of essential sulfur-containing amino acids.

The effect of heat processing on bigeye tuna and halibut at 115 and 124°C varying in F_0 values of 8, 21, and 32 min was reported by Tanaka and Kimura.[44] At 115°C, the electrophoretic patterns of proteins were similar in both fish and the bands of myosin heavy chain disappeared at any value of F_0. The actin and tropomyosin bands decreased when the F_0 value increased. At 124°C the protein degradation was smaller than that at 115°, because the thermal processing time necessary to attain the equal lethality was far shorter than that at 115°C.

Taking advantage of denaturation, heat induces the capability of fish muscle proteins for forming gels.[45] Thermal gelation of fish protein, for example, in making kamaboko, was due to myosin; light meromyosins combined with each other, after which heavy meromyosins combined to form the gel. Actin was degraded on heating, and the fragments aggregated to form a curd-like substance, so that actin had no gel-forming ability.[46] Heating and cooling cycles enhance the setting process for gelation of fish paste and improve textural quality.[47]

8.7 LIPIDS

Fish *lipids* are highly concentrated in polyunsaturated fatty acids (PUFAs), especially eicosapentaenoic acid (20:5 n-3, EPA) and docosahexaenoic acid (22:6 n-3, DHA). This composition leads to a high nutritional value of fish products associated with the well-known beneficial effects of n-3 PUFAs on human health. The n-3 PUFAs decrease the serum cholesterol and tryacylglycerol levels and prevent coronary heart disease.[48] Hydrolysis and main oxidation are the major alterations of fish lipids during thermal processing. Lipid degradation is often focused on the reactivity of PUFAs since they can produce a significant number of polar compounds, including volatile derivatives by action of heat via the process of lipid oxidation.[49] In this way, the highly unsaturated fatty acid composition renders fish flesh extremely susceptible to oxidation and rapid degradation during processes that involve thermal treatments. In addition, oxidation of n-3 fatty acids and the effect of oxidized lipids on proteins and amino acids in fish muscle cause loss of nutritional value.[50]

Cooking and sterilization provoke *lipolysis* and oxidation during fish canning, but there is also a significant effect of filling medium. Thermal treatments associated with fish cooking and sterilization decrease the initial lipid content of flesh mainly by loss of triacylglycerols.[2,51] Phospholipids are also affected, with choline

TABLE 8.2
Effect of Heating on the Content[a] of –SH Groups and S–S Bonds in Pollock and Mackerel Proteins

	Temperature, °C	Pollock				Mackerel			
		N[b]	–SH + S–S/2	–SH	S–S/2	*N*[b]	–SH + S–S/2	–SH	S–S/2
Untreated		12	11.5 ± 0.4	7.0 ± 0.5	4.4. ± 0.3	6	10.8 ± 0.3	7.2 ± 0.3	3.7 ± 0.4
Heated for 20 min	40	3	11.3 ± 0.4	7.1 ± 0.3	4.3 ± 0.4				
	50	3	11.3 ± 0.7	7.5 ± 0.1	3.9 ± 0.6	3	10.9 ± 0.4	8.1 ± 0.3	2.8 ± 0.2
	60	3	11.0 ± 0.2	6.6 ± 0.4	4.5 ± 0.5	3	11.4 ± 0.4	8.1 ± 0.1	3.3 ± 0.4
	70	3	11.6 ± 0.5	6.1 ± 0.2	5.5 ± 0.4	3	10.8 ± 0.5	7.2 ± 0.3	3.5 ± 0.7
	80	3	11.6 ± 0.5	6.3 ± 0.1	5.3 ± 0.5	3	10.8 ± 0.2	6.6 ± 0.3	4.1 ± 0.5
	95	3	11.6 ± 0.6	5.2 ± 0.5	6.5 ± 0.3	4	11.2 ± 0.4	6.1 ± 0.5	5.2 ± 0.4
	115	4	10.4 ± 0.3	3.9 ± 0.5	6.6 ± 0.2	2	9.9	9.9	6.3

[a]SH/16 g of *N*, average ± standard deviation.
[b]*N* = number of determinations.

Source: Courtesy of Opstevedt, J. et al., *J. Agric. Food Chem.*, 32, 929–935, 1984. With permission.

phospholipids affected the most during cooking, in particular lysoforms. Lipolitic enzymes in fish are mostly active at ordinary cold storage temperatures. Heat treatment resulting in inactivation of enzymes is of considerable practical importance. During fish thermal processes, hydrolysis of triacylglycerols gives as a result a significant increase of free fatty acids.[52] The application of ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectroscopy has shown a preferential stereospecificity of lipid hydrolysis in the internal position of the glycerol moiety after thermal stress, resulting in a larger increase of free DHA.[52] The ratio of 1,3-diacylglyceride and 1,2-diacylglyceride quantities confirms this finding. These results contrast with enzymatic hydrolysis during fish frozen storage, occurring preferentially in the sn-1 and sn-3 positions of triacylglycerols, with a consequent cleavage of saturated and monounsaturated fatty acids. After thermal processing, an increase in free PUFAs can be of special relevance for suffering oxidation. The most susceptible compounds at thermal stress are plasmalogens, 1-O-alk-1-enyl-glycerophospholipids.[53] At sterilization temperatures (115°C), the weak ether bonds of these compounds are broken, and as a result, the amount of plasmalogens in canned brine and canned oily tuna decrease by 50%. Plasmalogens have been more susceptible to damage during heat processing than their corresponding acyl derivatives. This behavior may be explained by the aldehydogenic chemical structure easily open to acidic attacks.

Overall quality and flavor of the thermally processed product can be highly influenced by lipid oxidation rending to rancidity. Initial raw composition, process conditions, and packing substrate have a special relevance. The canning process provokes increases of primary, secondary, and tertiary lipid oxidation products in canned tuna.[54] The highest thiobarbituric acid index (TBA-i) values were found in tuna canned muscle using brine as a dipping medium, thus indicating lower protection in the muscle kept in a highly aqueous environment than that kept using oily packing media.

^{13}C-NMR spectroscopy has been applied to elucidate the mechanism of lipid oxidation occurring during thermal treatment of fish.[55] Effects of temperature and time of processing have been studied by means of a model system of lipids extracted from salmon (*Salmo salar*) muscle to simulate industrial conditions of canning. Unsaturated fatty acids located at the sn-2 position of the glycerol moiety are most prone to suffering from oxidative damages. Regarding the mechanism of the reaction, results inferred from olefinic and methylenic resonances indicated a higher susceptibility of the closest allylic sites to the carbonyl group, followed by those placed near to the methyl terminal group. Unsaturations located in the middle of the carbon chain did not show notorious damages. The glyceryl region provided an unusual resonance at 53.4 ppm that could be assigned to a hydroxilic compound formed during oxidation.

Oxidation in fish during thermal processing has also been studied by determining volatile production with a static headspace gas chromatographic system.[56] The major *volatiles* formed included acetaldehyde, propanal, heptane, 2-ethylfuran, pentanal, and hexanal. The formation of *2-ethylfuran* had the highest independent contribution for the prediction of oxidative stability of fish muscle at 4 days at 40ºC and 150 min at 100ºC. The formation of 2-ethylfuran in oxidized n-3 PUFAs

in fish can be explained by the 14-hydroperoxide of eicosapentaenoate (20:5 n-3) and the 16-hydroperoxide of docosahexaenoate (22:6 n-3), which can undergo b-cleavage to produce a conjugated diene radical, which can react with oxygen to produce a vinyl hydroperoxide. Cleavage of this vinyl hydroperoxide by loss of a hydroxyl radical forms an alkoxyl radical that undergoes cyclization to produce 2-ethylfuran.

Associated with hydrolysis and oxidation, overprocessed canned samples, such as those subjected to sterilization treatments involving high temperatures and long times, lead to a significant decrease of n-3 fatty acids (110 and 130°C during 120 min). NMR techniques have been proposed as useful tools to select the optimal conditions of thermal fish processes based on minimum lipid hydrolysis and oxidation and maximum n-3 PUFA retention.[57] Dahl and Malcata[58] have employed a thermal oxidation model of sardine oil to predict oxidation stability of PUFAs. PUFAs with less than four double bonds were relatively stable to oxidation for up to 10 h at 50 to 70°C, and the qualitatively richest pattern of volatiles was obtained when the reaction was performed at 80°C.

Canned fish products in oily media showed dilution of the natural lipids of fish muscle by triacylglycerols from packing oils.[59] As result, a significant increase of the fatty acids present in vegetable oils used as dipping media, such as oleic and linoleic acids, is found in the final canned flesh. There is also an exchange of n-3 PUFAs from fish flesh to filling oil, resulting in the oil enriched in n-3 PUFAs. As regards hydrolysis, the extent and mechanism of the reaction seem to be independent of the filling medium used. Oxidation can be minimized by employing packing media containing natural antioxidants, such as extra virgin olive oil rich in polyphenols or certain vegetable oils rich in tocopherol isomers.[54,60] In tuna oxidized at 40 and 100°C, 400 ppm of the extra virgin olive oil polyphenols was an effective antioxidant, compared with 100 ppm of a 1:1 mixture of the synthetic antioxidants butylated hydroxytoluene and butylated hydroxyanisole. The extra virgin olive oil polyphenols were effective antioxidants when added to heated tuna muscle in the presence of either brine or refined olive oil. The extra virgin olive oil polyphenols had higher antioxidant activity in the brine samples than in the refined olive oil. Their hydrophobic character and their low solubility into an aqueous media may explain the higher antioxidant activity of extra virgin olive oil polyphenols in tuna packed in brine since they are totally adsorbed into fish flesh.

8.7.1 Volatiles

The *flavor* profiles of cooked fish differ in the aroma notes and in the intensity of these notes. 1-Octen-3-one, (Z)-1,5-octadien-3-one, (E)-2-nonenal, and (E;Z)-2,6-nonadienal play an important role in fresh fish-like odors due to their low odor threshold values.[61] During boiling and cooking, important thermal degradation of volatiles can occur in addition to the detection of off-flavor substances resulting from longer periods of frozen storage. Volatiles of canned tuna, canned salmon, dried and smoked fish, and boiled fish have been widely described.[62–65]

8.7.2 Effects of Heating on Formation of Cholesterol Oxides

Cholesterol is stable under normal conditions in air; however, it is oxidized by thermal stress and exposure to light to produce cholesterol oxides. Cholesterol oxides, including 7-hydroxycholesterol, 7-ketocholesterol, -epoxide, -epoxide, cholestane triol, and 25-hydroxycholesterol, were identified and quantified. These oxides are atherogenic, carcinogenic, and mutagenic compounds.[66–69] The oxidation of cholesterol during heating in an air oven at high temperature was studied by Osada et al.[70]; the cholesterol was stable for 24 h at 100ºC, but was unstable at temperatures up to 120°C. The cholesterol oxides in fish products were determined by gas–liquid chromatography and mass spectrometry by Ohshima et al.[71] These authors suggested that cholesterol oxidation in fish products proceeds in conjunction with oxidation of PUFAs during storage in air. The radicals produced from PUFA oxidation act as accelerators of the oxidation of cholesterol. The effects of grilling on formation of cholesterol oxides in seafood products were reported by Ohshima et al.[72]

8.8 LOW-MOLECULAR-WEIGHT COMPONENTS

8.8.1 Sugars

In general, the content of free sugars and sugar phosphates in fish muscle and shellfish is low. The phosphorylated sugars are unstable during cooking.[73] Free ribose can be involved in the browning of canned fish because of the reaction of carbonyl groups, such as reducing sugars or lipid oxidation products with an amino compound such as lysine. These reactions are significant in reducing the nutritive value, mainly when the fish is heated severely. Free ribose can be eliminated during cooking and the possible browning of the canned fish avoided.

8.8.2 Free Amino Acids

Free amino acids and creatine are the major components of the total nonprotein nitrogen (NPN) compounds in teleost muscle, and they are recognized as contributors to the flavor.[74] Free amino acids of fish are associated with autolysis and bacterial actions in the earlier stages of alteration.[75] Mackie and Ritchie[76] demonstrated that there was considerable variation in the concentration of amino acids along the length of fish, and variations were also found from the head-to-tail portions of cod fillets.

Free amino acids can be significantly affected by heating. Considerable loss of histidine, about 86%, after thermal processing of herring at 116ºC for periods of up to 5 h have been reported.[73]

The effect of cooking and sterilization on the free amino acids content in albacore was reported by Pérez-Martin et al.[77] After steam cooking, the losses were not significant. According to these authors, during the sterilization under standardized conditions ($F = 6$), the changes were not significant (Table 8.3);

TABLE 8.3
Effect of Sterilization Time on the Free Amino Acid Content in Albacore Muscle (mg/100 Dry Weight)

Amino Acid	Fresh	SD	Canned			
			115°, 60 min	SD	115°, 100 min	SD
Asp	36.9	4.7	32.7	4.2	32.1	4.4
Glu	55.7	5.2	49.3	4.8	37.3	5.1
Ser	34.5	5.8	30.5	5.0	31.0	5.4
His	2320.0	39.7	2050.1	37.6	1461.6	40.5
Gly	56.7	6.1	49.9	5.6	27.8	5.1
Thr	71.5	9.7	63.7	10.1	50.0	11.2
Arg	273.0	21.7	240.5	18.9	163.8	22.3
Tau	199.1	11.1	173.2	9.6	122.4	9.5
Tyr	49.3	3.6	42.4	3.9	31.0	3.4
Ala	80.6	3.2	70.2	3.8	58.9	4.0
Trp	97.1	4.1	83.6	4.4	76.7	3.8
Met	62.5	3.3	53.1	3.0	41.2	3.5
Val	26.6	3.1	23.6	2.9	16.0	2.8
Phe	150.5	3.9	134.0	3.3	117.5	3.0
Ile	48.1	5.1	40.9	4.3	38.4	3.6
Leu	68.8	5.7	60.2	5.1	48.1	4.9
Lys	109.3	5.6	95.2	4.8	81.1	5.1
Total	3740.2 a		3293.1 b		2434.9 c	

Note: Values followed by the same letter are not significantly different. SD = standard deviation, four samples. Albacore caught in 1985.

Source: Courtesy of Pérez-Martin, R.I. et al., *Z. Lebensm. Unters. Forsch.*, 187, 432–435, 1988. With permission.

however, when $F = 13$, significant differences were found, confirming the negative effect of the sterilization time. These authors suggest that analysis of the free amino acids would be useful to know the extent of thermal processing.

8.8.3 Amines

8.8.3.1 Total Volatile Bases

The *total volatile basic amines* (TVB-N) include *trimethylamine* (TMA), *dimethylamine* (DMA), ammonia, and other volatile nitrogenous compounds associated with the spoilage of marine products. TMAO is present in a large number of fish and shellfish, and it is generally accepted that TMAO is the main source of TMA and DMA. Endogenous enzymes in fish and exogenous enzymes produced by bacteria during frozen or ice preservation are responsible for the reduction of

TMAO to TMA and DMA. TMAO can be reduced by cysteine in the presence of hemoglobin or iron as the catalyst. TMA is associated with the fishy odor; however, this fishy odor is produced when TMA reacts with lipids. In gadoid frozen species, TMAO is reduced to DMA and formaldehyde (FA), which induces textural toughening of fish flesh.

The rate of thermal decomposition of TMAO varied with the fish species and was low in white fish and high in red-fleshed fish.[78] This difference was due to the different concentrations of hemoproteins, free amino acids, and –SH basis. The thermal decomposition of TMAO takes place at 55 to 60ºC in dark muscle and above 80ºC in ordinary muscle.

Precooking produces an increase in TMA, which is proportional to cooking time. Large concentrations of ammonia, DMA, and TMA were found in herring subjected to overprocessed conditions: heated for up to 5 h at 120°C.[79]

Tokunaga[80] studied the relationship between the freshness of raw albacore and the quality of canned albacore. The ratio of remaining undecomposed TMAO to the total amine content (TMAO + TMA + DMA) might be an index of freshness of the raw albacore. In the thermal decomposition of TMAO, TMA as well as DMA are produced in the ratio of 2:1, respectively. This author[80] suggested the use of the ratio of DMA over TMA (DMA-N/TMA-N) × 100 to evaluate the quality of canned albacore. This ratio was approximately 50% if the fish employed for canning was highly fresh, 40% when the fish was stored for 70 h before canning, and 30% or lower when the albacore was stored for about 116 h before canning. However, TMAO concentration in fish varies widely with season, size, and age of fish, and TMA is formed during thermal processing. Therefore, it is difficult to use TMAO as a reliable measure of the freshness of the raw fish that is used for canning.

Changes in volatile bases and TMAO during canning of albacore were reported by Gallardo et al.[81] (Table 8.4). The TVB-N levels increased during

TABLE 8.4
Changes in TVBs, Individual Bases, and TMAO during Processing of Canned Tuna in 120-ml Rectangular Cans

			Canned at		
Compounds	**Raw Fish**	**Precooked Fish**	**110°C, 90 min**	**115°C, 55 min**	**118°C, 40 min**
TVBs	280 (20)	340 (14)	450 (21)	430 (19)	410 (22)
Ammonia	250 (34)	310 (16)	420 (25)	410 (17)	380 (24)
Dimethylamine	2.4 (0.6)	5.2 (1.9)	7.0 (1.9)	7.4 (1.7)	7.7 (1.5)
Trimethylamine	4.4 (1.3)	13 (2.2)	16 (2.9)	17 (3.3)	19 (4.1)
TMAO	19 (6.3)	8.4 (4.9)	4.2 (2.5)	3.3 (1.9)	1.9 (2.1)

Note: Values are concentration (mg N kg^{-1} fish/canned contents) (standard deviation).

Source: Courtesy of Gallardo, J.M. et al., *Int. J. Food Sci. Technol.*, 25, 78–81, 1990. With permission.

cooking and sterilization. The effect of the process, in order of increasing TVB-N, was R < C < E118 < E115 < E110. The results suggest that under given conditions of thermal processing, the levels of TVB content may be of practical value in assessing the initial quality of albacore. If the thermal processing conditions are not known, high levels of TVB-N in canned product indicate either a poor quality of raw fish or overprocessing.

Determinations of the TVB-N in several fish species prior to cooking and after sterilization were carried out by Yeannes et al.[82] Increases in the contents of the bases were confirmed. Using different specimens of bonito with different degrees of spoilage, the contents of the volatile bases in the cooked bonito were significantly correlated with the values of the raw material when the processing conditions are held constant. A correlation between the bases content of sterilized bonito and the cooked product was detected too.

8.8.3.2 Biogenic Amines

Biogenic amines are aliphatic, alicyclic, or heterocicly organic bases of low molecular weight that have been found in different foods, such as cheese, beer, wine, fermented meat, and marine products. They are formed by action of bacterial enzymes on free amino acids, and the most important are histamine, putrescine, cadaverine, spermidine, spermine, tyramine, agmatine, tryptamine, and 2-phenylethylamine, which are produced by decarboxylation of free amino acids.

Histamine, produced by decarboxylation of histidine during microbial decomposition of scombroid fish, has received most of the attention. It is the main compound responsible for the intoxication named scombroid poisoning due to the ingestion of fish species such as mackerel, tuna, and mahi-mahi or pelagic species such as sardines and herring.[83] Putrescine and cadaverine have been reported to enhance the toxicity of histamine.[83]

The determination of the biogenic amines is important not only from the point of view of their toxicity, but also because they can be used as indicators of the degree of freshness or spoilage of food.[84]

Most of the biogenic amines are stable to thermal processing, and their presence in canned fish can be an index of the quality of raw material. The content of histamine, cadaverine, and tyramine was determined by Schulze and Zimmermann[85] in canned tuna and sardines. Concentrations of 7 to 13 mg/kg of histamine were detected in canned albacore, 14 to 36 mg/kg in canned skipjack, 20 to 40 mg/kg in canned mackerel, 25 to 48 mg/kg in canned sardines, and 24 to 55 mg/kg in saury pike.

Luten et al.[86] reported that histamine is stable during cooking. However, Sims et al.[87] reported that histamine formation could take place during sterilization, and they also found that thermal processing lowered histamine, putrescine, and cadaverine concentrations in skipjack tuna. Mietz and Karmas[88] proposed a chemical quality index (QI) based on biogenic amines, which reflected the quality loss in canned tuna:

$$QI = (HI + PU + CA)/(1 + SP + SM)$$

TABLE 8.5
Contents of Biogenic Amines (μg/g) throughout Canning Process ($n = 12$)

Amines (μg/g)	Raw Fish	Before Cooking	After Cooking	After Packing	End Product
HI	0.32 (O.62)*[a]	0.55 (1.44)*	0.040 (0.65)*	0.54 (0.90)*	0.63 (0.83)*
TY	0.32 (0.67)*	0.08 (0.18)*	0.24 (0.63)*	0.17 (0.35)*	0.15 (024)*
SE	1.80 (1.44)*	2.08 (2.06)*	2.32 (2.35)*	2.05 (2.42)*	1.80 (1.41)*
AG	0.94 (0.77)*	0.17 (0.44)*	0.15 (0.36)*	0.32 (0.53)*	0.40 (0.29)*
CA	0.25 (0.45)*	0.17 (0.31)*	0.33 (0.64)*	0.19 (0.32)*	0.21 (0.29)*
PU	0.29 (0.51)*	0.22 (0.28)*	0.27 (0.13)*	0.13 (0.20)*	0.32 (0.57)*
PHE	nd[b]	nd	0.10 (0.30)	0.27 (0.90)*	nd
TR	nd	0.11 (0.38)	0.12 (0.80)	0.01 (0.20)	0.12 (0.90)
SD	5.10 (1.74)*	4.31 (1.34)*	3.46 (1.21)*	3.51 (1.72)*	2.82 (1.29)**
SM	14.25 (5.91)*	19.91 (5.55)*	11.89 (3.34)*	12.89 (3.65)*	8.32 (2.67)**

[a]Mean value (standard deviation); values in the same column bearing the same number of asterisks are not different ($P > 0.05$); statistical comparisons were not performed for PHE and TR because these amines are found in only a low percentage of samples.
[b]nd = not detected (<0.25 μg/g for HI, PU, CA, AG, and PHE; 1 μg/g for SD, SM, TY, SE, and TR).

Source: Courtesy of Veciana-Nogués, M.T. et al., *J. Agric. Food Chem.*, 45, 4324–4328, 1997. With permission.

where QI is the quality index, HI is histamine, PU is putrescine, CA is cadaverine, SP is spermidine, and SM is spermine.

The increase in the quality index was correlated with the decrease of sensory scores on canned tuna.

Veciana-Nogués et al.[89] reported that no significant differences in thermal processing of tuna were found for histamine, putrescine, cadaverine, tyramine, and agmatine (Table 8.5). Only changes were detected for spermine and spermidine, which decreased after heat processing. For this reason, histamine, cadaverine, putrescine, and tyramine seem to be appropriated as quality indices to assess the raw material used in canned tuna.

8.8.3.3 Nucleotides

Fish spoilage has usually been determined by the measurement of the concentration of total basic nitrogen (TVB-N) and trimethylamine (TMA). However, the loss of freshness, which precedes microbiological spoilage, is associated with autolytic reactions. Freshness of fish muscle and the nucleotide degradation have been studied by Gill.[90] One of the most important biochemical changes is the hydrolysis of adenosine- 5' triphosphate (ATP). After the death of fish, the degradation of adenosine triphosphate (ATP) proceeds according to the following sequence:

$$ATP \rightarrow ADP \rightarrow AMP \rightarrow IMP \rightarrow HxR \rightarrow Hx$$

where ADP is adenosine diphosphate, AMP is adenosine monophosphate, IMP is inosine monophosphate, HxR is inosine, and Hx is hypoxanthine.

Most of the enzymes involved in the breakdown of ATP, after death, to IMP are autolytic. ATP is rapidly degraded to AMP and IMP by dephosphorylation. However, the degradation of IMP to HxR and then to Hx is mainly due to spoilage bacteria. The concentration of HxR and Hx increases with the length of the storage period. The dephosphorylation of IMP via HxR and Hx varies with the species and occurs within the period of edibility during ice storage. These changes are implicated in the loss of fresh flavors; IMP has been shown to impart a fresh flavor, and Hx produces flavors described as bitter. The concentrations of ATP and its degradation products are usually employed as indices of freshness of refrigerated seafood.[90–92]

The rate of formation of HxR and Hx varies in different species of fish; in some, HxR accumulates, and in others, the HxR is broken down rapidly and Hx accumulates.[93,94] The rate of breakdown of ATP and its derivatives is dependent on different factors, such as intraspecies differences,[95] the capture,[96] and seasonal variations. On the other hand, the breakdown of ATP and its derivatives depends on the time and storage temperature.

Hughes and Jones[97] reported that hypoxanthine is stable under the conditions of canning of herring, and suggested that hypoxanthine analysis is a practical value in assessing the freshness of raw material. Crawford[98] reported a comparison of the hypoxanthine contents of raw tuna and the canned product, and a significant relation was found. Gallardo[99] reported the heat stability of hypoxanthine during the canning of sardines.

Tokunaga et al.[100] and Gill[90] reported that IMP and HxR were relatively stable during the sterilization of fish. For tuna, which is an inosine-forming species, the IMP ratio (IMP/IMP + HxR + Hx) seems to be the most appropriate for determining quality. Veciana-Nogués et al.[89] showed that the IMP ratio in canned tuna was useful as a quality indicator of the raw material used in canned tuna. No significant differences were found between samples in contents of IMP, HxR, and Hx. These authors[89] confirmed that the IMP ratio can be used as a freshness indicator of the raw tuna used for canning. The IMP ratio obtained for these authors was much higher than 0.114, which had been proposed by Fujii et al.[101] as the minimum value for fish acceptance.

8.8.4 Ethanol

Ethanol has been used for many years as an objective indicator of seafood quality. Ethanol is produced from carbohydrates via glycolisis and by decarboxylation of amino acids. It is a common metabolite of a variety of bacteria and has been used as an index of quality for fish, including canned fish.[102–106] Although ethanol is volatile, it is heat stable and may be used to assess the quality of canned fish products.

8.9 EFFECT ON THE NUTRITIVE VALUE

In general, the nutritional value of the fish and shellfish is not seriously damaged during thermal processing.[73,107,108] Changes in nutritional quality of raw, precooked, and canned tuna were studied by Seet et al.[109] The cans were sterilized

at 115 and 121°C for 120 and 95 min, respectively. The amino acid concentration remained constant for raw, precooked, and canned tuna, except for histidine and sulfur amino acids. The protein digestibility decreased by 2.2% during thermal processing at 115°C and by 1.8% at 121°C.

The effect of heat processing on amino acids content in bigeye tuna and halibut processed at 115 and 124°C, varying in F values of 8, 21, and 32 min, was reported by Tanaka and Kimura.[44] No significant changes were detected in the overall composition and degradation of amino acids during thermal processing. For the study of the content of nutrients and availability of lysine in the manufacturing of canned tuna, two different sterilization times (60 and 90 min) were studied by Castrillón et al.[107] The net protein utilization was 83.6% for fresh bonito and 84.1% for canned tuna during sterilization for 60 min; however, when the time of sterilization was increased to 90 min, the effect was negative and the net protein utilization was 82.9%.

A more detailed study was carried out by Navarro et al.,[110] who demonstrated that overprocessing (115°C during 90 min) caused negative changes in the protein. It did not seem to affect lysine, since its availability does not decrease. However, it acted on some of the other less abundant amino acids, which upon deteriorating led to a decrease in the global nutritional utilization and damage to the protein quality.

Changes in the nutritional value of mussels during steam cooking for 15 min and sterilization at 115°C for 70 min were reported by Lema et al.[111] No significant differences for digestibility between mussels cooked by steam and sterilized mussels were found; however, the sterilization affected the biological value.

Lysine is the most sensitive of the amino acids and its availability serves as an index of damage even when it is not the limiting amino acid. Lysine has been widely investigated, although others such as histidine, cysteine, tryptophan, and arginine are also affected by heating. Hurrel and Carpenter[112] demonstrated that in fish, because of the small concentration of reducing sugars, the loss of lysine was slight; Seet et al.[109] reported that the amount of available lysine during precooking of albacore decreased about 2%, and there were no changes in available lysine in further sterilization by high-vacuum flame sterilization. However, when conventional sterilization was used, the canned tuna lost 10% of the total available lysine since the sterilization time to ensure commercial sterility was longer than that of the high-vacuum flame sterilization. However, none of these results allow isolated kinetic parameters to be calculated. Mathematical models for the prediction of the effects of heating on the availability of lysine and protein digestibility in fish products require a knowledge of kinetic parameters, to quantify the effects and to predict the quality of the canned fish.

Banga et al.[113] evaluate the changes in availability of lysine and protein digestibility during different thermal processings of albacore muscle and construct kinetic models that allow these changes to be predicted for a given treatment. According to these authors,[113] the values for the kinetic parameters indicate that the classical methods of sterilization of tuna — temperatures of retort under 125°C and F values under 12 min with z = 10°C — have only a slight effect on the

availability of lysine and protein digestibility. The computer simulation of the process with the software described in Banga et al.[114] also indicated no significant changes.

8.10 OPTIMIZATION OF THERMAL PROCESSING

The maximal retention of organoleptic property, quality, and nutritional value is essential for designing conditions of thermal fish processing.

Due to the kinetic character of chemical and physical reactions causing changes during the thermal processing of fish, research on mathematical modeling for the prediction of these changes and their optimization requires knowledge of kinetic parameters. These models allow for quantifying the effects of thermal processing and predicting the final quality, and they may be used in automatic control.

The prediction of precooking times for albacore by computer simulation was reported by Pérez-Martin et al.,[115] who developed a semiempirical model of precooking. A numerical simulation to predict the internal temperature profile of skipjack tuna during precooking and cooling was also performed by Zhang et al.[116]

The inactivation kinetics of microorganisms and quality factors show different temperature sensitivities. According to Lund,[24] thermal inactivation of micro organisms is much more dependent on the temperature than the losses of quality factors. In fish canneries, the thermal processing at constant temperature, which is effective, is applied at solid food as tuna. Optimal sterilization conditions and different numbers of methods have been developed for the prediction of nutrient degradation during thermal processing at constant temperature.[117–121]

The use of variable sterilization temperature could improve the quality and nutrient retention. Teixeira et al.[122] were the first to compare the advantages of a variable-temperature process over the traditional constant-temperature process. Banga et al.[114] developed a method for the optimization of the thermal processing of conduction-heated canned foods. These authors[114] obtained a significant increase of quality factor retention at the surface with variable-retort temperature profiles, against the optimum constant-temperature profile.

Silva et al.[123] optimized overall quality and the nutrient retention in foods preserved by heat through the use of two objective functions: volume average retention and volume average cook value.

8.11 CONCLUSIONS

In this review, an attempt has been made to include the more relevant research on the effects that fish thermal processing have on the main fish constituents, such as proteins, amino acids, and lipids, and on the sensory characteristics and nutritive value. The main literature about the use of mathematical models useful in the optimization of thermal processing of fish products and in enhancing quality was reviewed. It can be concluded from the available data in relation to the thermal degradation of nutrients and sensory characteristics that the sensory characteristics and nutritive value of heat-preserved fish products remained

satisfactory. In the future, the new advances in the basic sciences, mainly by the application of proteomics, metabolomics, nutrigenomics, and mass spectrometry, will contribute to characterizing and evaluating the chemical modifications of the proteins and others constituents in marine products during thermal processing. An improvement of the ability to predict the effect of thermal processing on the chemical degradation of constituents and loss of nutritional value can be expected.

NOMENCLATURE

D value, or decimal reduction time	Heat treatment time, expressed in minutes, required to reduce the number or concentration of spores, microorganisms, or quality factors to 10% of the original value.
F, or sterilizing value	Equivalent heat treatment time expressed in minutes required to achieve a reduction of the number of spores or vegetative cells of a particular microorganism.
F_0	Sterilizing value at reference temperature 121.1°C and $z = 10$°C.
z value	Temperature increment required to reduce the D value to 10% of the original one.

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9 Thermal Processing of Dairy Products

A.L. Kelly, N. Datta, and H.C. Deeth

CONTENTS

9.1 INTRODUCTION: WHY HEAT MILK?

Milk is a fluid product produced by female mammals that provides the nutritional requirements of the neonate. As such, it is remarkably rich in many essential food constituents, such as amino acids (supplied for ingestion in the form of protein), lipids, sugar (lactose), minerals, and vitamins. However, this richness also makes milk a fertile medium for the growth of microorganisms, which either spoil the product or present a risk of food poisoning or food-borne disease. In addition, there are a number of enzymes of different types (e.g., proteases, lipases) in milk that can contribute to undesirable changes during storage (e.g., lipolysis can induce rancidity), and treatment or intervention to inactivate or control such activities is often essential to the prolonging of the acceptable shelf life of dairy products.

Thus, the majority of milk consumed today is processed to ensure safety and prolong shelf life. The same applies to the huge range of products that can be made from milk, including cheese, fermented milks (e.g., yogurt), and food ingredients. A range of preservation strategies have evolved over the millennia that milk has been a part of the human diet; for example, preservation by fermentation was known in biblical times. However, by far the most common strategy to preserve milk is the application of heat (i.e., thermal processing), which will be the focus of this chapter. Milk may also be heated to establish specific product properties, e.g., inhibiting oxidation during storage of whole milk powder, or generating stronger gel structures in yogurt. Product-specific thermal processes will also be discussed here.

9.2 HISTORICAL DEVELOPMENT OF THERMAL PROCESSING OF MILK

The historical development of the thermal processing of milk was reviewed by Westhoff[1] and Holsinger et al.[2]

In the period 1864–1866, the famous French scientist Louis Pasteur discovered that the spoilage of wine and beer could be prevented by heating to around 60°C for several minutes; in recognition of this profoundly important work, mild thermal processes applied to milk are now referred to as *pasteurization*. Although pasteurization was originally developed to improve the stability and quality of food products, it soon became apparent that it offered consumers protection against hazards associated with the consumption of raw milk. Early in the 20th century, a particular benefit was a reduction in the risk of transmission of tuberculosis from infected cows, through their milk, to humans. Developments in technology and widespread implementation of pasteurization occurred early in the 20th century. The first commercial pasteurizers, in which milk was heated at 74 to 77°C, were produced in

Germany in 1882[1]; the first commercially operated milk pasteurizer was installed in Bloomville, NY, in 1893[2]; and the first law requiring pasteurization of liquid (beverage) milk was passed by authorities in Chicago in 1908.

Many early pasteurization processes used conditions not very different from those proposed by Pasteur; generally milk was heated to 62 to 65°C for at least 30 min, followed by rapid cooling to less than 10°C (such processes are now referred to as *low-temperature long-time* (LTLT) pasteurization). However, *high-temperature short-time* (HTST) pasteurization, in which milk is heated to 72 to 74°C and held for 15 to 30 sec, using a continuous-flow plate heat exchanger, gradually became the standard industrial procedure for the heat treatment of liquid milk. Compared to the LTLT process, the HTST process has the advantages of reduced heat damage and flavor changes, and increased throughput.[3]

Later developments in the thermal processing of milk led to the introduction (in the 1940s) of *ultra-high-temperature* (UHT) processes, in which milk is heated to temperatures of 135 to 140°C for 2 to 5 sec.[4] UHT treatments can be applied using a range of heat exchanger technologies (e.g., indirect processes using plate heat exchangers or direct processes where steam is injected into milk), and essentially result in a sterile product that is shelf stable for at least 6 months at room temperature. A key enabling technology to ensure long shelf life was the parallel development of aseptic packaging plants, where the sterile milk leaving the heat exchanger is packaged into a sterile hermetically sealed container under conditions that prevent recontamination.[5] Eventual deterioration of UHT milk quality generally results from physicochemical (e.g., *age gelation*) rather than microbiological or enzymatic processes.

Sterilized milk products may also be produced using in-container retort systems. In fact, such processes were developed before the work of Pasteur; in 1809, Nicholas Appert developed an in-container sterilization process for the preservation of a range of food products, including milk. In-container sterilization is generally used today for concentrated (condensed) milks; typical processes involve heat treatment at 115°C for 10 to 15 min.

In recent years there has been considerable interest in extending the shelf life of pasteurized milk.[6] This has given rise to the term "extended-shelf-life" (ESL) milk. While such milk can be produced by processes other than heat (e.g., microfiltration[7]), the most common type of ESL treatment is high-temperature treatment, mostly in the range of 120 to 130°C for a short time (<1 to 4 sec). The rationale for using these conditions was demonstrated by Ranjith,[8] who reported that treatment of milk at temperatures of ≤117.5°C resulted in high total bacterial counts (>10^6 cfu/ml) after 13 days, whereas milks treated at temperatures of ≥120°C had counts of <10^2 cfu/ml after storage at 7°C for >40 days. It appears that heating at ≥120°C is required to inactivate psychrotrophic spore-forming organisms such as *Bacillus cereus* and *Bacillus circulans*. The upper temperature limit for ESL processes, which Blake et al.[9] concluded was 134°C, is governed by the heat-induced chemical changes that cause flavor impairment; Glaeser[10] considered that the upper-limit heat treatment for ESL processes should be the lower limit for UHT, which in the EU is 135°C for 1 sec.

As stated above, the primary function of the thermal processing of milk is to kill undesirable microorganisms. Modern pasteurization is a very effective means of ensuring that liquid milk is free of the most heat resistant pathogenic bacteria likely to be present in raw milk; today, most health risks linked to the consumption of pasteurized milk are probably due to postpasteurization contamination of the product. UHT or in-container sterilized milks, on the other hand, are virtually free of even spore-forming thermophilic bacterial species.

9.3 OVERVIEW OF HEAT TREATMENTS APPLIED TO MILK

As with any food product, the choice of heat treatment applied to milk depends on a trade-off between, first, the degree of microbial inactivation required to ensure safety and extend the shelf life by an acceptable factor and, second, changes in quality of the product; these two consequences of heating are usually, in effect, inversely correlated.

Overall factors that should be considered in determining the heat treatment required for a particular product include:

- Postheating growth potential of spore-forming bacteria. For example, low pH conditions or storage at low temperatures suppress outgrowth of spore-forming bacteria; thus, products that include these additional hurdles, e.g., pasteurized or fermented milks, may not require as extensive heat treatment as higher pH products or products to be stored at room temperature.
- Consumer preference. For example, in some countries, such as Ireland and Australia,[11] consumer preference is clearly aligned toward pasteurized milk, and the more strongly cooked flavors associated with UHT milk are undesirable.
- Target market. For example, the requirements for processing of infant formulae are among the most stringent in the dairy industry, due to the vulnerability of that group of consumers to food-borne illness.

Heat treatments applied to milk are generally defined by the maximum temperature of heating and the holding time at that temperature. The processes most commonly applied to milk and dairy products are summarized in Table 9.1.[12,13,16]

9.4 EFFECTS OF HEATING ON MILK CONSTITUENTS

The primary constituents of milk include fat (as an emulsion), protein (a heterogeneous population, some of which are in colloidal form, while others are dissolved in the aqueous phase, including enzymes), lactose, salts, and vitamins. Milk is an exceedingly complex raw material for processing; it has a range of constituents whose nature, stability, and properties are changed by the types of heat treatments

TABLE 9.1
Types of Heat Treatment Applied to Milk and Their Microbiological Effects

Process	Typical Conditions	Heat Exchanger	Microbiological Effect	Typical Microbial Quality
Thermization	57–68°C for 15 sec	PHE	Destroys psychrotrophs	3–4 log reduction in psychrotrophs[a]
Pasteurization	63°C for 30 min	Batch	Destroys vegetative pathogens	Total plate count < 100,000 cfu/ml[b]
Pasteurization	72–74°C for 15–30 sec	PHE	Destroys vegetative pathogens	Total plate count < 100,000 cfu/ml[b]
Yogurt mix heating	85–95°C for 2–30 min	PHE/THE	Destroys all pathogens and most spores	—
Preheating for producing milk powder	70–135°C for 1 sec–5 min	PHE/THE/Other	Depends on treatment	—
High-temperature pasteurization	120–130 for <1–5 sec	PHE/THE	Destroys vegetative bacteria and most spores	—
UHT (indirect)	135–140°C for 3–5 sec	PHE/THE/SSHE	Destroys all bacteria, including spores	Total plate count < 100 cfu/ml after 15 d at 30°C[c]
UHT (direct)	135–140°C for 3–5 sec	Steam infusion or injection system	As UHT (indirect)	Total plate count < 100 cfu/ml after 15 d at 30°C[c]
In-container sterilization	115–120°C for 10–20 min	Batch or continuous (hydrostatic) retort	As UHT	Total plate count < 100 cfu/ml after 15 d at 30°C[c]

Note: PHE = plate heat exchanger; THE = tubular heat exchanger; SSHE = scraped-surface heat exchanger.

[a]Data from Pearce, L., in *Proceedings of Workshop on Revisiting Heat Resistance of Microorganisms in Milk*, Kiel, Germany, 2003, pp. 1–41.
[b]Data from Gallmann, P.U., in *Proceedings of the IDF World Dairy Summit Meeting on Extended Shelf Life (ESL) Milk*, Dresden, 2000, pp. 1–9.
[c]Data from Lewis, M.J., *Int. J. Dairy Technol.*, 52, 121–125, 1999.

applied to it. Many properties of milk (sensory, nutritional, and physicochemical) consequently change as a result of thermal processing.

Perhaps the most significant changes on heating milk are those that involve proteins. Most (70 to 80%) of the protein in milk is *casein*, a family of four largely hydrophobic proteins (α_{s1}-, α_{s2}-, β-, and κ-caseins). As is the case for many hydrophobic substances found in an aqueous environment, the caseins are found in milk in colloidal micelles (ranging from 50 to 500 nm in size (average, ~120 nm), with an average mass of ~10^8 Da; there are 10^{14} to 10^{16} micelles ml^{-1} milk). One of the caseins, κ-casein, is a glycoprotein with a hydrophilic sugar-rich C-terminal (often called the glycomacropeptide (GMP)); κ-casein is found at the surface of the micelle, where the GMP protrudes into the serum (forming the so-called hairy layer) and stabilizes the micelle by acting in a role analogous to the amphiphilic nature of a classical emulsifying agent. The hairy layer is negatively charged and is largely responsible for the steric repulsion that prevents casein micelles from aggregating.

The remainder (20 to 30%) of the proteins in milk are the so-called *whey proteins*, which are globular proteins found in the serum (aqueous) phase of milk; the major whey proteins are β-lactoglobulin (β-lg) and α-lactalbumin (α-la). In terms of thermal processing, β-lg is of particular significance; due to an uneven number of cysteine residues, β-lg possesses a free thiol group that, when the protein is in the native state, is located within the interior of the structure of the molecule. Heating to temperatures of >75°C, however, results in unfolding of the molecule and exposure of the thiol group, which can then undergo thiol-disulfide interchange reactions with disulfide bond-containing proteins (e.g., β-lg itself, α-la, κ- and α_{s2}-caseins, milk fat globule membrane proteins, and the indigenous milk alkaline proteinase, plasmin). Such interactions have profound implications for the quality of heated milk and dairy products such as yogurt. For example, binding of denatured β-lg to the casein micelle, via disulfide bond formation with κ-casein, fundamentally and negatively affects the rennet coagulation properties of milk, as will be discussed later. Denatured β-lg may also associate with κ-casein via hydrophobic interactions. Exposure of free thiol groups on denaturation of β-lg results in a cooked flavor of the milk, while providing antioxidant activity.

Interactions of denatured β-lg with plasmin greatly reduce the proteolytic activity in milk. The inactivation of milk enzymes is an intensively researched consequence of heating milk, due to the use of such enzymes as indices of the severity of heat treatment applied, as will be discussed in more detail later in this chapter.

Severe heating has a number of specific effects on the caseins, including dephosphorylation, deamidation of glutamine and arginine residues, and cleavage and formation of covalent cross-links; these changes may result in protein–protein interactions, which contribute to thermal instability.

Heat causes some alterations to the mineral balance in milk; for example, heating milk at medium or high temperatures causes precipitation of calcium phosphate and reduces calcium ion activity.[15] Heating milk also affects *lactose*, the nature and extent of such effects depending on environmental conditions and the severity of heating; heat-induced changes in lactose include degradation to

acids (with a concomitant decrease in pH), isomerization (e.g., to lactulose), production of compounds such as furfural, and interactions with amino groups of proteins (Maillard reaction). In the Maillard reaction, lactose or lactulose reacts with an amino group, such as the ε-amino group of lysine residues, in a complex (and not yet fully understood) series of reactions with a variety of end products.[16,17] The early stages of the Maillard reaction (condensation reactions between the carbonyl group of lactose and the -amino group of lysine of milk proteins) result in the formation of the protein-bound Amadori product, lactulosyllysine, which then degrades to a range of advanced Maillard products, including hydroxymethylfurfural (HMF), furfurals, and formic acid. The most obvious consequence of the Maillard reaction is a change in the color of milk (browning), due to the formation of pigments called melanoidins, or advanced-stage Maillard products. Extensive Maillard reactions can result in polymerization of proteins,[17] and also alter the flavor and nutritive quality of dairy products, in the latter case through reduced digestibility of the caseins and loss of available lysine.

Moderately intense heating processes applied to milk primarily cause the isomerization of lactose to lactulose. Lactulose, a disaccharide of galactose and fructose, is of interest as a bifidogenic factor and also as a laxative. More severe treatments (e.g., sterilization) will result preferentially in Maillard reactions. Products of heat-induced changes in lactose, such as lactulose and HMF, may be used as indices of heat treatment of milk.[18]

9.5 OVERVIEW OF THE MICROBIOLOGY OF MILK

Milk from a healthy cow is secreted free of microorganisms, but it becomes contaminated with many microorganisms during direct contact with various sources (Figure 9.1).[19] Three main types of microorganisms are the key factors for assessing quality and safety of heat-treated milk:

- Thermoduric/heat-resistant bacteria
- Bacteria that enter through postprocessing contamination
- Bacteria that can grow at refrigeration temperature

Raw milk has a short shelf life even under highly hygienic refrigeration conditions[20] and requires processing as soon as possible after arrival in the dairy plant to ensure the production of high-quality processed milk and dairy products. Heat treatment is the most common and single most effective industrial processing procedure for reducing bacterial numbers in milk, thereby enhancing its shelf life and ensuring the absence of pathogenic organisms.

The quality and safety of heat-treated milk depend on raw milk quality, processing conditions, postprocessing contamination, and storage temperature.[14] The former will be discussed here, while the latter factors will be considered later in this chapter.

Even if produced under highly hygienic conditions, raw milk contains a heterogeneous population of bacteria, some of which are pathogenic and others of which can cause spoilage during milk storage. Fortunately, pathogens are

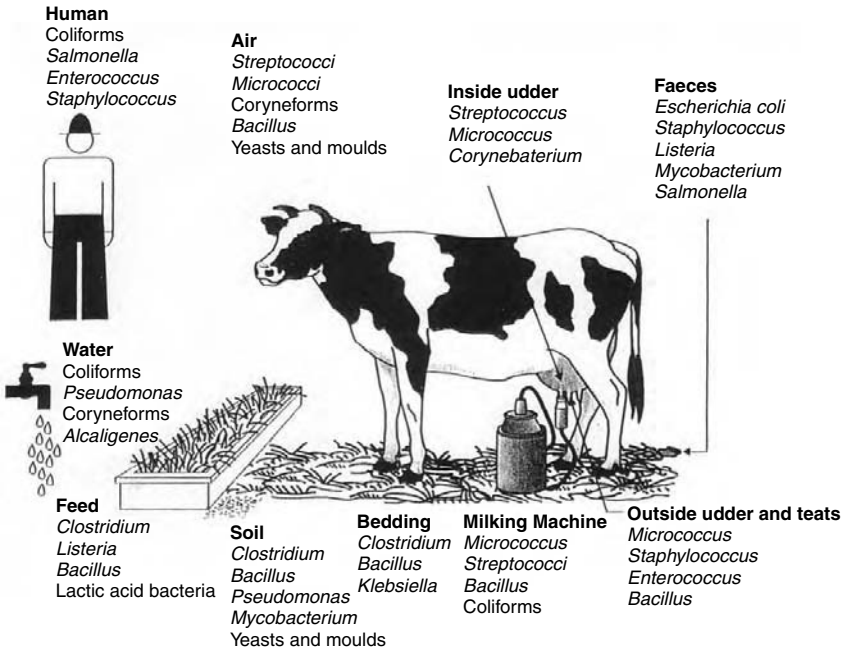

FIGURE 9.1 Sources of contamination of raw milk. (from Frank, J.F. and Hassan, A.N., in *Encyclopedia of Dairy Science*, Roginski, H., Fuquay, J.W., and Fox, P.F., Eds., Academic Press, London, 2002, pp. 1786–1796. With permission.)

generally not determinants of the shelf life of thermally treated milk and dairy products.[21,22] This is due to their low number in raw milk, their inability to grow at refrigeration temperatures, and their destruction by pasteurization.

In exception to the above generalization, one potentially pathogenic bacterium in raw milk, *B. cereus,* can be a significant spoilage agent due to the ability of its spores to survive pasteurization and the ability of some strains to proliferate in pasteurized milk at refrigeration temperature. This bacterium can produce enzymes such as a proteinase, which hydrolyzes casein to produce an intensely bitter flavor, and phospholipase, which hydrolyzes the phospholipids of the milk fat globule membrane and causes instability of the fat emulsion. In unhomogenized milk, this can cause the defect known as bitty cream, but this is not observed in homogenized milk. *B. cereus* in milk seldom causes food poisoning, as the contaminated product develops a strong, unacceptable flavor,[14] and also because toxigenic strains are seldom psychrotrophic. In addition, large numbers of this bacterium are required to produce food poisoning; Ryser[23] reported that most outbreaks of *B. cereus* poisoning were caused by contamination levels of at least 10^6 cfu/g.

In addition to *B. cereus*, other common types of spore-forming bacteria frequently present in raw milk are *Bacillus licheniformis* and *Bacillus stearothermophilus,* although the types and numbers of organisms vary considerably

between milks. For example, some husbandry practices, such as stall feeding of silage, are known to significantly increase the numbers of certain species. *B. stearothermophilus,* which is thermophilic and produces extremely heat resistant spores, causes a defect known as flat-sour spoilage in UHT milk stored at elevated temperature. In recent studies, a very heat resistant mesophilic species of *Bacillus* has been isolated from UHT milk products in several countries and has been named *Bacillus sporothermodurans.* Although it can multiply to a maximum of about 10^5 cfu/ml in milk without causing a change in its composition or sensory properties, its extreme heat stability and its ability to grow at room temperature make it a most unwelcome organism in dairy products.[24,25]

Psychrotrophic (i.e., able to tolerate cold) bacteria such as *Pseudomonas* spp. are very common in raw milk. These bacteria can produce extracellular enzymes such as proteinase, lipase, and phospholipase, when the counts of such bacteria exceed ~10^6 cfu/ml in milk. These enzymes can significantly and negatively affect the quality of milk and dairy products. A factor of particular significance is their high heat stability, which is much higher than that of the parent bacteria, with the enzymes frequently surviving processes that result in total elimination of the bacteria. For example, *Pseudomonas* proteinases can survive ultra-high-temperature (UHT) treatment (135 to 150°C for 2 to 8 sec) and cause bitterness and premature gelation in UHT milk.[26] *Pseudomonas* lipases can cause rancid off-flavors in cheese[27] and UHT milk,[28] and have been reported to cause a soapy off-flavor in flavored UHT milk recombined from milk powder containing residual enzyme.[21] These heat-stable enzymes do not present a problem in pasteurized milk and cream because these products have a short shelf life and are stored under refrigerated conditions. As will be discussed in the next section, thermization of raw milk when it arrives at a factory is used to extend the storage life of milk by controlling the growth of psychrotrophs, thereby reducing the likelihood of heat-resistant enzymes being present in subsequently processed milk and dairy products, e.g., milk powder.[29,30]

The microbiology of milk is obviously profoundly affected by the magnitude of heat treatment to which it is subjected. Milk heated at temperatures even slightly higher than those used for conventional HTST pasteurization, e.g., 80°C compared to 72°C, perhaps unexpectedly, has a lower keeping quality than pasteurized milk.[31,32] This has been attributed to activation of dormant spores present in raw milk[33] and destruction of the antibacterial enzyme lactoperoxidase.[34]

When the temperature of heat treatment is increased to 115 to 120°C for holding times of 1 to 5 sec, the number of spore-forming bacteria in milk and cream is reduced and the shelf life of the products is extended.[8,35–37] However, to eliminate the most heat resistant spores, much more severe heating is required. This is the basis of ultra-high-temperature (UHT) treatments, which heat milk at 135 to 140°C for 2 to 5 sec. Westhoff and Dougherty[38] studied the heat resistance of *Bacillus* spores in UHT milk and concluded that heating milk at 139 to 154°C for 9 sec was required to eliminate the most heat resistant aerobic mesophilic bacilli. This is similar to the conditions required for the inactivation of *B. sporothermodurans*: 148°C for 10 sec or 150°C for 6 sec.[39]

Several other bacteria that may be present in raw milk are of significance for specific products and heating processes; these will be discussed later in this chapter.

9.6 THERMIZATION OF MILK: TECHNOLOGY AND FUNCTIONS

Thermization is a subpasteurization operation sometimes applied to raw milk that is intended to be held after intake for extended periods of refrigerated storage before manufacture of certain products (e.g., Dutch-type cheese). The primary issue of concern in such cases is growth of psychrotrophic bacteria during cold storage, and consequent secretion of heat-stable extracellular proteinases and lipases by such bacteria into the milk, as discussed above.

Thermization, i.e., typically heating milk to 57 to 68°C for 15 sec, will inactivate the psychrotrophic bacteria and thereby prevent enzyme production.[40] Thermized milk has markedly better microbial quality during refrigerated storage than raw milk, but the net keeping quality depends on the precise heating regime applied and the raw milk quality; the natural antimicrobial system in milk (i.e., the lactoperoxidase–thiocyanate–hydrogen peroxide system) is unaffected by thermization.

Other thermization (i.e., subpasteurization) treatments may be used to prolong the shelf life of cultured milk products (either before or after packaging), by inactivating starter and other microflora in the product, preventing defects such as postacidification. Thermization also reduces the stability of extracellular proteinases and lipases produced by *Pseudomonas* bacteria to subsequent heat treatment, e.g., in UHT processes, by inducing so-called low-temperature inactivation.[41,42] However, in some cases, such low-temperature inactivation may be due to formation of enzyme–casein aggregates, rather than autoproteolysis, which can occur in the absence of milk proteins.[43]

It is possible that thermization also stimulates the germination of *B. cereus* spores, facilitating their inactivation by subsequent pasteurization. A process known as tyndallization involves heating milk in several successive heat treatments to successively germinate and inactivate spores; however, the efficiency of such processes has never been satisfactorily demonstrated, and they are rarely used.[22,32]

Thermization has little effect on the cheese-making properties of milk, and may in fact increase cheese yield by preventing premanufacture hydrolysis of milk protein by bacterial proteinases and by partially reversing low-temperature dissociation of β-casein and calcium from casein micelles.[44]

Potentially useful indicators for the efficiency of thermization in the ranges of 50 to 60°C or 60 to 70°C are the lysosomal enzyme α-L-fucosidase and the enzyme phospho-hexose-isomerase, respectively.[45,46] Inosine may also be used as an index of heating at 62°C, at which temperature its concentration increases with holding time, although measurement of this compound may not differentiate thermization from pasteurization processes.[40] Thermized milk should also retain active alkaline phosphatase, which allows it to be distinguished from pasteurized milk.

9.7 PASTEURIZATION OF MILK

9.7.1 Technology of Pasteurization

Pasteurization of milk is probably the largest-volume liquid processing operation in the modern food industry, and is consequently a highly optimized and controlled procedure. While a few plants (e.g., small cheese factories) may still employ the older low-temperature long-time (LTLT) process (heating milk to 62 to 65°C for 30 min), most processes today are of the high-temperature short-time type (HTST) (e.g., heating milk to 72 to 74°C for 15 to 30 sec).

HTST pasteurization is performed in plate heat exchangers, which are highly efficient due to extensive use of heat regeneration, whereby the majority of heat required to heat the cold incoming raw milk is supplied by the outgoing hot pasteurized milk, which is thereby cooled in the process. Regeneration is never completely efficient, and pasteurizers generally include a heating section where the milk is brought to the final pasteurization set temperature by a hot water circuit, and a final cooling section where the pasteurized milk is cooled to 5°C by chilled water. In a liquid milk processing plant, other unit operations such as separation (and standardization of fat content) and homogenization are often included in line with the pasteurizer, the milk being routed out mid-way through the regeneration section, when it is at the optimal temperature for these processes to be applied, without requiring separate heating and cooling of milk for that purpose.

Modern pasteurization plants include a number of safety features designed to ensure the safety of the final product and suitability for consumption. These include:

- Temperature sensors, at the end of the heating or holding sections, controlling a flow diversion valve that rejects milk that has not attained the required set temperature
- External insulated holding tubes to ensure correct holding times at the pasteurization temperature
- Booster pumps to increase the pressure of the pasteurized milk flowing through the regenerative heating sections, so that if leaks occur, pasteurized milk will flow into raw milk and not vice versa

The technology of pasteurization was described in detail by Kelly and O'Shea[3]; a diagram of a typical modern HTST pasteurization plant is presented in Figure 9.2.

The time–temperature combination traditionally used for HTST (72 to 74ºC for 15 sec) was based on the thermal inactivation kinetics of two bacteria (*Mycobacterium tuberculosis* and *Coxiella burnettii*), then considered to be the most heat resistant vegetative pathogenic bacteria likely to be present in raw milk; the similarity of their death kinetics to the inactivation kinetics of the indigenous enzyme, alkaline phosphatase, made that a particularly suitable indicator enzyme, or time–temperature integrator (TTI), for determination of the efficacy of pasteurization.

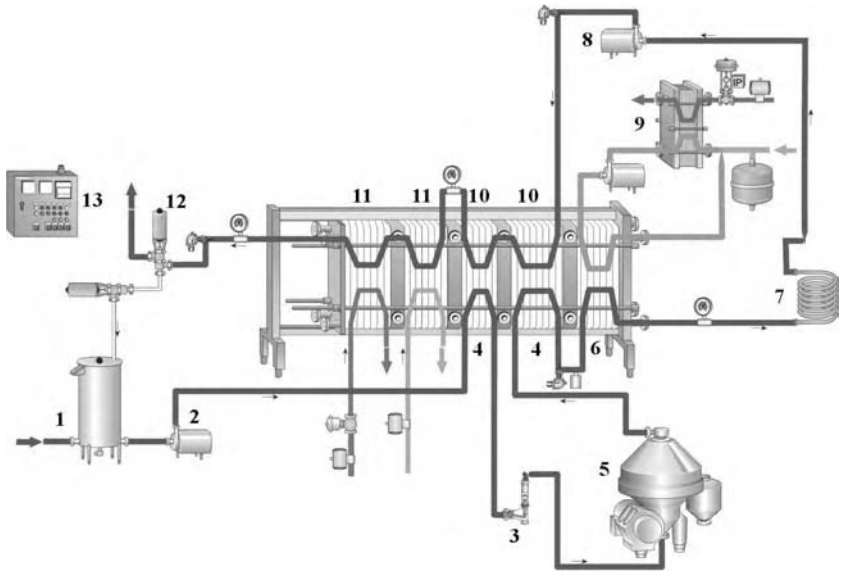

FIGURE 9.2 A complete milk pasteurization plant, including (1) balance tank, (2) feed pump, (3) flow controller, (4) regenerative preheating sections, (5) centrifugal clarifier, (6) heating section, (7) holding tube, (8) booster pump, (9) hot water heating system, (10) regenerative cooling sections, (11) cooling sections, (12) flow diversion valve. and (13) control panel. (Reproduced by courtesy of Tetra Pak A/B, Lund, Sweden.)

In recent years, evidence for the survival of *Listeria monocytogenes* and, in particular, *Mycobacterium avium* subsp. *paratuberculosis* (see later) in pasteurized milk has raised industry concern, and this has become the subject of ongoing research.[47,48]

9.7.2 Effects of Pasteurization on Milk Constituents

Overall, HTST pasteurization has little effect on the constituents of milk; whey protein denaturation is minimal (<5%) and the texture, flavor, and color of pasteurized milk should compare well to that of raw milk.[49] The extents of denaturation of immunoglobulins and agglutinins, which affect the antimicrobial and creaming properties of milk, respectively, are minor at 72°C, but increase at higher temperatures.

As mentioned above, the milk constituent of perhaps greatest significance in terms of pasteurization is the enzyme alkaline phosphatase.[50] A negative result (residual activity below a set maximum value) in a phosphatase test (assay) is regarded as an indication that milk has been pasteurized correctly.[51] Detailed kinetic studies on the thermal inactivation of alkaline phosphatase under conditions similar to pasteurization have been published.[52,53]

The antimicrobial lactoperoxidase system is affected little by pasteurization at 72°C, but higher-temperature treatments have progressively greater effects.[54] To test for overpasteurization (excessive heating) of milk, lactoperoxidase, being more heat stable than alkaline phosphatase and being inactivated at ~80°C, is often used as an indicator enzyme (Storch test[54]). Lactoperoxidase may also be used as an index of the efficacy of pasteurization of cream, which must be heated more severely than milk to ensure the killing of target bacteria, due to the protective effect of the fat therein. Detailed models for the inactivation kinetics of both alkaline phosphatase and lactoperoxidase in milk samples of different fat contents were recently developed by Claeys et al.[55] Recently, other enzymes have been studied as TTIs for heat treatments (particularly at temperatures above 72°C) that may be applied to milk; these include catalase, lipoprotein lipase, acid phosphatase, N-acetyl-β-glucosaminidase, and γ-glutamyl-transferase.[51,56]

9.7.3 Effects of Pasteurization on Milk Safety

The most important pathogens that can grow in milk at refrigeration temperature, together with their resistance to pasteurization, are summarized in Table 9.2.[22] As stated already, pasteurization was designed to destroy vegetative pathogenic microorganisms, and the twin hurdles of pasteurization and refrigeration are generally sufficient to ensure the safety of pasteurized milk. For example, *S. aureus*, a mastitis pathogen, produces a heat-stable enterotoxin that causes food poisoning after consumption of toxin-containing food. However, under normal circumstances, this pathogen does not pose a threat in pasteurized milk since it cannot grow or produce toxin at refrigeration temperatures and is readily killed by pasteurization. Similarly, while many strains of *Escherichia coli,* a commensal microbe found in the gut of cows and also in raw milk, can grow rapidly at refrigerated temperatures, one

TABLE 9.2
Heat and Cold Stability of Pathogenic Bacteria in Milk

Organism	Survives Pasteurization	Growth at 6°C
S. aureus	No	No
C. jejuni	No	No
Salmonella spp.	No	No
E. coli	No	?
L. monocytogenes	No	Yes
Yersinia enterocolitica	No	Yes
B. cereus	Yes (spores)	Yes[a]
Clostridium spp.	Yes (spores)	No[b]

[a]Certain strains only.
[b]Some nonproteolytic spp. can grow.

Source: Adapted from Muir, D.D., *J. Soc. Dairy Technol.*, 49, 24–32, 1996.

particular strain, *E. coli* O157:H7, a food-borne pathogen of international importance, is unable to grow in pasteurized milk at temperatures below 10°C.[57] In addition, it is readily destroyed by pasteurization, and hence consumption of pasteurized milk does not pose a significant risk for this pathogen.[58]

In terms of spore-forming bacteria that can be present in raw milk, *Clostridium perfringens*, a food poisoning bacterium, produces very heat resistant spores that survive pasteurization, but *C. perfringens* does not pose a health hazard in pasteurized milk due to the inability of the spores to germinate and grow at refrigeration temperature. In contrast, *B. cereus* in pasteurized milk has caused food poisoning outbreaks, as its spores can survive heat treatment, and some strains are capable of growing at low temperatures.[59] However, as was discussed earlier, this bacterium is rarely detected in milk stored below 5°C that has been processed in a properly maintained dairy plant.[60]

Thus, while hygienic milk production and handling, pasteurization, and refrigeration are effective measures to ensure the safety of milk, significant problems can arise if pathogenic organisms that can proliferate at low temperatures contaminate pasteurized milk (Table 9.3).

In 1985, an unusually large outbreak of salmonellosis in Chicago, involving more than 16,000 cases, was associated with the consumption of low-fat (2%) pasteurized milk[64]; a subsequent investigation concluded that the pathogen entered the milk as a postpasteurization contaminant. Similarly, *Campylobacter jejuni* in raw

TABLE 9.3
Major Disease Outbreaks Involving Pasteurized Milk

Causative Organism	Location	Year	Number of Cases	Cause	Reference
S. aureus	U.S.	1914–1942	29	PPC[a]	23
Campylobacter	U.K.	1978–1984	27	Improper	62
jejuni			3	pasteurization	62
				PPC	
Salmonella spp.	U.S.	1985	1600	PPC	23
E. coli	U.S.	1994	18	PPC	23
L. monocytogenes	U.S.	1983	49	Unknown	23
Yersinia	U.S.	1975	217	Poor raw	23
enterocolitica	U.S.	1982	172	material	23
	U.S.	1995	10	handling	23
	Europe	1985	36	PPC	63
				PPC	
				PPC	
B. cereus	Europe	1980	280	Unknown	59

[a]Postpasteurization contamination.

or inadequately pasteurized milk was implicated in several outbreaks of gastroenteritis in Great Britain from 1978 to 1984[61]; some cases were traced to pasteurized milk in glass bottles whose lids had been pecked by magpies and jackdaws, which are probable carriers of this bacterium.[65] *Yersinia enterocolitica*, which causes yersiniosis in children younger than 7 years of age,[62] is heat labile and completely inactivated by pasteurization[66]; however, several outbreaks of yersiniosis have been reported in the U.S. and Europe.[65] This bacterium can grow in milk during refrigeration, and thus poses a potential heath hazard in underpasteurized milk and milk contaminated with the organism after heat treatment.

Although *L. monocytogenes* is more heat tolerant than most other nonspore-forming pathogens, pasteurization should result in its total destruction[67]; however, some evidence exists of it being linked to a serious food poisoning incident involving pasteurized milk in the U.S. during 1983.[23]

As indicated in Table 9.3, most of the food poisoning outbreaks due to consumption of milk are believed to have been due to either inadequate heating or postheating contamination. One means by which pathogenic organisms can contaminate pasteurized milk is by leakage of raw milk into the pasteurized milk in the regeneration section of pasteurizers.[68] This should not occur in properly installed pasteurizers, where a booster pump prevents flow of milk from the raw into the pasteurized streams.

Maintaining proper hygiene in raw milk handling and ensuring adequate pasteurization can thus prevent contamination of pasteurized milk with pathogenic microorganisms. However, control of spoilage bacteria in pasteurized milk is more difficult. The main causative agents, thermoduric and psychrotrophic bacteria, are discussed below.

9.7.4 Effects of Pasteurization on Milk Shelf Life

Thermoduric organisms are those that will survive pasteurization. The main types of these organisms in milk and cream are shown in Table 9.4.

Common examples that can be isolated from pasteurized milk and cream include coryneforms, micrococci, and some streptococci, which all grow very slowly at refrigeration temperatures,[69] and also spore-forming organisms, such as *Bacillus* spp. whose spores can survive much more intense heating conditions, such as 80°C for 10 min. The spores can be activated, germinate, and grow in heat-treated products under certain conditions, subsequently causing spoilage. As mentioned above, some may even compromise the safety of the heat-treated product.

Postprocessing contamination (PPC) with Gram-negative, heat-sensitive psychrotrophic bacteria is the most important cause of spoilage in pasteurized milk and cream. These bacteria, which produce off-flavors due to enzymatic action when the bacterial count exceeds about 10^7 cfu/ml,[31,70] enter the product from nonsterile surfaces of processing and packaging equipment, the air, and packaging material. Constant monitoring of the PPC level with sensitive test methods such as the *Psychrofast* test[71] and strict attention to the cleanliness of surfaces with

TABLE 9.4
Heat-Resistant Organisms Recovered from Milk and Cream after Heat Treatment

	Isolates Recovered after Heating (%)			
	Milk		Cream	
Type of Bacteria	**63°C/30 min**	**80°C/10 min**	**63°/30 min**	**80°/10 min**
Bacillus spp.	54	61	55	65
Coryneform group	46	37	31	35
Other Gram-positive	0	2	0	0
Gram-negative	0	0	14	0

Source: Adapted from Phillips, J.D. et al., *J. Soc. Dairy Technol.*, 34, 109–113, 1981.

which the product comes in contact after heat treatment will ensure low contamination levels and maximize the shelf life of the product. PPC can be minimized by heating plant surfaces at 95°C for 30 min and packaging under ultraclean conditions, and completely avoided by applying aseptic techniques downstream of the holding tube. However, such facilities are expensive and not normally used for pasteurized milk. The presence of high counts of coliform bacteria in pasteurized milk is classically symptomatic of PPC.[72]

As mentioned earlier, psychrotrophic bacteria such as *Pseudomonas* spp. and their heat-stable enzymes can present particular problems for pasteurized milk products, either if growth and enzyme production has occurred before pasteurization or if PPC occurs.

9.7.5 Significance of Storage Temperature

Storage temperature has a vital role in determining the shelf life of heat-treated products. Ideally, pasteurized milk should be kept at or below 4°C; if the storage temperature is raised to 10°C, the shelf life is reduced by at least 50%.[4] Zadow[73] reported that shelf life is reduced to 50% by raising the temperature of products by only 3°C.

9.7.6 Emerging Issues

Mycobacterium avium ssp. *paratuberculosis* (MAP) (*M. paratuberculosis*) was discovered 100 years ago and is the causative bacteria of *Johne's disease* in cattle. Milk can be contaminated by MAP through the mammary gland of infected cows, but also, and more importantly, through contamination of milk during the milking process by feces from infected cows.[74]

Since MAP has also been implicated in Crohn's disease in humans,[75] reports of its possible survival during HTST pasteurization have caused some concern

and sparked research activity in several laboratories.[76] Progress has been slow because of difficulties in growing the organism; it is extremely slow growing (taking up to 4 months to culture for counting purposes[77]), and hence can be overgrown by any organisms whose growth is not inhibited during incubation. Trials to determine the resistance of this bacterium to pasteurization have yielded mixed results, with some laboratories reporting complete destruction under simulated commercial conditions, while others have reported survival of some organisms in some trials.[47,78–80] Inactivation during pasteurization appears to depend on the strain of the organism and the number of organisms present. Some strains can be inactivated completely by classical HTST conditions (72°C for 15 sec) at levels of 100 cfu/ml, but small numbers (4 to 16 cfu/ml) have been shown to survive higher-temperature (90°C for 15 sec) pasteurization of milk with an initial high (10^6 cfu/ml) MAP count.[47]

Increasing the holding time during pasteurization processes has been found to be more effective in inactivating MAP in milk than increasing the pasteurization temperature. Homogenization before pasteurization has been shown to increase the lethality of the heat treatment on MAP. These findings suggest that heat penetration is more important than the intensity of heat applied; this may be related to the tendency of the organism to form clumps.[79]

9.8 UHT PROCESSING OF MILK

9.8.1 Technology of UHT and Effects on Milk Constituents and Stability

UHT processing of milk involves heating milk in a continuous process to temperatures higher than 135°C for a few seconds, cooling rapidly, and *aseptically packaging* the milk into sterile containers.[81,82] The sequence of steps in UHT processing is shown in Figure 9.3.

UHT treatment must be sufficient to produce a commercially sterile product (one in which bacterial growth will not occur under normal storage conditions), but not severe enough to cause chemical changes that result in an unacceptable flavor, color, and nutritive loss. In general, the heating should be equivalent to a minimum of 9 log reduction of thermophilic spores (sometimes referred to as a *B* value*, >1) and a maximum reduction of 3% in the level of thiamine (sometimes referred to as a *C* value*, <1). The temperature and holding time commonly used for UHT processing are 138 to 140°C and 2 to 5 sec, respectively. Since the nominal holding time is the average time a particle spends in the holding tube, it is important to ensure that the time taken for the fastest particle is sufficient to inactivate the target microorganisms, i.e., *Clostridium* and *Bacillus* spores.

The microbiological failure rate for PPC in UHT products is quite low (0.02%).[84] Higher failure rates indicate significant inadequacies in the aseptic packaging step. Interestingly, Cerf and Davey[85] concluded that most bacteriological failures in UHT milk packages (which they reported as one to four per

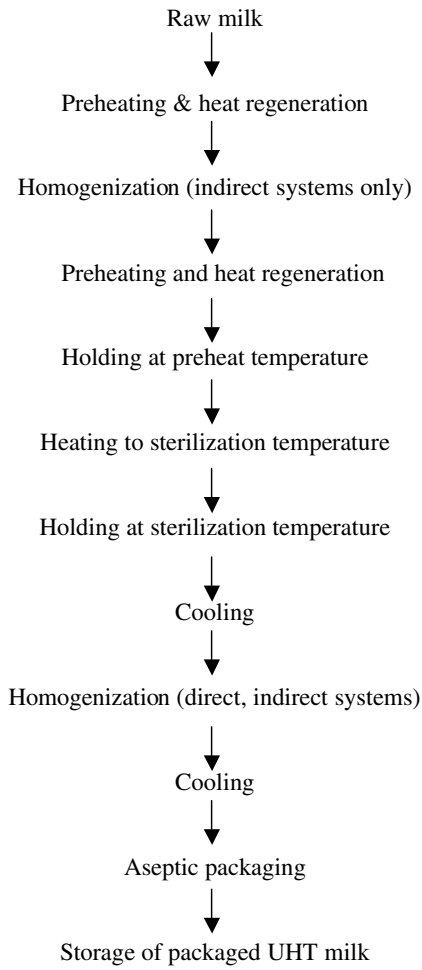

FIGURE 9.3 Steps involved in UHT processing of milk. (Adapted from Datta, N. et al., *Aust. J. Dairy Technol.,* 57: 211–227, 2002.)

100,000 packs) could be explained statistically on the basis of residence time distribution, whereby a very small percentage of spores pass through the holding tube too fast to be destroyed. This suggests that many of the failures may not be due to PPC.

The spores of some *Bacillus* species, such as *B. stearothermophilus* and *B. sporothermodurans*, are extremely heat resistant and can resist UHT treatment conditions. The latter species is of particular concern to the dairy industry, as it is mesophilic and thus can grow at the temperature at which UHT milk is normally stored. It has already caused the closure of some UHT processing plants.[86]

9.8.1.1 Heating Mode

Two main types of UHT processes are used commercially: direct heating, in which milk comes into direct contact with the heating medium, steam; and indirect heating, in which the heating medium, steam or superheated water, is separated from the milk by a stainless steel plate or wall of a tube. A less common type of indirect heating involves electrical heating of the stainless steel tubes carrying the milk. The electrical resistance of stainless steel causes what is known as joule heating, when an electrical current is passed through the walls of the tubes. In direct systems, heating to and cooling from the high temperature is very fast due to transfer of the latent heats of condensation and evaporation, respectively, between the steam and liquid milk. Cooling is achieved in a vacuum chamber. Direct heating requires sterilization temperatures 3 to 4°C higher than indirect heating to achieve an equal sterilization effect because of the greater heat input during the heat-up phase of indirect heating.[87]

Systems using a combination of direct and indirect heating are available commercially (e.g., the *High-Heat Infusion* system of APV[88] and the *Tetra Therm® Aseptic Plus Two* system of Tetra Pak).[83] These achieve better energy economy than conventional direct systems (due to greater heat regeneration) and cause less chemical damage, especially flavor change and burn-on, than conventional indirect UHT systems.[89,90]

9.8.1.2 Time–Temperature Profiles

The time–temperature curve or profile of a UHT process, which depends on the configuration of the plant, is a significant factor determining the quality of the final product. The greater the area under the curves at temperatures greater than about 80°C, the greater the chemical, i.e., quality, changes induced in the milk. The time–temperature profiles for some UHT systems are shown in Figure 9.4. However, it should be noted that each UHT installation will present a unique profile.

9.8.2 Effects on Milk Constituents

9.8.2.1 Proteins and Fat

UHT processing causes a slight increase in the size of the casein micelle due to its association with denatured whey proteins and calcium phosphate. The extent of the increase depends on the time and temperature of processing and the pH of the milk.[82] This phenomenon can lead to a chalky or astringent defect in UHT milk (especially if heated by steam injection), which can be eliminated by homogenization after the high-heat treatment.[91]

On treatment at UHT temperatures, β-lactoglobulin irreversibly denatures and interacts with the casein micelle, particularly with κ-casein, and reduces the susceptibility of UHT milk to rennet coagulation. Denaturation of β-lactoglobulin is one of the key effects of UHT heating and controls the major

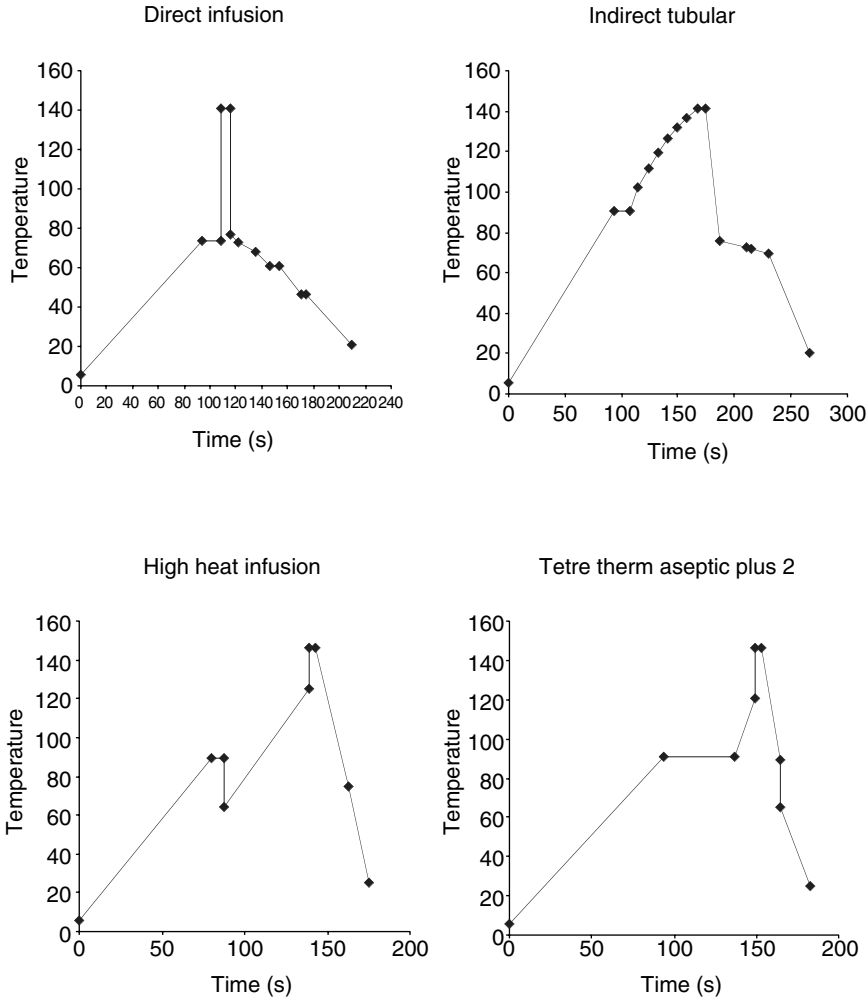

FIGURE 9.4 Time–temperature profiles of various heating modes in UHT processing. (Adapted from Deeth, H.C., and Datta, N., *Encyclopedia of Diary Science*, Academic Press, 2002, pp. 2642–2652.)

properties of UHT milk and products made from it. For example, volatile sulfydryl compounds are liberated and influence the flavor of the heated milk, deposits form within the heat exchangers, and plasmin, which may cause deterioration of the product, is inhibited.[82,92] The extent of denaturation of β-lactoglobulin in UHT milk can vary from as low as 35% in direct plants to close to 100% in indirect plants.[93]

UHT processing causes virtually no physical or chemical changes in the structure, properties, or nutritional value of milk fat.

9.8.2.2 Enzyme Inactivation

The milk alkaline proteinase, plasmin, and its inactive precursor, plasminogen, have considerable heat resistance. They are more susceptible to inactivation by indirect UHT processing than by direct heating; 19% of the original plasmin and 37% plasminogen activity remained in directly processed milk, while no residual plasmin activity and 19% of the plasminogen remained in indirectly processed milk.[94,95] Heat-stable proteinases from pseudomonads were reported to retain 20 to 40% of their activity after exposure to UHT conditions of 140°C for 5 sec.[96]

9.8.2.3 Protein–Sugar Interactions

UHT treatment causes extensive Maillard reactions in milk; products of such are useful as indicators of the thermal history of the UHT milk and for predicting the sensory and nutritional quality of UHT-processed milk.[97,98]

9.8.2.4 Minerals and Vitamins

UHT processing transfers minerals from the aqueous phase to the casein micelle and reduces ionic calcium levels by 10 to 20%. This, in addition to the interaction of whey proteins with the casein micelle, reduces the susceptibility of UHT milk to coagulation by rennet. Some calcium phosphate is rendered insoluble at the high temperatures used in UHT heating and deposits on the surfaces of the heat exchanger (fouling).

The fat-soluble vitamins (A, D, and E) and some of the water-soluble vitamins (pantothenic acid, nicotinic acid, riboflavin, and biotin) are largely unaffected by UHT treatment, but losses of 20 and 30%, respectively, in thiamine and vitamin B_{12} can occur during UHT treatment.[82] The levels of ascorbic acid and folic acid are markedly reduced in UHT milk containing a significant level of oxygen during UHT processing and storage.[99]

9.8.2.5 Flavor Compounds

At least two different types of flavors develop in UHT milk: the cooked or heated flavor, which develops during processing, and the stale flavor, which develops during storage. Volatile sulfur compounds produced mainly from denatured lactoglobulin are responsible for the cooked flavor, which disappears rapidly in the presence of oxygen or oxidizing agents. Aliphatic aldehydes are major contributors to the stale flavor. UHT milk kept at 25°C has a maximum flavor acceptability between 3 and 5 weeks, that is, after the cooked flavor disappears and before the stale flavor appears.[100]

9.8.3 Physical Stability of UHT Milk

In contrast to pasteurized products, storage temperature has a less significant effect on the shelf life of UHT products, as bacterial contamination is rare. However, the temperature of storage has a significant effect on the shelf life of these products

through its effect on their physicochemical properties.[101] Several changes that can occur in UHT milk during storage will be discussed in this section.

9.8.3.1 Gelation

Gelation during storage is a common problem of UHT milk, which ultimately limits its shelf life.[87] A major initiating factor is partial proteolysis of the caseins, by either plasmin or residual heat-resistant bacterial proteinases. Milk sterilized by direct heating gels more rapidly during storage than milk treated by indirect methods.[94] This effect appears to be due to the greater inactivation of the proteinases and greater stabilization of the casein micelle by complexation with denatured whey proteins during the more severe indirect heating. The addition of sodium hexametaphosphate (0.1%) to raw milk before processing delays the onset of gelation of UHT milk during storage.[101]

9.8.3.2 Fat Separation

Despite homogenization of milk in the UHT process, a layer of fat occasionally develops on the surface of the milk during storage. Less fat separation occurs in milk processed with direct steam injection than with indirect heating,[102] due to the additional homogenization effect of the steam injection.

9.8.3.3 Sedimentation

Sedimentation in UHT milk is due to destabilization of casein micelles. The amount of sediment increases with the time and temperature of heating and with the time and temperature of storage.[103] The pH of the milk is very important, as severe sedimentation occurs at pH < 6.5. Sedimentation occurs more readily in concentrated milk than in normal-strength milk, but less in reconstituted milk.[82] Goat's milk is particularly susceptible to sedimentation, which has been attributed to its high ionic calcium content. Sediment volume decreases with increasing homogenization pressure and addition of chemicals such as trisodium citrate or disodium hydrogen phosphate (0.025 to 0.1%) to raw milk.[104]

9.9 IN-CONTAINER STERILIZATION OF MILK AND CONCENTRATED MILK

In-container sterilization (e.g., in bottles, cans, or jars), as mentioned earlier, is one of the oldest thermal processing strategies applied to milk, predating even the work of Pasteur. Today, most processors producing long-life milk use UHT systems, due to the advantages of high-throughput and continuous operation. In addition, the long times for which products are exposed to high temperatures in sterilization processes result in extensive deterioration in the quality of the products (e.g., extensive development of brown colors due to Maillard reactions and creation of strong cooked flavors due to production of volatile sulfydryl compounds from β-lg). Typical treatment conditions used for in-container sterilization processes for dairy products are 110 to 120°C for 10 to 20 min.[105]

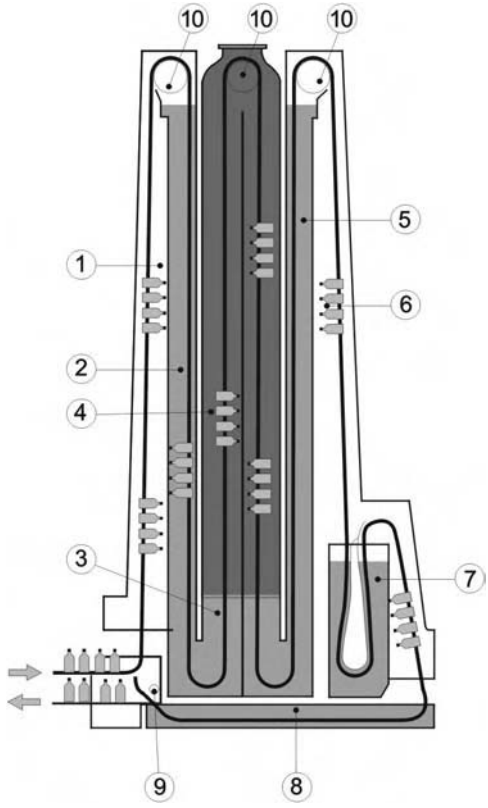

FIGURE 9.5 Hydrostatic vertical continuous sterilizer showing (1–3) heating stages, (4) steam-filled sterilization section, (5–9) cooling stages, and (10) upper shafts and wheels. (Reproduced by courtesy of Tetra Pak A/B, Lund, Sweden.)

The products most commonly treated in-container today are sterilized concentrated milk and sweetened condensed milk. In the former case, long shelf life is achieved by sterilization applied to the packaged product; in the latter, thermal treatment reduces the microbial load of the product, but microbial growth is ultimately prevented by the effect of added sucrose on the osmotic pressure in the medium.

Sterilization has traditionally been applied in autoclaves or batch retorts; however, in most plants today, continuous sterilization in hydrostatic retorts is used. A diagram of a hydrostatic tower sterilizer is shown in Figure 9.5; the principle of such systems is as follows. A central chamber, in which sterilization is achieved, is maintained at sterilization temperature by steam under pressure, which is counterbalanced on the inlet and discharge sides by columns of water that generate a hydrostatic pressure sufficient to maintain the conditions of temperature and pressure required for sterilization. The water in the inlet leg is warmed to achieve preheating of the product, while that in the discharge leg is cooled and

serves to reduce the temperature of the containers and their contents poststerilization. Presterilization of product in a UHT-type process may be applied before packaging, to reduce the heat load that needs to be applied in the hydrostatic retort.

Other designs of continuous retort for sterilization of milk products include horizontal sealed rotary-valve retorts, in which product is passed through a steam zone in which sterilization is achieved, and horizontal continuous rotating autoclaves (cooker-coolers). In the latter system, the design incorporates three cylindrical vessels at different pressures and temperatures through which the product containers pass in a helical manner, thereby progressively moving through the retort, while simultaneously being rotated, to increase rates of heat transfer and reduce thermal damage.

While, as discussed already, milk is a relatively heat stable system, under certain conditions it can be coagulated during the process of sterilization; the mechanism of heat-induced coagulation of milk (i.e., the heat stability of milk) has been the subject of considerable amounts of research.[106,107]

The heat stability of milk (expressed as the number of minutes at a particular temperature, e.g., 140°C, before visible coagulation of the milk occurs — the heat coagulation time (HCT)) is highly dependent on pH, with large differences in heat stability being apparent over quite a narrow range of pH values (Figure 9.6).[108] Indeed, pH is probably the most significant factor influencing the heat stability of milk. Most milk samples show what is referred to as a type A heat stability–pH profile,

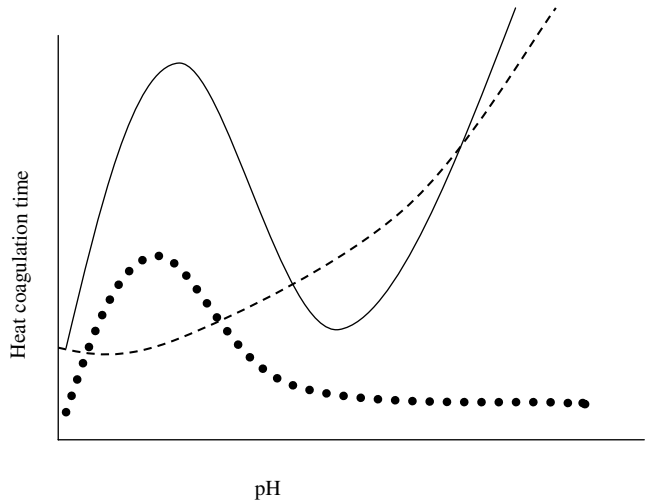

FIGURE 9.6 Heat coagulation time (HCT)–pH profiles of typical type A bovine milk (whole line) and type B serum protein-free milk (dashed line), as determined at 140°C, or concentrated milk (dotted line), as determined at 120°C. (From Fox, P.F. and Kelly, A.L., in *Proteins in Food Processing*, Yada, R., Ed., Woodhead Publishing, New York, pp. 29–71, 2004.)

with a pronounced minimum and maximum, typically around pH 6.7 and 7.0, respectively; heat stability decreases on the acidic side of the maximum and increases on the alkaline side of the minimum. The rare type B profile does not exhibit a minimum, and heat stability increases progressively throughout the pH range 6.4 to 7.4.

As well as pH, a number of other factors affect the heat stability of milk.[106,107] These include:

- Levels of Ca^{2+} or Mg^{2+}, reduction of which increases stability in the pH range 6.5 to 7.5
- Hydrolysis of lactose, which increases heat stability throughout the pH range
- Addition of κ-casein, which eliminates the minimum in a type A profile
- Addition of β-lactoglobulin to type B milk, which converts it to a type A profile
- Addition of phosphates, which increase heat stability
- Addition of oxidizing agents, which convert a type A to a type B profile, or reducing agents, which decrease heat stability
- Presence of alcohols and sulfydryl-blocking agents, which reduce the heat stability of milk

Concentrated (e.g., evaporated) milk is much less thermally stable than unconcentrated milk and its heat stability profile, normally assayed at 120°C for that reason, is quite different. It shows a maximum at ~pH 6.4, with decreasing stability at higher and lower pH values (Figure 9.6). The possibility that concentrated milk will coagulate on sterilization may be reduced by preheating the milk, adjustment of the pH of the milk, or addition of stabilizing salts (e.g., polyphosphates).

9.10 THERMAL PROCESSING DURING MANUFACTURE OF OTHER DAIRY PRODUCTS

9.10.1 Evaporation and Spray Drying

The two largest bulk-commodity milk powders produced today are whole milk powder (WMP) and skim milk powder (SMP); a number of different heat treatments may be applied to milk before evaporation prior to manufacture of milk powder. While the principal objective of such heating is to ensure the safety of the final powder, the functionality and applications of the powder are also largely determined at this point. For example, SMP is frequently classified on the basis of its content of remaining native whey protein; milk used for manufacture of so-called low-heat powders has been mildly heated, and the powders contain a high proportion of native whey protein, while high-heat powders have low levels of native whey protein due to more severe heating during processing.

The subsequent applications of SMP are largely determined by its heat classification. For example, for cheese making, low-heat powders are recommended, as denatured whey protein would interfere with the rennet coagulation process (see below). On the other hand, for yogurt, where denatured whey proteins can become a structural element of the acid gel, high-heat powders are favored.

Evaporation plants are typically equipped with flexible thermal processing capabilities, with heat exchangers capable of treating milk at different temperatures, with different holding times, to allow production of powders of different heat classifications on a single plant. Preheating may be performed using any of a range of heat exchangers, including plate heat exchangers and spiral heat exchangers wrapped around the tubes in the evaporator itself, or using very short time steam injection heating systems. Direct-heat exchangers are preferred over indirect systems, as biofilms of thermophilic bacteria may develop within indirect-heat exchangers.[109] *B. cereus* spores in milk powder are a particular health hazard because both reconstitution and pasteurization can induce their germination and outgrowth.

Denaturation at later stages of the powder manufacturing process (e.g., during evaporation or spray drying) is relatively minor compared to that caused at the preheating stage.[110] The rate of the increase in temperature during preheating may affect whey protein interactions. Slower indirect-heating favors whey protein–whey protein interactions and higher overall denaturation of whey proteins than more rapid direct-heating methods, which favor extensive casein–whey protein interactions.[109]

The properties and applications of the major heat classification groups of SMP are outlined in Table 9.5.[111]

In manufacture of WMP, heat classification is not used; the milk is generally heated to 85°C to inactivate indigenous lipase activity and expose antioxidant-free sulfydryl groups.[112]

9.10.2 Yogurt and Cheese Manufacture

Severe heat treatment is undesirable for many cheese varieties, especially hard varieties such as cheddar, principally due to denaturation of whey proteins. Denatured whey protein can interfere with both the primary stage of rennet coagulation (i.e., hydrolysis of the Phe_{105}-Met_{106} bond of κ-casein) and later gel assembly and structure development, in both cases due to steric hindrance at the surface of the micelle due to denatured β-lactoglobulin bound to κ-casein. Cheese made from milk that has been heated under conditions more severe than conventional pasteurization is generally regarded as yielding an inferior quality product, with defects in flavor and texture.

Nonetheless, there has been significant interest in this area, due to the economic advantages of incorporating whey protein in the curd and thereby increasing cheese yield. Process modifications that can be used to compensate in part for the negative effects of severely heating cheese milk include adjustment of the pH of the heated milk to ~6.2, to favor the action of chymosin and

TABLE 9.5
Food Applications of Skim Milk Powder in Different Heat Classes

Heat Classification	Heat Treatments Applied	WPNI[a]	Functional Properties	Food Applications
Low heat	70°C for 15 sec	>6.0	Solubility, lack of cooked flavor	Recombined milk, milk standardization, cheese
Medium heat	85°C for 1 min	1.5–6.0	Emulsification, foaming, water absorption, viscosity, color, flavor	Ice cream, chocolate, confectionery
	90°C for 30 sec			
	105°C for 30 sec			
High heat	90°C for 5 min	<1.5	Heat stability, gelation, water absorption	Recombined evaporated milk
	120°C for 1 min			
	135°C for 30 sec			
High-high heat	>120°C for >40 sec	<1.5	Flavor, water binding, color	Bakery, recombined evaporated milk

[a]Whey protein nitrogen index.

Source: Adapted from Kelly, A.L., O'Connell, J.E., and Fox, P.F., *Advanced Dairy Chemistry,* vol. 1, *Proteins*, 2nd ed., Kluwer Academic–Plenum Publishers, 2003, pp. 1027–1062.

solubilize some heat-precipitated CCP. Alternatively, heat and pH adjustment may be applied to whey to yield a microparticulated whey protein precipitate, which can be added to cheese milk and thereby incorporated into the curd (the *centri-whey process*).[113]

For soft cheese or acid-coagulated cheese varieties (e.g., cottage cheese or Quarg), severe heat treatment and high levels of whey protein denaturation are favored and applied quite commonly. Similarly, in the case of fermented milks (e.g., yogurt), high-heat treatment (e.g., 85 to 95°C for 2 to 30 min) is commonly used to induce extensive whey protein denaturation and association with caseins, in addition to destroying pathogenic and spoilage organisms; in such cases, the denatured whey protein acts as a structural element in the gel and gives a firmer texture that is less likely to synerese (i.e., expel whey) during storage.[114–116] The denatured whey proteins also become susceptible to aggregation during acidification, as their isoelectric point is approached.[117] Attempts have been made to use UHT heating (which also denatures whey proteins) for yogurt manufacture, but the resulting yogurt has lower viscosity and gel strength than yogurt made by the conventional process.[118]

9.11 CONCLUSIONS

Milk is a complex product from chemical, physicochemical, enzymatic, and microbiological perspectives. Its potential to act as a vector for food pathogens and its inherent tendency to spoil rapidly, even at refrigeration temperatures, necessitate rapid processing to preserve and stabilize the product and protect the consumer. Heat treatment is one of the oldest means for achieving these goals, and a suite of different thermal processes, applied using a range of heat exchanger and process technologies, now exists in the modern dairy industry. However, heating milk has a range of other effects on its constituents and characteristics, which must be considered as part of the net implications of applying any thermal process to milk.

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10 UHT Thermal Processing of Milk

Pamela Manzi and Laura Pizzoferrato

CONTENTS

10.1 INTRODUCTION

Nowadays, milk is nearly always thermally processed before consumption. The main purpose of heating is to make milk safe for human consumption (by killing pathogenic bacteria) and to extend its shelf life (by killing microorganisms and inactivating enzymes).

In the European Union, according to Council Directive 92/46/EEC,[1] industrial heat treatments of milk can be classified, depending on temperature and time of heating, into:

- *Pasteurized milk* obtained by means of a treatment involving a high temperature for a short time (HTST, at least 71.7°C for 15 sec) or a pasteurization process using a different time and temperature combination to obtain an equivalent effect.
- *Ultra-high-temperature (UHT) milk* obtained by applying a continuous flow of heat at high temperature (not less than 135°C) for a short time (but at least 1 sec). This treatment has the aim to destroy all residual spoilage microorganisms and their spores, thus considerably extending milk shelf life, permitting milk to be transported or held for a long period before using. According to the European law, no deterioration should be observed in the UHT milk product after 15 days in a closed container at a temperature of +30°C; where necessary, provision can also be made for a period of 7 days in a closed container at a temperature of +55°C. Two main types of UHT thermal processing are distinguished: direct and indirect heating. If the UHT milk treatment process is performed by direct contact of milk and steam (*direct UHT*), the steam should be obtained from potable water. Moreover, the use of this process must not cause any dilution of the treated milk. In the *indirect UHT* thermal processing, tubular, plate, or scraped-surface heat exchangers are employed to transfer heat to milk.
- *Sterilized milk* heated and sterilized in hermetically sealed wrappings or containers, the seal of which must remain intact.

Obviously, during the heating process numerous changes in the chemical composition and in the physical and organoleptic characteristics of milk occur, even if heating conditions are now optimized to maintain as much as possible original milk quality. Some of these heat-induced changes are reversible, such as lactose mutarotation, alterations in ionic equilibrium and protein conformation, casein association, agglutination of fat globules, and fat crystallization, while others are irreversible, such as denaturation of whey proteins and their interaction

with casein micelles, the Maillard reaction, and changes in fat globule composition and vitamin content.[2–4]

Several heat-induced markers (e.g., bioavailable lysine, furosine, hydroxymethylfurfural, lactulose) related to these modifications have been developed in recent years to determine the quality of milk. These so-called heat-damage indicators can be used to control and check the heat treatments given to milk.

In this chapter, we focus on milk subjected to the ultra-high-temperature (UHT) treatment process, which is today the most common thermal treatment technique for milk. In particular, we discuss heat-damage indicators related to alterations in UHT milk nutrient composition (carbohydrates, protein, lipids, vitamins, and minerals) and to the Maillard reaction, as well as the combined use of some of these indicators. We further discuss the safety and organoleptic aspects of UHT milk in relation to its thermal treatment.

10.2 EFFECT OF UHT TREATMENT ON MILK NUTRIENTS

10.2.1 Carbohydrates

Lactose is the main carbohydrate in milk (about 4.8% in cow's milk); it is a disaccharide composed of D-glucose and D-galactose linked by 1-4 beta-glycosidic bond. Other carbohydrates present in milk include free monosaccharides (glucose, fructose, and galactose), aminosugars (glucosamine and galactosamine), and oligosaccharides. Levels of milk sugars can change as a consequence of heat treatment and storage.[5]

10.2.1.1 Lactose

Lactose can isomerize to lactulose (4-O-β-galactopyranosyl-D-fructose) in heat-treated milk via the Lobrey de Bruyn–Alberda van Ekenstein transformation. Lactulose isomerization is catalyzed by free amino groups of casein and is strictly dependent on time of heating, heating temperature, and pH.

Lactulose content in milk can be determined enzymatically (detection limit = 100 mg/l) as well as by gas chromatographic analysis (detection limit = 10 mg/l). Recently, an enzymatic-spectrophotometric method with higher detection sensitivity has been developed.[6] This method, with a detection limit of 2.5 mg/l, is particularly useful in samples with low lactulose content. Using this new method, Marconi and coworkers[6] analyzed 90 milk samples from different heat treatments: lactulose content ranged from 2 to 1146 mg/l (Table 10.1).

Normally, lactulose does not occur in fresh milk and highly pasteurized milk, but only in UHT and sterilized milk. Lactulose content is therefore considered a suitable indicator of heat treatment.[7] Recently, it has been proposed to stipulate a lactulose content of less than 600 mg/l for UHT milk and more than 600 mg/l for sterilized milk.[8,9]

A recent study on market milks of Czech origin has shown that lactulose content differs significantly ($P < 0.01$) among milk types (liquid and powder).[10] The authors

TABLE 10.1
Content of Lactulose (mg/100 ml) in Different Heat-Treated Milk Samples

Minimum	Maximum	Mean	Type of Treatment	References
5	10		UHT direct	3
15	75		UHT indirect	3
4	15		Pasteurized	3
49	114	74	Sterilized	6
28	42	35	UHT indirect	6
13	24	17	UHT direct with injection system	6
9	12	11	UHT direct with infusion system	6
3.2	7.9	5.8	High-temperature pasteurized	6
0.2	0.6	0.4	Pasteurized	6
		36	High-temperature pasteurized	10
		230	Dried milk	10
		2451	Condensed milk	10
19	62		UHT, whole milk	11
		64	Sterilized, whole milk	11
		115	Sterilized, low-fat milk	11
		12	UHT direct	12
25.0	45.6		UHT indirect	12
		112	Sterilized	12

further found that lactulose levels in all the UHT milk samples analyzed were below the proposed limit (600 mg/l) necessary for differentiation of UHT from sterilized milk.[10] Average contents were found to be very low (35.5 mg/l) in high-temperature-treated milk (Table 10.1), low in dried milk (229.7 mg/kg), and very high in condensed milk (2451.3 mg/l).[10]

This research confirms the earlier work of Mosso and coworkers,[11] who analyzed lactulose in 14 samples of UHT milk and 2 samples of sterilized milk. For the UHT milk samples (whole, skimmed, and partially skimmed), lactulose content ranged from 18.6 to 62.0 mg/100 ml. The two sterilized milk samples had lactulose contents of 115 mg/100 ml (showing a brown color) and 64 mg/100 ml.[11]

During storage, lactulose concentration in UHT milk can either decrease (via beta-elimination to galactose, tagatose, and formic acid) or increase (via lactose isomerization), the former process being more temperature dependent than the latter.[13] Andrews[13] found that light did not affect lactulose concentration during milk storage at 18°C for 115 days. Lactulose formation increased as a direct function of OH concentration and lactose concentration, but was unaffected by protein concentration or dissolved oxygen.

Recently, lactulose has also gained interest in the field of clinical nutrition. Being an indigestible sugar, lactulose has been found to promote the growth of *Bifibacterium bifidus*, and hence could be useful as a prebiotic compound.[14]

10.2.1.2 Free Monosaccharides and Aminosugars

To verify whether galactose might be used as an indicator to distinguish between different thermal processes applied to milk, Romero and coworkers[15] examined the evolution of galactose in four commercial whole UHT milk samples (two directly and two indirectly heat-treated products) during storage at temperatures of 6, 20, 30, 40, and 50°C until milk expiration date (90 days). Galactose concentration (determined by an enzymatic method) remained constant only in samples stored at 6°C, while the concentration progressively increased at all other storage temperatures. No significant differences in galactose formation were observed between samples with respect to direct or indirect heat treatment or initial galactose content.[15]

Troyano and coworkers[16] found that the content of monosaccharides (glucose and galactose) and aminosugars (N-acetylglucosamine, N-acetylgalactosamine, and myo-inositol) ranged from 2 to 14 mg/100 ml in just-processed UHT milk. Some authors have observed an increase in monosaccharide and aminosugar content depending on time and temperature of storage,[16] the increase being particularly clear in UHT milk derived from raw milk with high psychrotrophic activity.

Storage effects on the levels of galactose and N-acetylglucosamine in UHT milk were investigated in two commercial and two experimental batches of UHT milk (whole and skim) stored at 10 to 30°C for 120 days.[17] In agreement with the above-cited research, an increase in galactose and N-acetylglucosamine contents with time was observed, the increase being more pronounced at higher storage temperatures. Increase in monosaccharide content is probably due to dephosphorylation of the respective sugar phosphates (levels of which decrease at 10 to 20°C), although the authors hypothesized that during storage at 30°C, changes in galactose levels may also be due to other processes, possibly involving glycosidases.[17]

With the aim to understand the biochemical processes taking place during the shelf life of UHT milk, Recio and coworkers[18] studied changes in the free monosaccharide fraction and noncasein N contents of five batches of commercial UHT milk during 3 months of storage. They observed that during storage, milk batches with high residual proteolytic activity showed a considerable increase in galactose, N-acetylglucosamine, and N-acetylgalactosamine with time, whereas glucose and myo-inositol contents remained unaltered. No changes occurred in batches with slight or negligible proteolytic activity.

10.2.2 Proteins

Milk proteins can be classified into two main fractions: casein (about 80% of total milk protein) and whey proteins (about 20%). The casein fraction, composed of alpha-s1-, alpha-s2-, beta-, and kappa-caseins, precipitates at pH 4.6. In particular,

kappa-casein can be hydrolyzed by rennin to give para-kappa-caseinate that is insoluble in the presence of calcium ions and precipitates as a curd. Usually casein exists in colloidal particles, so-called casein micelles, containing calcium and phosphorus, some enzymes, citrate, and milk serum.

Whey proteins do not precipitate at pH 4.6; they are water soluble and sensible to temperature. The main components of whey protein are beta-lactoglobulin, alpha-lactalbumin, bovine serum albumin, and immunoglobulins. Beta-lactoglobulin represents about 50% of the total whey protein and is the main whey protein in bovine, ovine, caprine, and buffalo milks, while alpha-lactalbumin is the principal protein in human milk.

10.2.2.1 Denaturation of Whey Protein

Several physical and chemical changes occur in whey protein during thermal processing of milk, and these changes (denaturation) affect the functional and sensory properties of milk. During the heating process, whey proteins containing sulfhydryl residues undergo various changes resulting in the formation of (1) a protein complex between beta-lactoglobulin and kappa-casein, with consequent modification of rennet coagulation behavior and heat stability, (2) typical off-flavors, and (3) unusual amino acids (lysinoalanine).[19] In particular, under certain conditions of concentration and pH, beta-lactoglobulin is able to form gels.[20,21]

Whey proteins show different thermal stabilities: alpha-lactalbumin > beta-lactoglobulin > bovine serum albumin > immunoglobulins. While denaturation of alpha-lactalbumin can be a good parameter to describe high-temperature treatments, such as sterilization, denaturation of beta-lactoglobulin is useful to describe thermal treatments from pasteurization to UHT processing.[4,22]

Alpha-lactalbumin is frequently chosen as an indicator of heat treatment. To characterize its native and heat-denatured forms, monoclonal antibodies specific in inhibition enzyme-linked immunosorbent assay (ELISA) have been proposed.[23] Using this method, it is possible to differentiate among raw, pasteurized, UHT, and sterilized milk even if the alpha-lactalbumin concentration of the original raw milk is unknown. However, as mentioned above, this technique is mainly suited to detect UHT treatment and sterilization because of the heat stability of alpha-lactalbumin.[23]

Fukal and coworkers[24] investigated the use of immunochemical probes to discriminate among different heat treatments of milk. They raised polyclonal antibodies against 10 immunogens: 5 native milk proteins, alpha- + beta-casein, kappa-casein, whole casein, alpha-lactalbumin, and beta-lactoglobulin, and the corresponding 5 pasteurized milk proteins. Their results showed no significant differences in the immunoreactivity of anticasein antibodies in heat-treated milk compared to raw milk. In contrast, using a combination of antibodies against native alpha-lactalbumin and beta-lactoglobulin, immunoreactivity decreased in heated samples and allowed ($P < 0.001$) a categorization of milk as raw, pasteurized, UHT treated, or bath sterilized.[24]

Irreversible denaturation of whey proteins during heating of milk under commercial processing conditions has been widely studied. Oldfield and coworkers[25]

observed that native protein concentration decreased with increased heating time at all temperatures studied. Kinetics and thermodynamics of denaturation varied among the whey proteins: temperature dependence was revealed for alpha-lactalbumin and beta-lactoglobulin. Aggregation of lactoglobulin was due to disulfide linkages, while aggregation of alpha-lactalbumin was apparently more complex, involving formation of disulfide-linked aggregates and hydrophobic interactions.[25]

10.2.2.2 Proteolysis

During UHT milk storage, one of the main problems limiting shelf life is gelation. *Gelation* is caused by modifications of casein micelle aggregation, producing a three-dimensional network. The mechanism is not completely known, but it is probably due to proteolysis induced by either heat-resistant native proteinases (plasmin) or microbial proteinases. While plasmin, a native alkaline serine proteinase, is almost completely inactivated by the UHT process, its precursor, plasminogen, is particularly resistant to heat. Plasminogen is converted to plasmin by an activator whose activity increases after heat treatment.[26] Usually plasmin attacks beta-casein and alpha-2-casein, while the microbial proteinases prefer to attack kappa-casein. Note that as little as 1 ng of bacterial proteinase/ml is sufficient to cause gelation of UHT milk during storage.[27]

It is possible to discriminate between the types of proteolysis by reversed-phase high-pressure liquid chromatography (RP-HPLC) and the fluorescamine method: peptides produced by bacterial proteinases are less hydrophobic and elute earlier on RP-HPLC than those produced by plasmin activity. Acid precipitation allows fractionation of peptides; in the pH 4.6-soluble fraction are total proteolysis peptides, whereas the 12% trichloroacetic acid (TCA)-soluble fraction contains those generated by bacterial proteinases only. If proteolysis is caused by plasmin, this may be a sign of the UHT processing conditions (notably direct UHT processing) being too mild; if proteolysis is caused by bacterial proteinases, this may be a sign of low quality of raw milk.[26]

Effects of heat treatment on the plasmin system in milk, with particular reference to plasminogen activators derived from somatic cells, were studied in depth by Kennedy and Kelly.[28] Milk samples were heated at various temperatures (63 to 138°C) for set times (10 to 90 sec), simulating industrial procedures. Results showed that thermal plasmin inactivation is a first-order reaction, under UHT treatment, and that plasmin is less stable in high (800,000 cells/ml) than in low (<150,000 cells/ml) somatic cell count milk. On the contrary, results also showed that at lower temperatures (63 to 90°C), plasmin is slightly more stable in high than in low somatic cell count milk. Moreover, plasminogen activators derived from somatic cells were confirmed to be stable over the entire range of temperatures studied.[28]

The correlation between para-kappa-casein and related peptides, and proteolysis was recently investigated in stored raw, pasteurized, and UHT milk samples.[29] Para-kappa-casein-derived compounds were observed in raw and pasteurized milk stored at 6°C for more than 5 days, and in UHT milk stored at 20°C for 30, 60,

or 90 days. The presence of these compounds was attributed to the action of proteinases from psychrotrophic bacteria on kappa-casein.[29]

Garcia-Risco and coworkers[30] investigated the effect of storage on proteolysis. They studied protein degradation and distribution of caseins and whey proteins in the soluble (supernatant fraction) and colloidal phases (pellet fraction) during storage for 5 months at room temperature in six commercial UHT milks using capillary electrophoresis and sodium dodecyl sulfate polyacrilamide gel electrophoresis (SDS-PAGE). During storage, a decrease of all caseins and, in particular, kappa-casein was observed due to proteolytic activity.

Cauvin and coworkers[31] found that storage temperature did not significantly affect proteolysis of casein during storage of UHT milk, although casein concentration decreased and proteose–peptone concentration increased in UHT milk samples from two factories, stored at 4°C and room temperature for 3 months. This was attributed to plasminogen-derived activity.

The effect of homogenization of milk on proteolysis varies depending on whether it precedes or follows heating. Homogenization of milk *before* UHT treatment has been found to decrease activities of proteinase, glycosidase, and phosphatase during storage. During homogenization, casein and whey proteins interact with the fat globule membrane, the morphology of casein micelles changes, giving rise to small micellar particles, and a complex formation between kappa-casein and beta-lactoglobulin occurs. All of these aspects may be responsible for the reduced proteolytic degradation observed in homogenized UHT milk samples.[32] In particular, heat-induced binding of the whey proteins alpha-lactalbumin and beta-lactoglobulin to milk fat globule membranes has been studied: alpha-lactalbumin behavior did not change with temperature and the total amount of protein bound was approximately 0.2 mg/g fat. On the other hand, beta-lactoglobulin interaction with milk fat globules did increase with temperature between 65 and 85°C, from 0.2 to 0.7 mg/g fat.[33]

Homogenization *after* heating facilitates proteolysis in skim milk that contains high levels of soluble beta-lactoglobulin and kappa-casein, with mainly kappa-casein susceptible to degradation. In contrast, whole milk samples show the lowest levels of proteolysis, probably due to an increased complex formation between kappa-casein and beta-lactoglobulin.[34]

10.2.2.3 Free Amino Acids

Heat treatments could potentially affect the content of free amino acids in milk. However, concentration of free amino acids in milk heated by thermization/pasteurization, UHT, and sterilization processes are reported to be not markedly influenced by temperature or holding time during processing.[35]

Gandolfi and coworkers[36] investigated occurrence in milk of free and bond D-amino acids. Significant amounts of free D-alanine, D-aspartic acid, and D-glutamic acid were found in raw cow's milk. The amount of D-amino acids in milk did not increase by pasteurization, UHT treatment, or sterilization. In contrast, D-alanine content in raw milk samples increased during cold storage at 4°C, and hence it was

TABLE 10.2
Content of Lysinoalanine (mg/1000 g Protein) in Different Heat-Treated Milk Samples

Minimum	Maximum	Type of Treatment	References
Up to 15		Pasteurized	38
Up to 400		UHT	38
4	24	Raw	40
17	47	Pasteurized	40
13	69	High pasteurized	40
49	186	UHT	40
224	653	Sterilized	40
<0.4		Pasteurized	41

suggested that D-alanine might be considered an indicator of bacterial milk contamination.[36] Indeed, the presence of D-amino acids in milk, and in food in general, can be ascribed not only to thermal racemization, but also to microbial activity.[37]

In processed foods some unusual amino acids can be detected that do not naturally occur in raw foods. Their presence is due to processing conditions, such as heat and alkali treatments of foods. In particular, the production of lysinoalanine, an unnatural amino acid, is a two-step process consisting of: (1) production of dehydroalanine from the degradation of cystine, O-phosphoserine, or O-glycoserine, and (2) reaction of dehydroalanine with the free amino group of lysine to form lysinoalanine.[38] The molecule of lysinoalanine seems to reduce protein digestibility due to inhibition of proteolytic metalloenzymes.[38] Moreover, lysinoalanine formation causes a decrease in lysine bioavailability for nutritionally important, high-lysine proteins such as casein.

The presence of lysinoalanine in milk-based infant formulas[39] and in different processed milks[40] has been investigated in order to verify whether lysinoalanine, determined by HPLC method, can be a good indicator of heat treatment of milk. Results confirmed that lysinoalanine content is lower in raw and pasteurized milk than in UHT milk (Table 10.2). Lysinoalanine can also be utilized as a sensitive indicator in dairy products in which caseinate has been added.[41]

10.2.2.4 Protein Quality and Digestibility

Heat treatments might also negatively affect milk nutritional quality and, in particular, protein digestibility. Efigenia and coworkers[42] evaluated the effect of heat treatment on milk nutritional quality for samples of raw, pasteurized, domestic-boiled, and UHT milk: fat, protein, and N contents were not significantly modified by any of these treatments. Protein efficiency ratio, digestibility, and *in vitro* liver protein synthesis, studied by feeding trials in rats, were unaffected by heat treatments, with the exception of a lower rate of protein synthesis in the liver of rats fed with boiled milk.[42]

Alkanhal and coworkers[43] studied the modification of protein digestibility and quality in UHT milk during storage by comparing apparent digestibility, true digestibility, biological value, and net protein utilization in Sprague-Dawley rats fed with pasteurized, fresh UHT, and reconstituted (obtained from skim milk powder) UHT milk, all stored for 0, 3, or 6 months at 37°C, as a source of protein in their diet. Results of this study are reported in Figure 10.1. Interestingly, biological value and net protein utilization of pasteurized milk did not change with storage time, while biological value and net protein utilization of UHT milk were lower for stored milk than directly used (0-month) milk. Protein quality of

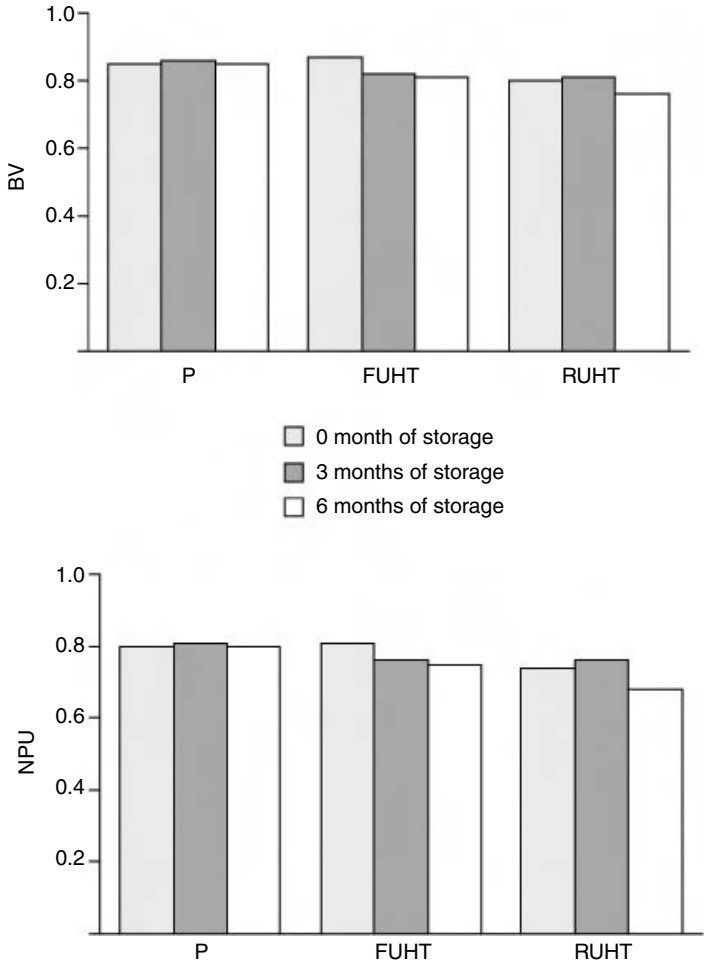

FIGURE 10.1 Biological value (BV) and net protein utilization (NPU) of pasteurized (P), fresh UHT (FUHT), and reconstituted UHT (RUHT) milk during storage. (Modified Alkanhal, H.A. et al., *Int. J. Food Sci. Nutr.*, 52, 509–514, 2001.)

reconstituted UHT milk was poorest at all storage times, and further declined after 6 months of storage (Figure 10.1).

Effects of heat treatment on protein digestibility and *lysine availability* of pasteurized milk (72 or 85°C for 15 sec) and UHT milk (140°C for 3 sec or 130°C for 10 sec) were also studied.[44] Lysine loss was the highest in UHT milk and correlated with heat severity, although the degree of lysine loss was not sufficient to affect milk nutritional values. *In vitro* protein digestibility was highest in milk pasteurized at 72°C. Results suggested that in severely heated milk samples, lysine availability and protein digestibility decrease simultaneously.[44]

Sakai and coworkers[45] evaluated three types of commercial heat-treated milk samples — low-temperature long-time (LTLT) milk, high-temperature short-time (HTST) milk, and UHT milk — for their peptic digestibility. The intact proteins of casein decreased rapidly upon peptic digestion without showing any differences among the milk samples differently treated, while alpha-lactalbumin was more resistant to peptic digestion than casein in LTLT and HTST milks and, to a lesser extent, in UHT milk. Beta-lactoglobulin in LTLT and HTST milk was resistant to peptic digestion, but easily digested in UHT milk.[45]

10.2.2.5 Inactivation of Endogenous Milk Enzymes

Milk contains *enzymes* that have the ability to catalyze specific chemical reactions. In milk both endogenous and exogenous enzymes are present: *endogenous enzymes* are mainly hydrolases (lipase, the heat-stable plasmin, and alkaline phosphatase, destroyed by minimum pasteurization temperatures), and *exogenous enzymes*, generally heat stable, are produced by psychrotrophic bacteria. As expected, enzyme activities can be considerably affected by thermal processing.

Girotti and coworkers[46] analyzed raw, pasteurized, and UHT milk samples with different fat contents and cream samples for xanthine oxidase (EC 1.1.3.22). In pasteurized milk, xanthine oxidase activity depended on fat content, while in UHT milk, enzyme activity completely disappeared due to heat treatment.

Martin and coworkers[47] studied adenosine deaminase (EC 3.5.4.4), which oxidatively deaminates adenosine to inosine, in model and practical experiments. Activity of adenosine deaminase in milk increased up to about 75°C, but was no longer evident at 85°C. Activity was present in short-time heated milk samples, but not in high-temperature and UHT milk samples. Adenosine deaminase showed a higher thermal stability than alkaline phosphatase, and its activity was not influenced by homogenization.[47]

Zehetner and coworkers[48] studied the stability of four endogenous milk enzymes, alpha-L-fucosidase (EC 3.2.1.51), phosphohexoseisomerase (EC 5.3.1.9; glucose-6-phosphate isomerase), phosphodiesterase I (EC 3.1.4.1), and alpha-mannosidase (EC 3.2.1.24) during heating (temperature range of 52 to 86°C) for heating times up to 1600 sec. At a heating time of up to 800 sec, alpha-fucosidase was inactivated at temperatures between 52 and 62°C and phosphohexoseisomerase at temperatures between 56 and 66°C. Phosphodiesterase I was inactivated under pasteurization conditions, and alpha-mannosidase was inactivated

within the lower range of high-temperature pasteurization. Measurement of the activities of the four endogenous milk enzymes in commercial heat-treated milk samples showed no enzyme activity in 21 UHT milk samples, and in 18 pasteurized milk samples only phosphodiesterase activity (30%) could be detected.[48]

10.2.3 Lipids

Milk can be described as an oil-in-water emulsion with the fat globules dispersed in the continuous serum phase. The total fat content of milk, which reflects the energy requirements of the newborn, ranges from 3.5% (cow and woman) to 50% (aquatic mammals) according to the species, and varies with breed, age of the animal, stage of lactation, and type of feed.[20] The lipids associated with the milk fat globule are mostly (98%) triglycerides; the other lipids amount to less than 2% of the total, and of this, around 0.5% is diacylglycerols and monoacylglycerols, the balance being made up of phospholipids, sterols, free fatty acids, and traces of other substances such as the fat-soluble vitamin.

The heat load influence on milk will depend on the total fat content because fat affects the viscosity of milk and therefore hinders heat transfer. Pellegrino[49] evaluated the effect of fat content on heat-induced changes for bulk milk (>20 t) with different fat contents, either pasteurized or UHT processed under direct or indirect industrial conditions. Results indicated that fat did indeed protect milk components against tested heat-induced changes (lactulose formation, decreased furosine levels, and whey protein denaturation).

10.2.3.1 Fatty Acids

The *saturated* fatty acids are about 63% of total milk fatty acids, and in particular, the short-chain fatty acids, butyric, caproic, caprylic, and capric acid (C4, C6, C8, and C10, respectively), are abundant (8 to 9%) in ruminant milk fat. *Short-chain* fatty acids are responsible for the characteristic dairy flavor and aroma, and they can contribute either to the desirable aromas of some cheeses or to rancid flavor.

About 40% of total fatty acids consists of the saturated C16 palmitic and C18 stearic acids, the remainder of the saturates being mainly lauric (C12) and myristic (C14) acid. Among the *unsaturated* fatty acids, C18:1 oleic acid is abundant (approximately 30% of total fat), but the percentage can vary with the feed of the animal (higher in summer with pasture).[19] The level of polyunsaturated fatty acids is lower in ruminant milk than in monogastric milk. In particular, cow's milk fat contains low levels of the polyunsaturates C18:2 linoleic (2.4%) and C18:3 linolenic (0.8%) acid.[19]

In milk a small amount of *trans* fatty acids (unsaturated fatty acids with at least a double bond in *trans* configuration) occurs; their presence is due to the hydrogenation action of the microorganisms of the rumen.[50]. Generally, *trans* fatty acids have been found to increase low-density lipoprotein (LDL) cholesterol and decrease high-density lipoprotein (HDL) cholesterol, and a relationship between risk of coronary heart disease and high intake of *trans* fatty acids has been hypothesized.[51,52]

In contrast, *Butyrivirus fibrisolvens*, a microorganism of the rumen, is able to convert linoleic acid into 24 isomers, most of which, such as 9-*cis*, 11-*trans* octadecadienoic acid (rumenic acid) — the main isomer in ruminant milk fat, are responsible for beneficial effects (conjugated linoleic acid (CLA)).[53] Actually, in the last decade, several favorable biological activities of CLA have been hypothesized:[54] CLA is thought to possess anticarcinogenetic properties[55] and the capacity to modify lipid metabolism[56] and prostaglandin production in specific tissues.[57] Milk fat is a good source of CLA (0.6%); according to Creamer and MacGibbon,[20] New Zealand milk contains the highest level, probably due to breeding cattle mainly on pasture.

UHT treatment can increase levels of free fatty acids in milk, with a consequent increase in acid degree value (ADV). Choi and Jeon[58] studied free fatty acids and ADV in direct and indirect UHT milk samples during 12 weeks of storage at 23°C. The total amount of free fatty acids increased slightly during storage from 77.9 to 86.2 ppm and from 127.1 to 141.2 ppm in directly and indirectly processed UHT milk, respectively. The higher concentration of free fatty acids observed for indirectly processed UHT milk was ascribed to the more severe heat treatment and the resulting higher lipolysis. Acid degree value increased from 0.62 to 0.77 meq KOH in 100 g fat in directly processed UHT milk and from 1.39 to 1.50 meq KOH in 100 g fat in indirectly processed UHT milk.[58]

Milk fat, even if it is composed mainly of saturated fatty acids, can undergo oxidative reactions. UHT milk samples processed at 140°C, stored at 9, 15, 25, 35, 45, and 55°C, were analyzed for changes brought about by lipid oxidation and proteolysis.[59] The thiobarbituric acid (TBA) value of these samples increased from 0.012 to 0.021, 0.023, 0.032, and 0.065 after 16 weeks of storage at 15, 25, 35, and 45°C, respectively, reaching 0.22 after 12 weeks of storage at 55°C. The level of free amino groups, expressed as glycine, was 18.14 μmol/ml in the fresh sample, increasing to 21.92, 23.08, 28.40, 33.56, and 36.06 μmol/ml of milk after 16 weeks of storage at 9, 15, 25, 35, and 45°C, respectively, reaching 32.90 μmol/ml of milk after 12 weeks of storage at 55°C. Both proteolysis and lipid oxidation were strongly related to storage temperature and could be described by zero-order reaction kinetics. A storage temperature of 35°C was found to be critical for proteolytic changes.[59]

10.2.3.2 Stability of Fat Globules

Another class of lipids in milk is phospholipids, which even if present in small amounts (less than 1%), are essential in the formation of fat globules. These fat globules (ranging from 0.1 to 15 μm in diameter) are surrounded by a membrane that stabilizes the fat globules in an emulsion within the aqueous environment of milk. Mechanical agitation can disrupt the membrane, thus allowing the formation of larger fat globules, while homogenization of milk is able to decrease the size of fat globules (below 1 μm).

The fat membrane is made up of a lipid fraction, a protein fraction, trace metals, and enzymes. Phosphatidylcholine, phosphatidylethanolamine, sphingomyelin, triacylglycerols, diacylglycerols and free fatty acid, cerebrosides,

and sterols are the basis of the lipid fraction. The protein fraction of the membrane consists of up to 40 polypeptides (15,000 to 240,000 Da), the enzyme xanthine oxidase (20%), butyrophilin, and several minor proteins. The relative amount of the protein fraction can vary according to the season.[60] As the heat treatment of milk can induce interaction between the fat globule membrane and the milk protein, some authors[60] have investigated the behavior of fat membranes during heat treatment. Their results show that polymerization occurs via intramolecular disulfite bonds of xanthine oxidase and butyrophilin during heat treatment.

Separation of the fat layer adversely affects shelf life of UHT milk. In order to investigate the effect of homogenization on formation of the cream layer in UHT milk, Hillbrick and coworkers[61] examined milk samples obtained by indirect UHT treatment, using plate heat exchangers, and direct UHT treatment, using steam injection. All milk samples, stored upside down at 20°C for 2 weeks, showed a cream layer, but the layer thickness was negatively correlated to pressure of homogenization (0, 17.3, 34.5 MPa; $P < 0.05$). When homogenization pressure remained the same, particle size distribution and thickness of fat layers were similar, regardless of UHT plant configuration used. The authors concluded that homogenizing milk after or before heating produces milk of similar microstructure that forms cream layers of similar thicknesses during storage. Nevertheless, it was recommended that UHT milk be homogenized *before* treatment with high temperature, to avoid use of aseptic homogenizers.[61]

Corredig and Dalgleish[62] studied interactions between milk fat globules and proteins in milk samples obtained by HTST (80 to 95°C for 24 and 90 sec), UHT (120 to 135°C/4 sec), and direct steam injection (DSI) (120 to 140°C/4 sec). A sharp increase in the fat globules' specific surface area was observed for DSI milk. For the HTST and UHT milk samples, it was found that with increasing temperature, an increasing amount of whey protein was bound to casein micelle systems. A negligible amount of whey protein was bound to micelles in DSI-treated milk.

Changes occurring in soluble phosphoglycerides in UHT milk during storage (at 10, 20, and 30°C for up to 4 months) were evaluated in comparison with pasteurized milk samples.[63] Glycerophosphocholine and glycerophosphoethanolamine disappeared during storage in UHT milk manufactured from raw milk of poor microbial quality, while alpha-glycerophosphate increased. UHT milk samples manufactured from raw milk of better microbial quality and submitted to severe heat processes did not display changes in phosphoglycerides during storage.[63]

10.2.4 Vitamin

During processing, milk, as other foods, can suffer vitamin losses not only due to heat, but also due to exposure to oxygen, light, and pH variations, or combinations of these factors. Vitamins A, D, and E, beta-carotene, and vitamins of the B complex, present in raw milk, are generally stable to heat, and UHT thermal processing does not modify their content.

10.2.4.1 Ascorbic Acid (Vitamin C)

Ascorbic acid (vitamin C) content of cow's milk is about 10 to 20 mg/l. Ascorbic acid content is somewhat higher for sheep milk, but all the same, 25% of this vitamin is lost during pasteurization. In UHT milk, the content of vitamin C depends on the treatment, the presence of oxygen, and storage conditions.

While milk is not regarded as a reliable or important source of vitamin C in the human diet, vitamin C is of interest here because of its potential as a heat-damage indicator. Indeed, vitamin C is heat sensitive, and in the presence of oxygen or enzymes, it is oxidized to dehydroascorbic acid, with a lower vitamin C activity, and other inactive degradation products. Note, however, that heat treatments may cause enzyme inactivation, microorganism destruction, and oxygen removal, thus indirectly improving vitamin stability. This double action of heat treatment has been hypothesized to explain unexpected results of a study analyzing ascorbic acid in milk samples in Italy. In this study, processed milk samples were obtained from Italian central dairies operating under standardized conditions: pasteurization HTST at 72, 75, 80, 85, and 90°C for 15 sec, and sterilization UHT at 140°C for 3 sec.[64] After milk collection, heat treatment, transportation, and sampling in the laboratory, the ascorbic acid retention was low at low pasteurization temperatures and increased with increasing pasteurization temperature. The maximum value was 80 to 85°C; at higher temperature (90°C and UHT), ascorbic acid content decreased.

High pasteurization temperatures apparently stabilize ascorbic acid, especially close to 80°C, when by exclusion of oxygen from milk, a protective action takes place. Indeed, at 80 to 85°C peroxidase is inactivated and other enzymes do not survive. Heat processing can also reduce the microbial population of the product, and a good correlation ($r = 0.99$) has been observed between ascorbic acid content and residual bacterial population.[64]

10.2.4.2 Vitamins of the B Complex

Heat treatment causes slight or no variation in riboflavin content (B2), and no significant difference in riboflavin content can be detected between raw and UHT milk samples. Tagliaferri and coworkers[65] studied the behavior of vitamin B2 in milk subjected to different heat treatments (pasteurization at 75, 82, or 89°C, direct or indirect UHT). No significant vitamin losses were observed, and the authors concluded that vitamin B2 is not a reliable heat index. Indeed, vitamin B2 losses in milk are mainly caused by other factors, especially exposure to sunlight or fluorescent light.[65]

Study of vitamin B1 (thiamine) in milk subjected to different heat treatments (pasteurization at 75, 82, and 89°C, direct and indirect UHT) showed similar results: significant loss of vitamin B1 due to the heat treatment was not observed. Therefore, vitamin B1 is also not a suitable indicator of thermal processing-induced changes in milk. More intense heat treatments (e.g., sterilization, boiling, autoclaving) are necessary to induce vitamin B1 losses in milk.[66]

Several folate fractions have been identified in milk samples with HPLC analysis, including tetrahydrofolic acid, 5-methyltetrahydrofolic acid (5-MTHFA), the main form, and 5-formyltetrahydrofolic acid.[67] There is significant seasonal variation in the total folate concentration of milk, with a peak occurring in summer.

Oxygen is known to induce degradation of 5-methyltetrahydrofolic acid. Effects of the presence of different oxygen levels on the thermal degradation of 5-MTHFA in the UHT region at 110, 120, 140, and 150°C were investigated in a buffer model food system.[68] Results showed that in the presence of oxygen, the overall folate degradation is a second-order reaction; Arrhenius activation energy values for aerobic and anaerobic degradation were 106 and 62 kJ/mol, respectively. Results confirmed the importance of degassing milk before heat treatment to maximize recovery of folate.[68]

The concentration of folate-binding protein (FBP), which might have an impact on folate absorption, is significantly lower in UHT milk and fermented milk, both of which are processed at temperatures of >90°C, than in pasteurized milk.[69] Wigertz and coworkers[70] investigated the relation between retention of 5-methyltetrahydrofolate and folate-binding protein (FBP) concentration. Raw and pasteurized milk samples contained similar amounts of FBP: 211 and 168 nmol/l, respectively, while UHT-processed milk and yogurt, both processed at high temperatures, contained only 5.2 and 0.2 nmol/l FBP, respectively. All folates in raw and pasteurized milk were found to be protein bound, while folates in UHT-processed milk and yogurt occurred freely. Raw milk, pasteurized milk, UHT milk, and yogurt contained 44.8, 41.1, 36.1, and 35.6 μg/l 5-methyltetrahydrofolates, respectively, after deconjugation. It was concluded that significant losses of 5-methyltetrahydrofolates take place as a result of processing. Results supported the equimolar ratio of FBP and folates in raw and pasteurized milk.

Heat processing of milk reduces the amount of 5-methyltetrahydrofolate and the concentration and folate-binding capacity of FBP.[70] What can be the implications of FBP denaturation on folate bioavailability in milk and to what extent this denaturation can affect folate retention during processing and storage are questions that need further investigation.[71]

10.2.4.3 Fat-Soluble Vitamin: Beta-Carotene, Retinol, and Vitamin E

The beta-carotene content of milk varies markedly, depending on the animal species, feed, and season (e.g., fresh pasture is richer in carotenoids than hay or silage). A naturally yellowish color of cow's milk is associated with the presence of carotenoids. Milk of goat and buffalo does not contain carotenoids, probably because of a different animal metabolism, and usually dairy products from these animals are whiter than cow products. The beta-carotene content of milk is unaffected by UHT processing.

The main form of vitamin A in milk, *all-trans retinol*, comprises a beta-ionone ring with a side chain composed of two isoprene units and four double bonds in the *trans* configuration. Among retinol *cis* isomers, *13-cis retinol* has the largest

biopotency (75%) relative to the all-*trans* retinol, while *9-cis retinol* has a biological activity of only 19%.[72] The other isomers have even lower vitamin A activities. As a consequence, these compounds should be quantified separately in order to obtain a more accurate vitamin A assessment in nutritional studies.

Even if vitamin A is generally considered a heat-resistant compound,[73,74] data about retinol stability sometimes are contradictory, depending on whether the analytic method employed involved separation of the isomers. Indeed, some authors report no significant vitamin A losses from UHT processing,[75] while others, using chromatographic methods that allow separation of vitamin A isomers, do report significant losses.[76]

Samples of raw milk, not subjected to thermal processing, from various species show no conversion of the predominant all-*trans* isomers to *cis* isomers.[77] On the other hand, the most ubiquitous 9-*cis* and 13-*cis* isomers, resulting from all-*trans* retinol isomerization reactions, are observed in many types of dairy products, including cheeses, UHT milk, margarine, and butter, in varying concentration, depending on processing and storage conditions.[76,78,79] Given the natural variability of the all-*trans* retinol content in raw unprocessed milk, it has been proposed to express the degree of isomerization due to milk processing by the ratio 13-*cis*/all-*trans* retinol.[80]

Panfili and coworkers[80] found an average 13-*cis*/all-*trans* retinol ratio of 2.6% for pasteurized milk undergoing a mild heat treatment (high-quality milk), while pasteurized milk treated with a temperature ranging from 72 and 76°C for 15 sec showed an average 13-*cis*/all-*trans* retinol ratio of 6.4%. Milk subjected to more severe heat treatments showed a higher degree of 13-*cis* isomerization (a 13-*cis*/all-*trans* retinol ratio of 15.7% for UHT milk and 33.5% for sterilized milk), which is consistent with increased thermal interconversion of the retinol isomers. Also, in pasteurized and UHT creams, the 13-*cis* isomer level appeared to be related to heat treatment (13-*cis*/all-*trans* retinol ratio of 3.0% for pasteurized cream and 14.4% for UHT cream).[77]

Also, Murphy and coworkers[81] found significant differences ($P < 0.01$) in *cis/trans* isomerization between pasteurized and UHT milk samples. On average, UHT milk showed a higher degree of isomerization than pasteurized milk, while sterilized milk samples showed the highest degree of isomerization.

Cis/trans isomerization could also be directly promoted by light, with the relative amounts of the different *cis* isomers depending on the wavelength and the light permeability of the container.[81] A comparison among glass, plastic, and paperboard containers showed no significant loss of all-*trans* retinol in milk contained in paperboard boxes, while the rate of loss was significantly lower in plastic than in glass containers.[81]

Actually, sterilized milk in plastic bottles had lower 13-*cis*/all-*trans* ratios than sterilized milk in glass bottles, probably because of different light permeability of the packaging, confirming results obtained by other authors.[81]

In general, values of all-*trans* retinol and 13-*cis* retinol are useful for a more complete evaluation of the nutritional quality of milk and dairy products, while the degree of isomerization, expressed by the ratio 13-*cis*/all-*trans* retinol, can

represent an indicator of the treatment the product has undergone, relative to the lipid fraction and in particular to the unsaponifiable fraction. This indicator can support the already proposed treatment indices regarding protein and carbohydrate modifications.[3,4]

Lim[82] studied the effects of storage (10 days at 4 to 5°C or 180 days at –20°C) and season on the vitamin A (retinol and beta-carotene) content of low-temperature long-time (LTLT) pasteurized and UHT (aseptically or nonaseptically filled) milk. Vitamin A contents of LTLT, UHT nonaseptically, and UHT aseptically filled milks were, respectively, 40.9, 41.7, and 47.0 µg/100 ml in summer, and 23.2, 27.2, and 26.6 µg/100 ml in winter. No significant difference in vitamin A contents between LTLT and UHT milks was observed, either before or after storage. Vitamin A losses were greater in all milk types when stored at –20°C for 180 days than at 4 to 5°C for 10 days.[82]

Tocopherols (vitamin E) are sensitive to oxidation, heat, and light, but usually small or no losses of alpha-tocopherol (the most important E vitamers) are observed after UHT treatments.[83,84] Alpha-tocopherol losses from 3 to 14% were observed in UHT milk after 1 month of storage at 30°C, losses increasing with longer storage time.[83] In a recent, unpublished study, we observed no losses of alpha-tocopherol and retinol in UHT milk at 8°C, a temperature typical of a home refrigerator, which stresses the importance of storing UHT milk refrigerated (0 to 4°C) after opening.

10.2.5 Minerals

The most common cations (positively charged ions) in milk are K, Na, Ca, and Mg. The most common anions are chloride and inorganic phosphate; citrate, sulfate, carbonate, and bicarbonate are also present, but in lesser amounts. Of these minerals, K, Na, and Cl are almost entirely diffusible, while Ca, Mg, inorganic phosphate, and citrate are nondiffusible and associated with the casein micelles.

Milk salts thus exist in an equilibrium between the liquid and colloidal phase: this equilibrium can be affected by processing. In particular, the distribution of *diffusible salts* (low-molecular-weight ions and complexes) and *nondiffusible salts* (bound to proteins) can be modified by acidification, addition of salts, heat treatment, high pressure, ultrafiltration, and cold storage.[85] Heat treatments cause a decrease in soluble salt content, and conversion of a mineral from the liquid to the colloidal form is proportional to heat treatment severity.[85]

De La Fuente and coworkers[86] analyzed samples of commercial UHT whole milk and skim milk (n = 41) for contents of total and soluble minerals (Ca, P, and Mg). Wide intervals of variation in mineral distribution were found, which the authors attributed to the nature of the samples and the processing conditions.

When acid whey is obtained from pasteurized, UHT, or sterilized milk, *calcium* recovery is at least 80% of total milk calcium. Ionic calcium represents about 50% of total calcium in all whey extracts. Total calcium in whey from UHT-treated samples is lower than that from pasteurized samples, probably due

to modifications of calcium chemical form induced by heating. The severity of heat treatment does not significantly affect the ionic calcium percentage in whey.[87]

Levels of Se, Fe, Cu, Zn, Na, K, Ca, and Mg were investigated in 3 samples of six different kinds of sterilized (UHT) whole milk and in 151 samples of fresh milk collected in the Canary Islands.[88] In raw milk, average mineral levels were: Fe (0.515 mg/l), Cu (0.0769 mg/l), Zn (4.41 mg/l), Na (534.1 mg/l), K (1424 mg/l), Ca (1653 mg/l), Mg (113.9 mg/l), and Se (16.44 μg/l). Mean concentrations of Fe and Zn were significantly lower for UHT milk than for raw milk. The Se content was similar for UHT and raw milk, but the Cu level was significantly higher in UHT than in raw milk. Mean concentrations of Na, K, and Mg in raw and sterilized milk were not significantly different.[88]

In order to investigate the effect of heat treatments, and the resulting protein denaturation, on mineral bioavailability, Hagemeister and coworkers[89] conducted a trial with Goettingen minipigs feeding with different heat-treated milk samples. Trials with raw, pasteurized, or UHT-sterilized milks showed no significant effect of either pasteurization or UHT sterilization on bioavailability of Fe, Cu, or Zn from milk.

10.3 MAILLARD REACTION IN UHT MILK

The most studied chemical reaction in heat-treated milk is, undoubtedly, the Maillard reaction, in which amino groups (mainly casein-bound lysine residues) and reducing sugars (mainly lactose) are the main reactants.[90] The Maillard reaction consists of several steps, strictly dependent on temperature, pH, water activity, and type of sugar and amino group involved.[91]

In the early stage of the Maillard reaction, condensation of the reactive free amino group of lysine with the free carbonyl group of lactose occurs, via formation of a Schiff's base, which is subsequently transformed via the Amadori rearrangement into the Amadori product (ε-deoxyketosyl compounds). In milk, this Amadori product is lactulosyl-lysine (bound to protein).

The initial stage of the Maillard reaction has important nutritional consequences: formation of lactulosyl-lysine represents a considerable loss of biologically available lysine. The amount of lysine loss in the Maillard reaction has been proposed as a marker of the severity of heat treatment.[90]

The Maillard reaction, on severe industrial treatments, can carry on with the Amadori product undergoing a cleavage, leading, through different pathways, to many reactive compounds. In the final stages of the Maillard reaction, polymeric reactions lead to brown pigments (melanoidins), responsible for food odors and flavors.

10.3.1 Furosine: An Early Maillard Reaction Index

The early stage of the Maillard reaction can be monitored through the amount of furosine (ε-N-2-furoylmethyl-L-lysine) in milk. Furosine arises from acid

hydrolysis (6 *N* HCl at 110°C for 24 h) of lactulosyl-lysine.[92] Furosine detection can be performed by several methods: reversed-phase HPLC,[93–95] microbore (1.0 mm i.d.) and narrow-bore (2.0 mm i.d.) reversed-phase HPLC,[96,97] or capillary electrophoresis.[98,99] Furosine can be considered a good indicator of the earliest stage of the Maillard reaction because it gives an assessment of unavailable lysine produced during heat treatment of milk.[100]

In Italy, the furosine level in pasteurized milk is regulated by law and should not exceed 8.6 mg/100 g protein.[101] No legal limit has been set for the furosine level in UHT milk. This is probably due to the concurrent use of different types, direct and indirect, of UHT processes that lead to large variations in furosine levels in UHT milk available on the Italian market.[49] Indeed, Panfili and coworkers[80] found that furosine content of Italian UHT milk ranged from 66 to 263 mg/100 g protein. These data are comparable to those found in other countries (Table 10.3).

Ferrer and coworkers[102] studied the furosine content in store-brand and name-brand UHT milk from the Spanish market; furosine levels ranged from 65.5 to 310.6 mg/100 g protein for store-brand and from 40.3 to 50.7 mg/100 g protein for name-brand UHT milk (Table 10.3). In Belgium, Van Renterghem and De Block[103] determined furosine in direct UHT milk and indirect UHT milk, using either a plate heat exchange system or tubular heat exchange system. Furosine content in direct UHT milk ranged from 35 to 109 mg/100 g protein. In the tubular system, the furosine level ranged from 118 to 193 mg/100 g protein, while in the plate system, data were scattered within the range of 108 to 240 mg/100 g protein (Table 10.3).

TABLE 10.3
Content of Furosine (mg/100 g Protein) in Different UHT Milk Samples

Minimum	Maximum	Countries	Type of Treatment	Reference
66	263	Italy	UHT	80
3.0	3.2	Europe	Raw milk	93
3.5	4.8	Europe	Pasteurized	93
56	200	Europe	UHT	93
297	415	Europe	Sterilized in bottle	93
65	311	Spain	UHT, store brand	102
40	51	Spain	UHT, name brand	102
35	109	Belgium	UHT direct	103
118	193	Belgium	UHT indirect, tubular	103
108	240	Belgium	UHT indirect, plate	103
220	372	Belgium	Sterilized	103
28	53		UHT direct, 25°C storage	104
51	67		UHT indirect, 25°C storage	104

Rattray and coworkers[104] studied UHT direct and indirect milk during storage, and their results also showed that the amount of furosine is higher for indirect heat treatment than for direct treatment (Table 10.3), probably due to the higher amount of heat applied in the indirect process and to the temporary dilution effect of steam in the direct process.

It is noted that standardization of milk protein will affect furosine as an index of heat processing. While fat standardization of milk is already a common practice in the dairy industry, steps are being undertaken to also standardize the protein content. There are several methods to alter protein concentration of milk: addition of ultrafiltrate milk retentate or permeate and addition of fractions of whey protein.[105] Rattray and coworkers[104,106] have found that milk protein standardization through addition of acid whey permeate results in lower levels of furosine than protein standardization obtained with skim milk permeate. This difference is probably due to a decrease in both lactose and protein concentrations when using acid whey permeate, while skim milk permeate only causes a decrease in protein.

10.3.2 Furfural Compounds: Intermediate Maillard Reaction Indices

Intermediate compounds of the Maillard reaction may be formed in heated milk, but only in very small amounts compared to the Amadori product. Among these compounds, the furfurals must be included. In particular, hydroxymethylfurfural (HMF) and other furfural compounds (furfural, furylmethylcetonem, and methylfurfural) can be generated during heat treatment of milk or storage at inadequate temperature.

From a chemical point of view, HMF is the product of the dehydration of hexoses (free or linked to protein) due to the presence of concentrated acids. HMF is formed not only from Amadori compounds, but also from sugars (lactose isomerization). It is considered a good index of the severity of milk heat treatment[107] and is suitable as a marker of the most severe heat treatments (UHT and sterilized milk).

Traditionally, HMF is determined by a colorimetric method,[108] but this method has low specificity. At present, capillary electrophoresis[109] and RP-HPLC[110] appear to be the most powerful techniques for HMF determination. The analytical separation of HMF can be achieved by micellar electrokinetic chromatography (MEEC) employing sodium dodecyl sulfate as the anionic surfactant or by a simple isocratic HPLC method using reversed-phase microbore columns.[111]

Using HMF as a marker, Ferrer and coworkers[102] observed differences between store-brand and name-brand UHT milk. Free HMF was found to be present only in store-brand UHT milk, levels ranging from 8.24 to 50.9 μg/100 ml of milk, probably due to lower milk quality.

Several factors possibly affecting the use of HMF as a marker have been investigated. In particular, the total HMF level in milk appears to be affected by

milk fat concentration.[107] The HMF level in commercial UHT milk (stored below 50°C) is also related to temperature and time of storage, and increases with higher temperature.[112]

10.3.3 Fluorescent Products: Advanced Maillard Reaction Indices

According to Van Boekel,[91] several Maillard products are fluorescent. Fluorescence is typical of intermediate products; they show an initial phase of fluorescence development followed by a decrease. On the basis of this concept, an alternative method to evaluate the severity of milk heat treatment is based on the fluorimetric measurement of denaturated proteins (290-nm excitation and 340-nm emission) and of the fluorescent advanced Maillard reaction products (330-nm excitation and 420-nm emission). It has been suggested that fluorimetric measurement of tryptophan can be considered a marker of protein denaturation during heat treatment, because it is well correlated with beta-lactoglobulin, while fluorescent Maillard products can reflect the loss of nutritional quality during processing.[113–115] The fluorimetric measure of tryptophan is more helpful for milk subjected to mild heat treatment (pasteurization), while the fluorescent Maillard products (pyrrole and imidazole derivates) are more significant for indirectly heated UHT milk (Figure 10.2). Using the data represented in Figure 10.2, we find a correlation of $r = 0.94$ between furosine content and fluorescence of Maillard advanced products in the direct and indirect UHT milk samples analyzed.

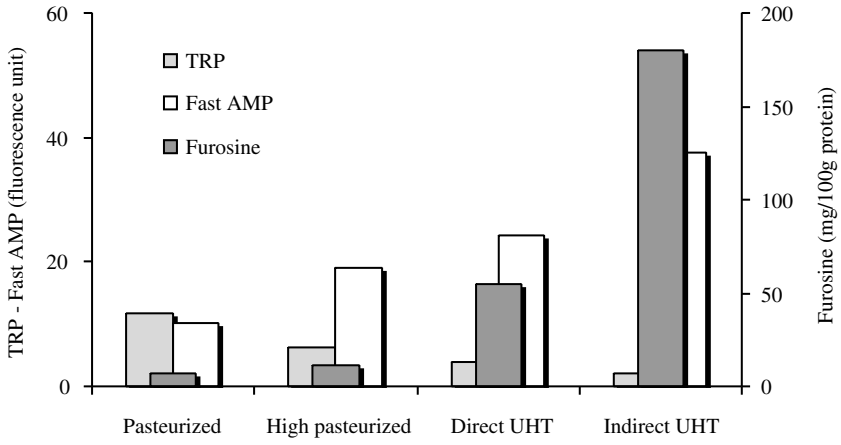

FIGURE 10.2 Fluorescence of advanced Maillard products (fast AMP) and tryptophan (TRP) and furosine content in different heat-treated milk samples. (Modified from Birlouez-Aragon, I. et al., *Int. Dairy J.*, 8, 771–777, 1998.)

10.4 HYPHENATED MARKERS OF UHT TREATMENT

Milk heat treatments can produce very complex effects among milk constituents. Simultaneous study of several heat-induced parameters improves the classification of industrial processed milks and provides deeper knowledge of what actually happened in heat-treated milk.

Both furosine and lactulose are good thermal indicators of heat damage.[116] In a detailed study, Pellegrino and coworkers[117] compared the extent of Maillard reaction and lactose isomerization in 46 samples of direct and indirect UHT milk and in-bottle sterilized milk processed under defined conditions. The authors found that evaluation of the ratio furosine/lactulose gives good results only in milk subjected to high temperature, because in pasteurized milk the Maillard reaction is predominant. With values of furosine rising up to 50 mg/100 g protein, the relation between furosine and lactulose was well described by a linear regression line ($r = 0.994$). High correlations between lactulose and furosine levels were also observed in 160 samples collected from the European market.[117]

Pellegrino and coworkers[117] also evaluated the effect of preheating (80 to 90°C) in the UHT process using the furosine/lactulose ratio. The preheating procedure can negatively affect milk quality because during this process the Maillard reaction can carry on, while lactulose is not produced. Indeed, the consequence of preheating was a shift of the regression line toward high levels of furosine; this could also explain why the ratio furosine/lactulose of some commercial samples fell out of the confidence limits of the regression line.

Thus, the combined measure of furosine (describing early Maillard reaction) and lactulose (describing extent of lactose isomerization) values for sterilized milk is useful to provide additional information about the thermal history of the product. For instance, high pH values of raw milk enhance lactose isomerization but do not affect furosine, while milk drying, prolonged preheating, and long storage promote intensive Maillard reaction.[117] Lactulose and furosine levels can also be used to distinguish between UHT, pasteurized, and in-container sterilized milks, as well as to detect illegal use of reconstituted milk powder during UHT milk production, resulting in higher furosine values with little change in lactulose content.[118]

Mortier and coworkers[119] have evaluated various parameters of heat damage (furosine, lactulose, beta-lactoglobulin, alkaline phosphatase, and lactoperoxidase) in different kinds of Belgium milk (154 samples) submitted to either thermization, pasteurization, direct UHT, indirect UHT, or sterilization. According to their results, the direct UHT process is less severe than the indirect UHT process. Interestingly, about 60% of the indirect UHT milk samples studied had a lactulose content exceeding the proposed limit of 600 mg/l.[8,9]

Panfili and coworkers[80] studied the relation between the *cis/trans* retinol ratio and the furosine level for different types of heat-treated milk to validate the *cis/trans* retinol ratio as an index of thermal stress. The degree of retinol isomerization (*cis/trans* retinol ratio) was found to be positively correlated ($r = 0.84$) to the furosine index of raw, pasteurized, UHT, and sterilized milks. Recent research, involving a larger number of milk samples (Figure 10.3), shows an even

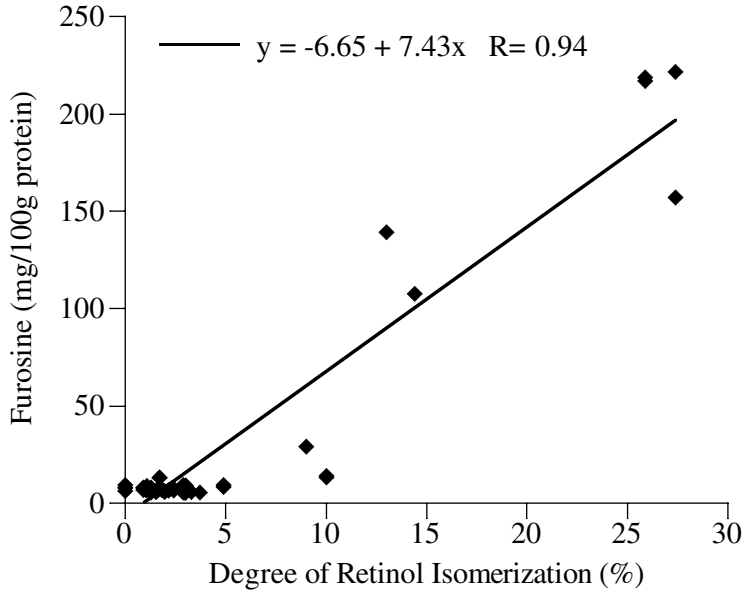

FIGURE 10.3 Correlation between furosine content and degree of retinol isomerization in various milk samples. (Manzi, P., Panfili, G., and Pizzoferrato, L., unpublished data.)

better correlation between retinol isomerization and furosine level ($r = 0.94$) and demonstrates that the degree of retinol isomerization can be a useful index of thermal stress, especially for mild heat treatments (P. Manzi, G. Panfili, and L. Pizzoferrato, unpublished data).

10.5 SAFETY

10.5.1 Bacteria

As regards microbiological safety, control points for milk products are raw material quality, processing conditions (temperature and time), postprocessing contamination, and storage temperature. For ambient stable UHT products, the main concern is with heat-resistant spoilage *bacteria*, such as *Bacillus stearothermophilus* and *Bacillus sporothermodurans*.[120,121]

Gallardo and coworkers[122] examined the microbiological quality of 10 samples each of pasteurized, UHT, and sterilized milks from Spain. Total aerobic counts, total *Enterobacteria*, total coliforms and *Escherichia coli*, sulfite-reducing *Clostridia*, *Staphylococcus aureus*, *Salmonella* spp., *Shigella* spp., *Clostridium perfringens*, and yeasts and fungi were determined. All samples complied with Spanish microbiological standards.

Guida and coworkers[123] recently analyzed 72 samples of direct UHT milk (135°C for 1 sec), classified into great, middle, and small commercial delivery,

for the presence of mesophylic bacteria according to European law.[1,124] About 14% of total milk samples analyzed were out of range, in particular, 25% from great distribution, 17% from middle distribution, and none from small distribution. The authors suggested that contamination could be due to heat-resistant spores or after-packaging contaminations.

10.5.2 Aflatoxins

The contamination of food with *aflatoxins* is a notorious problem. From epidemiological studies it is known that aflatoxins are toxic and carcinogetic compounds. Human exposure to aflatoxins can result from ingestion of contaminated food. Aflatoxin M1 (AFM1), a hydroxylated metabolite of aflatoxin B1 (AFB1), can be present in milk via animals consuming feed contaminated with AFB1. AFB1 has been classified as class 1 or human carcinogen and AFM1 as class 2 or probable carcinogen.[125] Because milk represents a main constituent of the diet of children and growing young, i.e., the population most at risk, it is necessary to monitor the contamination of aflatoxin in milk. Current regulations for AFM1 in milk have been established by the Food and Agriculture Organization (FAO):[126] permissible levels range from 0.05 to 0.5 ppm.

Heat processing of milk should not affect the AFM1 concentration because AFM1 is heat stable (decomposition temperature ranges from 237 to 306°C). Nevertheless, published data on the effect of heat treatment on milk AFM1 levels seem to be contradictory.[127] This can be due to the fact that AFM1 is not stable in milk (contamination disappeared after 6 days storage at 0°C), and not all methods used to determine AFM1 have the same accuracy, precision, and sensitivity.

Martins and Martins[128] investigated the occurrence of AFM1 in raw and UHT commercial milk in Portugal. Only two UHT-treated milk samples exceeded the limit of 0.05 ppm, while the other 68 UHT-treated milk samples had low AFM1 levels (from <0.005 to 0.05 ppm). According to these authors, findings are similar in other European countries and data are not worrisome for public health, even though they recommend that more samples should be analyzed.

In Greece, levels of aflatoxin M1 were recently investigated in samples of raw, pasteurized, UHT, and concentrated milks collected in supermarkets.[129] Of the 297 samples analyzed, only 2 samples of cow's milk, 1 sample of sheep's raw milk, and 2 samples of concentrated milk exceeded the limit of 50 ng/l. Results suggest that current regulation of aflatoxin M1 levels in milk in Greece is effective.

In Italy, the presence of aflatoxin M1 has been assessed in 127 milk samples (UHT, pasteurized, raw) from the Campania and Calabria regions. Several milk samples (14%) contained aflatoxin M1 levels that exceeded the EU limit of 50 ng/l.[130]

A recent study on milk produced in Argentina showed very low AFM1 contamination of milk.[131] The authors ascribed this finding to cow feeding practices; in Argentina, pasture is the ordinary practice, while in most other countries cows are stabled.

In Brazil, Garrido and coworkers[132] investigated the presence of M1 and M2 aflatoxins in 60 UHT and 79 pasteurized commercial milk samples collected from supermarkets. None of the milk samples were found to be contaminated with aflatoxin M2, but aflatoxin M1 was detected in 29 samples (20.9%) at levels of 50 to 240 ng/l. Occurrence of aflatoxin M1 was high in both commercial pasteurized and UHT milk. The contamination level, according to MERCOSUR Technical Regulations, should not be considered a serious public health problem, even if in some cases it exceeded the limit (50 ng/l) permitted by the EU.

10.5.3 Chemical Contamination

Environmental contamination caused by human activities (industrial processing, packaging procedures, accidents during transport, storage before consumption) can affect milk safety. Chemical pollution, in particular by organic substances (e.g., polychlorinated biphenyls (PCBs)), is one of the major problems. This is a well-known concern, and worldwide, quality control structures focus on identifying hazards and periodically surveying milk all along the supply chain. While data on chemical contamination of breast milk are abundant in the international scientific literature, food chain monitoring results are seldom published. This is unfortunate, as availability of these results would be useful for the whole scientific community.

Milk and cheeses, collected from Washington, D.C., area retail stores, have been analyzed for polychlorinated dibenzo-p-dioxin and dibenzofuran contamination.[133] Contaminants were identified and quantified, and expressed in international toxic equivalent (I-TEQ). Milk contamination ranged from 0.05 to 0.12 I-TEQ. Similar values have been observed in milk collected in rural areas with no apparent sources of contamination.[134] In particular, the I-TEQ values found for the Washington milk samples are higher than the I-TEQ values of German milk.[135]

In Italy, Fabietti and coworkers[136] examined 35 commercial milk samples for the presence of the principal aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes). Milk samples were collected from different dairies and included pasteurized whole, semiskimmed, and skim milk, and UHT whole and semiskimmed milk. Levels of the two most common aromatic hydrocarbons (benzene and toluene) were relatively low (0.12 to 100 μg/kg), while levels of ethylbenzene and total xylenes (meta + ortho + para) were below the detection limit of 0.05 μg/kg. Benzene and toluene levels were higher in whole and semiskimmed milk than in skim milk. No differences were observed between pasteurized and UHT milk with similar fat contents. Results indicate that levels of aromatic hydrocarbons in commercial milk in Italy are similar to those found in other foods and are sufficiently low to consider milk safe from the point of view of chemical contamination.[136]

10.6 SENSORY QUALITY

UHT milk, either freshly prepared or stored, has a sensorial characteristic called cooked note. Stale and oxidized flavors occur due to formation of aldehydes and ketones.

Valero and coworkers[137] studied the evolution of *volatile components* of commercial whole and skim UHT milk during 4 months of storage. Sensory analyses showed a decrease in quality during storage either in whole or skim milk, and after 3 months of storage there was a slight stale flavor.

The concentration of volatile compounds, such as aldehydes and ketones, provides discriminant information about storage time and storage temperature of whole and partially skimmed UHT milk. Some volatile compounds, such as acetone, 2-butanone, 2-pentanone, 2-heptanone, 3-methylbutanal, pentanal, hexanal, heptanal, dimethyl disulfide, toluene, and limonene, are reportedly useful to differentiate milk subjected to different heat treatments.[138]

In whole milk, 2-pentanone and 2-heptanone occurred during heat treatment, and dimethyl sulfide and dimethyl disulfide were responsible for the cooked note. Skim milk, instead, showed a different pattern of volatile compounds with hydrocarbons representing the main group.[138,139]

During storage, UHT milk develops off-flavors due to the release of lower-chain-length fatty acids by psychrotrophic microorganisms. Indeed, in UHT milk samples, stored at 22 and 37°C and monitored over 33 days, volatile and free fatty acids showed a sharp increase after 13 to 14 and 20 to 21 days, respectively, due to lipases from psychrotrophic spores.[140] Hence, good-quality raw milk should be used for UHT milk to prevent rancid flavor development.[140] Actually, it is known that milk with a high acid degree value has an acceptable lipolyzed flavor.[58]

Iwatsuki and coworkers[141] examined the effect of pasteurization temperature on sensory properties of UHT milk (treated at 120, 130, or 140°C for 2 sec); the sensory analysis of the milk was conducted by an expert panel. Using multiple regression analysis, it was found that the palatability of UHT milk is judged mainly on aroma and aftertaste, freshness, and intensity of milk flavor. Results of sensory and principal component analyses showed that milk body, related to milk flavor, viscosity, and fattiness, becomes stronger with increasing UHT temperature.[141]

Sensory properties and palatability of UHT milk (heated at 130°C for 2 sec) were also evaluated as a function of homogenization pressure.[142] Evaluation of sensory properties by an expert panel and principal component analysis indicated that milk homogenized at lower pressure has greater fattiness, body, milk flavor, sweetness, and thickness. Palatability, as judged by a panel of housewives, improved when milk was homogenized at low pressure. In terms of physicochemical properties, the authors found that with increased homogenization pressure, fractionation of fat globules occurs, resulting in an increase in viscosity, degree of whiteness, and refractive index for the UHT milk.[142]

10.7 CONCLUSIONS

Alterations in the chemical composition of milk due to thermal processing are extremely complex. They depend on the composition of the raw milk, time and temperature of thermal processing, other processing conditions (e.g., homogenization), and time and temperature of storage. Some heat-induced chemical

alterations affect milk nutritional quality (e.g., lysine loss, isomerization of all-*trans* retinol), some the physical appearance (e.g., casein proteolysis), and others the organoleptic characteristics.

As regards safety of UHT milk, contamination with heat-resistant bacteria, aflatoxin, and chemical compounds remains of some concern. The problem here is not so much with thermal processing, but with the quality of the raw milk, provided processing and domestic handling procedures are properly performed. Continuous monitoring seems warranted.

The growing scientific interest in heat-induced modifications of chemical, biological, and sensorial characteristics of UHT milk is a response to the growing consumer demand for information on food quality and food safety. This aspect will be more and more important in the future, when development of milk products, as other foods, will be specifically planned on consumer concerns.

A comprehensive description of the heat-induced changes will be necessary to allow more complete milk labeling, extending to nutritional and functional components. This will be a new, important challenge for the food chemist.

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11 Thermal Processing of Canned Foods

Z. Jun Weng

CONTENTS

11.1 INTRODUCTION

Thermal processing of canned foods can be divided into two major process methods: *in-container sterilization* and *in-flow sterilization*. The in-flow process refers to aseptic processing and aseptic packaging, which are covered in the previous chapter. The in-container process generally refers to the canning process, in which the prepared food is filled into a package before sealing and sterilization. The food could be packaged in metal cans, glass bottles, plastic bottles, retortable pouches, retortable cartons, rigid and semirigid plastic containers, etc. Although the canning process started from Nicholas Appert's time in 1810,[1] food processing via the canning process still provides a universal and economic method for preserving and processing foods. It is one of the most convenient and safe food products in today's life.

The customer eating trends and the food retail trends (such as Wal-Mart) are the key drivers on impacting the canning industry. Today's consumer requires foods to be safe, fresh-like in quality, healthy, nutritional, novel, ethnic, and convenient. The most pervasive consumer trend in the food industry is the increasing demand for convenience foods. The general trend of the average meal preparation time in the U.S. has fallen from 30 to 15 min.[2] Convenience and quality are the primary drivers that strongly affect every aspect of the food canning process, including food formulation, packaging, and processing. In this section, we are going to discuss the recent development in the sterilizer systems for thermal processing of canned foods, the latest thermal process calculation methods, and computer-based thermal process real-time control methods for ensuring food safety and quality.

11.2 CURRENT CANNING STERILIZATION SYSTEMS

The basic flowchart of canning operation is shown in Figure 11.1. The food is formulated first and filled into a container. The container could be a metal container, glass jar, plastic bottle, retort pouch, etc. After filling, the container is hermetically sealed. The sealed product then undergoes a sterilization (or pasteurization) process to obtain the scheduled food safety (commercial sterility or desired lethality F^{z}_{Tref} value) and the desired quality. The sterilization process is the critical control point for ensuring food safety. The sterilizer should be able to consistently deliver the commercial sterility to every canned product from batch to batch.

There are many types of sterilizers or retorts used in the canning industry.[3,4] The most common sterilizers used in the canning industry are batch retorts,

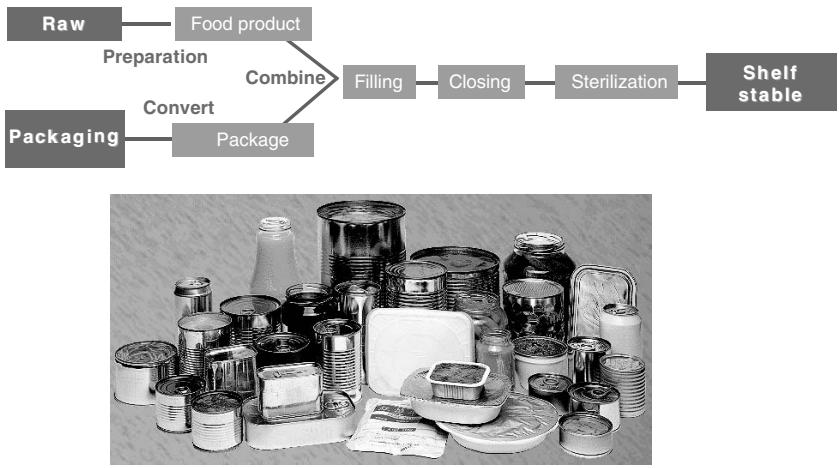

FIGURE 11.1 The general flowchart of canning process and canned foods in various package formats.

TABLE 11.1
Sterilization Applications for Different Heat Transfer Modes and Packages of Canned Foods

Operation	Equipment Types	Product Flexibility	Container Flexibility
Continuous sterilizers	Rotary reel and spiral	Convection + semiconvection	3-piece cans and some 2-piece cans
	Hydrostatic	Conduction	All cans, jars, and bottles
Batch retorts	Still	Convection + conduction	All cans
	Semiautomatic		Flexible packages
	Automated batch		Glass jars and bottles

continuous hydrostatic sterilizers, and continuous rotary (reel-and-spiral) sterilizers. Modern batch and continuous sterilizers continue to evolve to maximize the process efficiency and product quality, and to adapt various packaging containers, such as nitrogen-containing retortable pouch, easy-open cans, retortable cartons, etc. Based on the product heat transfer characteristics and the packaging materials, the application of various sterilizers can be grossly summarized in Table 11.1. System and system life cycle cost, production throughput, product quality and uniformity, packaging material and geometry, variation of container sizes, and future package trends are among the most important factors when choosing a proper sterilization system. The high-temperature short-time (HTST) process, generally aided by the rotational process, usually is considered for maximizing the product quality and throughput. However, some products, such as canned seafood, are sensitive to heat and shear force; thus, a proper sterilization temperature needs to be properly optimized.

11.2.1 Batch Retort

The batch retort represents the most versatile and flexible sterilization system to meet the increasing market demand on the product innovation. It is used for both conduction-heating and convention-heating products. Almost every kind of packaging formats used in the canning industry can be properly processed in a batch retort. The batch retort is usually classified into still retort and rotary retort based on the agitation mode. Generally, the rotational batch retort uses the end-over-end rotation mode to enhance the product heat transfer in the container, and thus increase the product throughput and quality. Different heating media and heating methods, such as steam, steam–air mixture, water cascading, water spray, or water full immersion, are used in various batch retort systems.[3]

The major development in the batch retort is perhaps in handling various packaging materials and the system automation. Modern batch retort provides independent control of temperature and pressure for protecting the package integrity

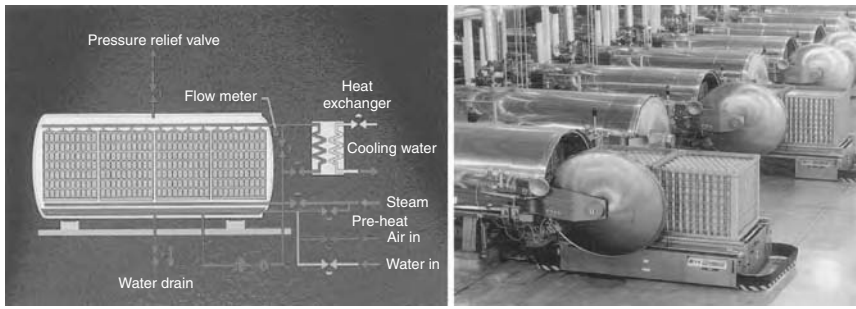

FIGURE 11.2 Steam Water Spray Automated Batch Retort System. Left: System concept view. Right: Fully automated SWS system with automatic loading/unloading system. (From FMC FoodTech. With permission.)

during heating and cooling phases. One of these batch retorts is the water spray batch retort, which is increasingly used in the modern canning industry. In these retorts, water usually is stored in the bottom of the retort vessel and circulated by a pump with a high flow rate and sprayed (or cascaded) on the packages. Usually the water is indirectly heated by steam through a heat exchanger in the circulation line. The primary application of this system is for the food packaged in a container that requires overpressure for balancing the internal pressure, such as pouches, bottles, pressurized cans, etc. Figure 11.2 (left) shows a typical Steam Water Spray™ (SWS) Automated Batch Retort System. Both superheated water spray and steam are used as the heating medium, and air is used as overpressure for balancing the product internal pressure. The system utilizes direct steam injection for ensuring fast and uniform come-up. The high-velocity water intensely sprays from various angles a mix of steam, water, and air and creates a homogenous temperature distribution inside the vessel. The system uses an indirect cooling method, and the sterile water is cooled over a plate heat exchanger, which saves water, water treatment chemicals, and energy. The system is controlled by the LOG-TEC® Process Management System, which can automatically correct process deviations using its embedded mathematical models, such as NumeriCAL®, without intervention of an authorized person.

There is an increasing demand toward fully automatic retort loading and unloading for reducing the labor cost. It is not uncommon that the entire cook room, with a dozen batch retorts, is operated by one supervising person (Figure 11.2, right). Wider ranges of process times, temperatures, and pressures can often be selected for economically processing products in fully automated batch retorts.

The major concern on the batch retorts perhaps is the product quality uniformity within a single batch and from batch to batch. It is common in a single batch that the outer layer products in a basket are usually processed more severely than those inside the basket, which may result in a nonuniform quality distribution of the processed products. Product throughput and energy consumption are also

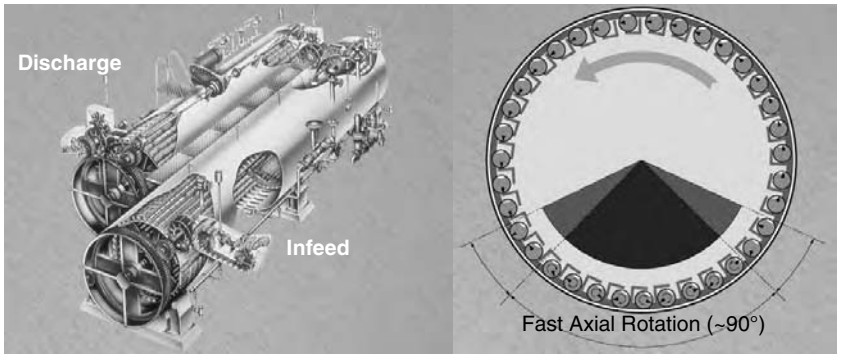

FIGURE 11.3 The process principle of FMC FoodTech continuous rotary (reel-and-spiral) sterilizer system. Left: System cut-away diagram. Right: Induced convection heating.

major concerns. To obtain a desired throughput, many batch retorts are often necessary, which requires plant floor space and increases the energy consumption, especially during venting and come-up phases.

11.2.2 Continuous Rotary Sterilizer

The continuous rotary sterilizer is a fully automated continuous processing system designed for high product throughput, lower energy consumption, and more uniformity of processed product quality. The continuous rotary sterilizer system uses the induced heating principle by intermittently rotating the can along its axis (side), and thus increases the rate of heat penetration (Figure 11.3). The system enables use of the high-temperature short-time process principle for maximizing the product quality and throughput.

The seamed cans enter the line directly from the closing machine. A feed device delivers the cans via the infeed valve to the rotating reel of the sterilizer. The reel, working in conjunction with the stationary spirals in the shell, carries the cans through the cooking and cooling system.[4] Since each container travels exactly the same trajectory, its process time and temperature profile and cooling profile are exactly identical. Uniform cooking/cooling and uniform quality for every container can thus be ensured. The continuous rotary sterilizer is widely used in the food industry. More than 7500 FMC FoodTech continuous rotary shells have been placed in production around the world since 1921 for processing more than half of the world's canned foods. The major applications are for fruit, vegetables, ready meals, soups, infant formula, and dairy products. Depending on the process time and can size, the system can deliver up to 1500 cans per minute.

To meet the industry demands on reducing the overall cost and increasing the consumer convenience, the continuous rotary sterilizer is consistently evolving. Figure 11.4 shows the FMC FoodTech continuous rotary sterilizer, with overpressure capability for handling different packaging formats, such as plastic containers,

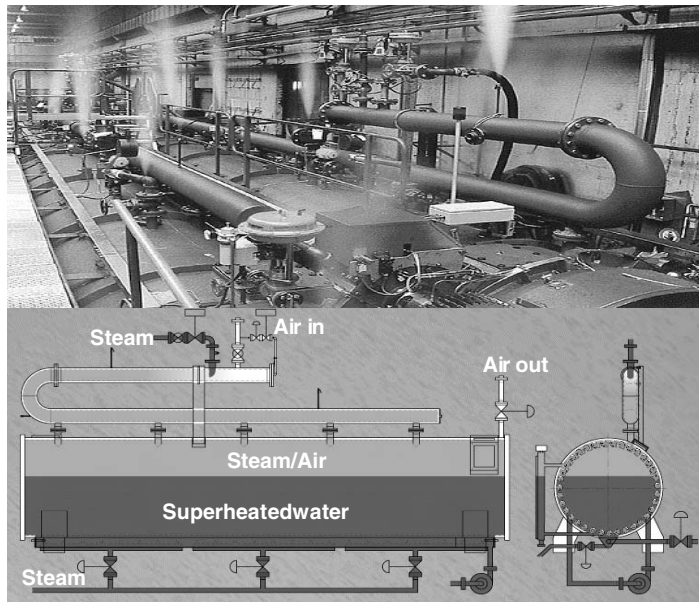

FIGURE 11.4 FMC FoodTech continuous rotary sterilizer with overpressure capability. Top: System in operation. Bottom: System processing principle. (From FMC FoodTech. With permission.)

reduced metal plate thickness, peelable lids and easy-open ends, etc. These packaging formats require overpressure to balance the can internal pressure during processing. Superheated water with circulation and the steam–air mixture (top portion) at the same temperature are used as the heating media. The air serves as the overpressure to balance the product internal pressure during processing. Steam and air are mixed in an overhead mixing tube and introduced into the cooker shell over the whole length (Figure 11.4, bottom). A pure steam–air mixture has also been successfully used to process pressure-sensitive products, such as rigid plastic containers. In this case, the steam and air are mixed by the reel rotation and can movement.

In 2003, FMC FoodTech introduced a large-diameter, high-volume continuous rotary pressure sterilizer line with 2.84 m (112 in.) diameter (Figure 11.5). Comparing to the traditional continuous rotary pressure sterilizer, with a diameter of 1.47 m (58 in.), the can holding capacity is nearly doubled. This 100% larger capacity vessel allows the continuous rotary pressure sterilizer to operate at higher processing volumes without doubling up on machinery, and thus increases the production efficiency and simplicity.

The continuous rotary sterilizer is an ideal system for processing products that require large throughput with limited can size variation. The system generally requires a cylindrical container with limited can diameter and can height variation for each application. Since the product content is intensely mixed by rotation, it may also not be suitable for those products sensitive to the shear force.

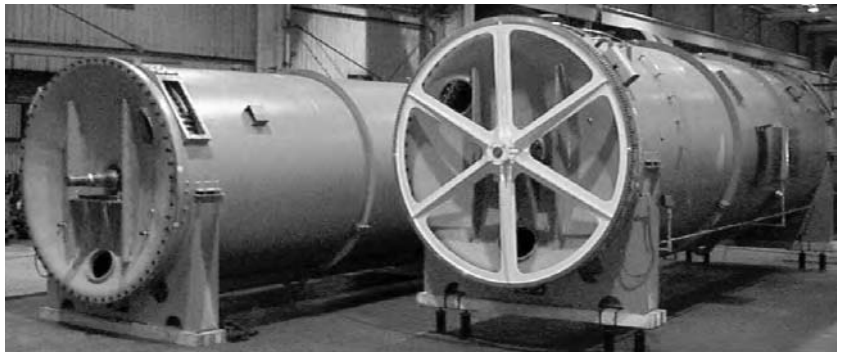

FIGURE 11.5 Large-diameter (2.84-m) continuous reel-and-spiral rotary pressure sterilizer system. (From FMC FoodTech. With permission.)

11.2.3 Hydrostatic Sterilizer

The hydrostatic pressure sterilizer is another kind of continuous container-handling system used in the food canning industry (Figure 11.6). This type of sterilizer is particularly well suited for processing products that require long cook and cool times and high container throughput, and for those that derive little or no benefit from container agitation. The hydrostatic sterilizer operates on the hydrostatic pressure principle, with the pressure of saturated steam in the chamber (steam dome)

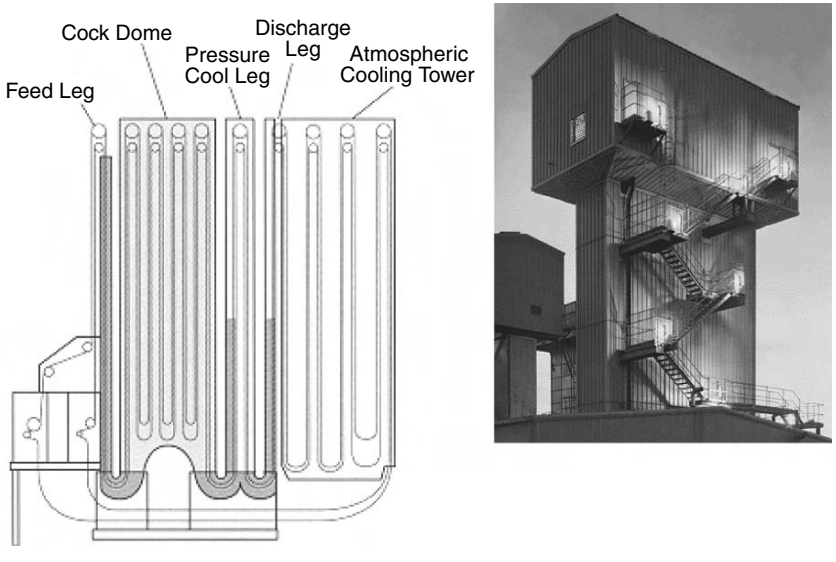

FIGURE 11.6 Continuous hydrostatic sterilizer. Left: Standard steam chamber with pressure cool. Right: A hydrostatic sterilizer in operation. (From FMC FoodTech. With permission.)

balancing the weight of two water columns (feed and discharge legs) adjacent to the steam dome (Figure 11.6, left). Typical products presently being sterilized in the hydrostatic sterilizer include baby foods in jars, pet foods, soup, pumpkin, canned meat and stews, beverages, etc. Typically, a sack of containers is mechanically transferred onto a carrier, which is attached to a moving chain (conveyor). The product is conveyed through a temperature-controlled hot-water column (feed leg), a controlled steam chamber (steam dome) set to a processing temperature, a precool discharge water column (discharge leg), and a water-cascading cooling system, and finally exits the system at the container unloading station. The speed of the conveyor is controlled such that the residence time of each carrier in the steam dome meets the scheduled process time (and thus scheduled lethality) at the minimum required temperature parameters assigned by a competent process authority. Generally, in an ideal and well-controlled process, all products processed in a hydrostatic sterilizer receive exactly the same time–temperature process treatment and a uniform sterility.

The hydrostatic sterilizer can be used to sterilize products packaged in metal cans, glass jars, plastic bottles, and lately the retortable pouch, with the capability of agitating the product for faster heat transfer. However, the initial investment for such a system is usually higher than other systems, and the system is usually limited to a certain range of can sizes (diameter), which depend on the designed carrier profile.

11.3 THERMAL PROCESS CALCULATION FOR FOOD SAFETY

The sterilization process is the critical control point for ensuring food safety and often is a critical unit operation on maximizing the production efficiency or throughput. Establishment of a proper thermal process is based on the knowledge of the heat resistance of microorganisms and the heat transfer rate of a specific product. Process modeling and calculation software play an important role in optimizing sterilization processes while ensuring food safety. There is an increasing interest in the canning industry in using new process modeling and process calculation methods for food safety and for optimizing the product quality and process efficiency.[1,5]

11.3.1 Principles of Thermal Process Calculation

The calculation of the sterilization value, or the F^{z}_{Tref} value, of the canned foods is based on the microbial death kinetics of first-order reaction under lethal temperatures and the product temperature at the critical point, or the slowest-heating zone (cold spot), in the slowest-heating container. Equation 11.1 is widely used for the canned food thermal process evaluation and calculation,[1,6,7] in which the first-order thermal inactivation kinetics of the microorganism and traditional z value model are used:

$$F^{z}_{Tref} = \text{value} = \int_0^t 10^{(T-Tref)/z} dt \tag{11.1}$$

where T is the slowest-heating zone product temperature in a container, t is the heating and cooling time, T_{ref} is the reference temperature for the microorganism of concern, and z is the thermal characteristic of the target microorganism in the lethal temperature range.

For the low-acid canned foods (pH greater than 4.6 and a_w greater than 8.5),[8] the commercial sterility is achieved by destruction of all pathogenic organisms together with nonpathogenic spoilage microorganisms, such as *Clostridium sporogenes* (PA 3679), so that the canned foods can be shelf stable under normal storage room temperature.[4,8] In the canning industry, the F_0 value is often used for the low-acid canned foods and refers to the sterilization value (F^z_{Tref} value) with a z value of 10°C (18°F) and a reference temperature (T_{ref}) of 121.1°C (250°F). The z value of 10°C is used as the thermal characteristic for the pathogenic microorganism, *Clostridium botulinum* spores. The *C. botulinum* spore is the most heat resistant pathogen and produces the most deadly toxin if it is allowed to grow. It is the target pathogenic microorganism to be killed during thermal processing for low-acid shelf-stable canned foods.

Equation 11.1 is also used for the thermal process calculation of low-acid canned foods with an extended refrigerated shelf life, and for shelf-stable canned acid (such as fruits) and acidified foods under normal storage conditions. In this case, the food industry sometimes uses the pasteurization value (P^z_{Tref} value) instead of the sterilization value (F^z_{Tref} value), since foods generally are processed below or around 100°C. For the acid or acidified foods, the process is used to kill all organisms affecting the shelf stability of the products stored at ambient temperature. For the low-acid foods stored under refrigerated conditions, the process is used to kill the vegetative pathogenic bacteria together with *C. botulinum* spores of nonproteolytic types *B*, *E*, and *F* for an extended shelf life. The thermal characteristics of the most thermal resistant pathogens or the target pathogen need to be carefully studied for each application. In some cases, the z value may not be constant in the lethal temperature range. For example, the *C. botulinum* spores of nonproteolytic type *B* in the surimi product show a broken thermal death time (TDT) curve, or two z values, with $z = 7.0$°C for temperature less than 90°C and $z = 10$°C for temperature above 90°C.[9]

Recently there are some challenges on the validity of the first-order thermal inactivation kinetics of the concerned microorganisms.[10] The major concern was the non-log-linear survivor curve, or the shoulder-and-tail phenomenon under constant heat treatment. Instead of the traditional first-order thermal inactivation kinetics model, various alternative thermal inactivation kinetic models for microbial survivor curves have been proposed.[10–12] These alternative kinetic models could fundamentally change the traditional thermal process calculation methods, such as the Ball formula method,[13] and need to be scientifically challenged. Instead of using the traditional F^z_{Tref} value for the food safety evaluation, a new concept, food safety objective (FSO), has been introduced.[10] The FSO defines the maximum frequency or concentration of a microorganism hazard in a food at the time of consumption that will provide an appropriate level of protection. Obviously, these trends challenge the traditional mathematical methods in thermal processing calculation.

11.3.2 Thermal Process Calculation Models and Software

There are a number of mathematical methods proposed for thermal process calculations.[14] In calculating the sterilization value at the slowest-heating zone in the container, all proposed mathematical methods are based on Equation 11.1. The difference, though, is on how the product temperature (T) at the slowest-heating zone is obtained. The general method uses the physically measured product temperatures only (called physical simulation), whereas the mathematical models use mathematical models for predicting the product temperatures. The obtained product temperatures are then utilized in Equation 11.1 for integrating the sterilization value. Thus, the process calculation methods could be divided into following four categories based on product temperatures obtained:

- The general method using physically measured time–temperature data[1,6]
- The semiempirical mathematical methods using a constant heating or cooling retort temperature, such as the Ball formula method,[13,15] Hayakawa method,[14] Stumbo method,[1,14] Gillespy method,[14] etc.
- The theoretical models, such as pure conduction- or convection-heating models[15,16] and computational fluid dynamic (CFD) models, based on Navier–Stoke's equations[17,18]
- The innovative models for handling variable retort temperatures

The general method purely utilizes the physically measured product temperatures in lethal rate integration (Equation 11.1). Numerical integration procedures such as Simpson's rule or the trapezoidal method are often used for integration purposes. Since the actual least lethal zone product temperatures are used in the calculation, it is the most accurate method for evaluating a given set of heat penetration data. However, the general method is generally not recommended for thermal process development (or design), since it represents the process instance that is under evaluation. The daily process conditions, such as the initial product temperature variation, the retort process temperature stability, the come-up profile, and the cooling profile, may vary from cycle to cycle. The retort could be only partially loaded, and the process might experience sterilization temperature deviations. These variations could lead to uncertainty of the food safety of the delivered process.

Except for the general method, almost all published methods used mathematical models to correlate the retort temperatures to the product temperatures. Except some simple heat transfer modes, such as pure convection- or pure conduction-heating products, the majority of canned food products exhibit complicated heat transfer modes. Therefore, the majority of mathematical methods were based on semiempirical equations such as the Ball formula method[13–15] by using heating and cooling factors (*jh, fh, jc, fc* …). The Ball formula method has been used in the food industry for more than half a century, and is still widely used in the

canning industry. It is flexible in terms of ranging initial product temperatures and retort temperatures in process design. It can be used for any kind of foods packaged in any kind of containers, since it introduces a dimensionless factor, *j* value (*jh* or *jc*), which is used to correlate the initial product temperature and is independent of the retort temperatures within a reasonable range. However, because of time limitations when Ball developed his method half a century ago, there were some assumptions made in his mathematical model,[13,15] such as $jc = 1.41$, $fc = fh$, etc. For conduction-heating products, the Ball formula method often results in underestimating the actual lethality value (conservative). However, in many cases, when the product *jc* value is substantially less than 1.41, such as for products packed in the thin pouch, the Ball formula method could lead to overestimating the actual product lethality value. Moreover, the Ball formula method only handles the constant process temperature. It is in the food industry's interest to have a properly optimized thermal process for the product quality and efficiency.[5,19]

11.3.3 Innovative Model

With rapid development in the information technologies, the more sophisticated mathematical modeling methods, which can handle variable process retort temperatures (classified as innovative models) for canned food thermal process calculations, have been discussed and published in the literature.[20–25] NumeriCAL[26] and CTemp[27] are two typical examples of software packages used in the food industry. The major advantages of these published methods are that they can handle various complex heat transfer modes and the variable process temperatures, and thus the process temperature deviations.

Since it was introduced in 1988, NumeriCAL software is adopted by almost all major food processors for thermal process evaluation and thermal process design of canned foods in North America, and its benefit of increasing process efficiency and product quality has been recognized in the food industry.[19] Its modeling results are accepted by both the Food and Drug Administration (FDA) and U.S. Department of Agriculture (USDA) regulatory agencies. The NumeriCAL core algorithm (J. Manson, personal communication, 1991) is based on the finite difference method for handling the variable retort process temperatures. Since NumeriCAL utilizes heating and cooling factors, it is capable of simulating product temperatures at a single point inside a container for any transient heat transfer mode and for any type of food packaged in all styles of containers. Figure 11.7 shows Windows®-based NumeriCAL software, version 3.0.[26] It consists of two major modules: analyze and calculate modules. The analyze module is used to analyze the heat penetration data and to develop NumeriCAL heating and cooling factors for the worst-case container. There are a number of nonlinear optimization methods embedded in the model, which can be used to automatically fit the heat penetration curve. The calculate module is used for the thermal process calculation (or thermal process design) and thermal process deviation analysis.

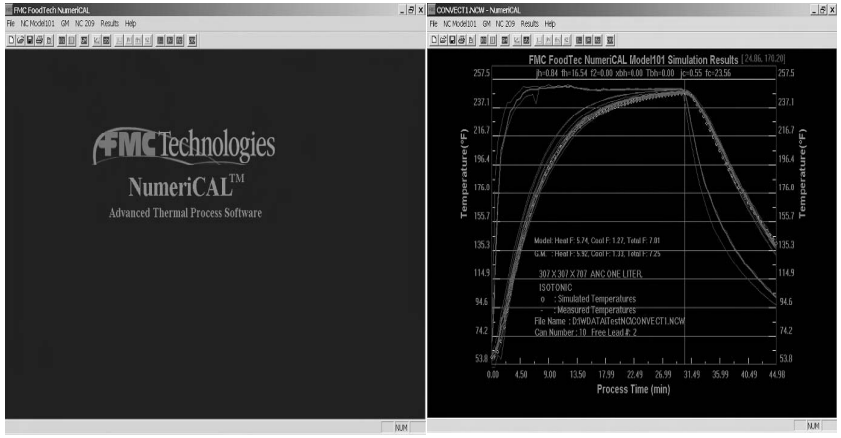

FIGURE 11.7 Microsoft Windows-based NumeriCAL software (version 3.0) designed for thermal process modeling and calculation. Left: Front page. Right: Process modeling.

It is not the purpose of this chapter to describe each method. It is important, however, that software used for thermal process calculations be properly validated, and that a validation program based on the software life cycle approach be used (John W. Larkin and Steve Spanik, personal communication, 2004). The software key components, especially the core algorithm, that are critical to the safety of the process should be validated to a high degree.[28] The software validation for the automated controller system has been discussed in the literature.[28–32]

11.3.4 Challenge Thermal Process Calculation Software

Thermal process development of canned foods in the food industry generally involves two steps: modeling and calculation. Process modeling is to fit or model a set of heat penetration data for developing heating and cooling factors, such as Ball and NumeriCAL methods or other physical parameters. The second step is to use these obtained parameters for the process calculation or process design. Basically, the second step is the model prediction step, since it predicts the new thermal process time and temperature for other process conditions, such as different initial product temperature and process retort temperature, and for the process temperature deviation analysis. It is important that the parameters (*jh*, *fh* …) used in the new process development are properly validated for each application.

Figure 11.8 shows an overview of verification through the software life cycle activities.[29] The left-hand side of the flowchart describes software design activities, and the right-hand side of the flowchart describes various stages of testing activities. Testing activities consist of two methods: black box (the functional test)

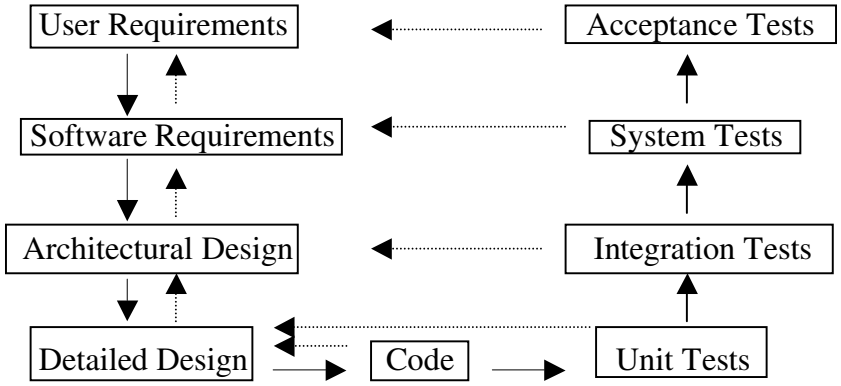

FIGURE 11.8 Overview of verification through the software life cycle activities. Verify: Dashed arrow line. Sequence: Solid arrow line.

and white box (the structural test) tests.[29,30] The white box testing method is used to check and verify the correct paths through the program code. This activity is generally performed by those who can access and understand the source code. A modern software development tool, such as Visual C++ from Microsoft, is typically an integrated development environment for coding, debugging, and execution. In particular, the line-by-line execution feature in the debugging mode enables software developers to check the execution result of every statement and its logic. Each statement of code needs to be successfully executed at least once during this testing stage. The black box test method is used to test the results generated by the software. It is done by inputting a given set of input parameters to the software and checking the accuracy of the output results, such as predicted temperatures and lethality value. The black box test can usually be performed by end users or thermal process specialists. Those components that influence and are critical to the safety of the process must be validated to a higher degree than those components that are not critical to the safety of the process.[28]

A mathematical model used for thermal process calculation needs to be validated in its accuracy and predictability for the product and process delivery application system selected. There are a number of methods to validate the stability and accuracy of the developed mathematical model itself. The analytical solution to the governing heat transfer equation in a special condition (e.g., constant processing and cooling temperatures) is a method often employed to challenge the theoretical model. The microbial challenge is another method used to challenge the model, where the physical measurement is difficult to perform, such as in the multiphase aseptic processing system. However, the majority of mathematical models used for thermal processing of canned foods were tested against the physical measurement data, such as temperatures.

Weng[33] presented a case study on challenging the NumeriCAL model for thermal process calculations. He provided a list of user requirements that are critical in thermal process calculations for food safety and production efficiency:

1. The software/model should be able to model the entire heat penetration curve, including heating and cooling portions for various heat transfer modes packaged in various containers, with general method accuracy on lethality value calculations for products exhibiting either simple or broken semilogarithmic heating or cooling curves, and with *jh* value less than 1.0 to (but not limited to) around 50.
2. The software/model should be able to determine or predict new processes with the following variations under a reasonable range:
   - Different process temperatures (RT) and initial product temperatures (IT)
   - Variable come-up temperature profiles
   - Variable retort temperatures
   - Large g value (*g* is the temperature difference between retort temperature and the slowest-heating zone product temperature at the end of heating)
   - Variable cooling profiles
3. The software/model is able to handle various process temperature deviations.
4. The software/model is able to incorporate various thermal inactivation kinetic models of the microorganism of concern.

The NumeriCAL model was extensively challenged[33] against variables such as the initial temperature, the retort temperature, the various come-up retort temperature profiles, the cooling temperature variations, larger g values,[34] and the various process temperature deviations. Figure 11.9 shows one of the typical NumeriCAL modeling results for canned beef chunk in gravy processed in a hydrostatic sterilizer with a NumeriCAL *jh* value of 4.70 and *jc* value of 1.00 due to rapid depressurization during initial cooling. The thermocouple tip was impaled into the geometric center of the beef chunk, which was located at the geometric center of the container during the sterilization process. The product shows a broken semilogarithmic heating curve, and the model-simulated product temperatures (including cooling phase) agree well with the measured product temperatures. It is noted that from Figure 11.9 to Figure 11.13 the product temperature of the heating portion is plotted in the well-known inversed logarithmic scale,[1,7,13] which is labeled in the left *y* axis; the cooling portion is plotted in the logarithmic scale, which is labeled directly on the cooling curve; and the retort temperature is plotted in the linear scale, which is labeled in the right *y* axis for comparison purposes.

Figure 11.10 shows a case study on the model simulation results for different initial product temperatures. The left curve is the modeling results for developing heating (*jh*, *fh*) and cooling (*jc*, *fc*) factors with an initial product temperature of 29.5°C. The right curve is the predicted product temperatures under a different

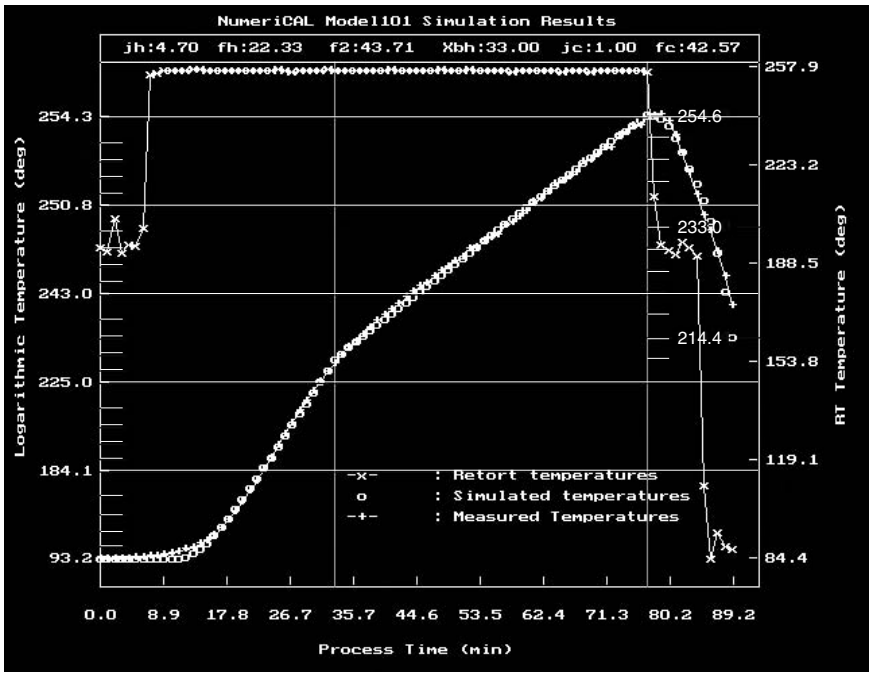

FIGURE 11.9 A typical NumeriCAL modeled product temperature profile (°F) for canned beef chunk in gravy (300 × 405 can size) processed in a hydrostatic sterilizer *(jh* = 4.70, *fh* = 22.33, *f*2 = 43.71, *xbh* = 33.00, *jc* = 1.00, *fc* = 42.57).

initial product temperature (15.2°C higher) by using the same input heating and cooling factors as the left curve. The agreement between the predicted and measured product temperatures (Figure 11.10, right curve) suggests that the model predictability is not affected by the initial product temperatures within the range studied.

Figure 11.11 shows the chocolate drink packaged in 15.5-fluid oz glass bottles and processed in 119.4 and 125.6°C retort temperatures, respectively. The left curve shows modeling results on developing NumeriCAL heating and cooling factors (*jh* = 1.56, *fh* = 10.50, *jc* = 0.73, *fc* = 10.86). This set of heating/cooling factors was then used to predict the production temperature for a higher retort sterilization temperature (125.6°C), as shown in the right curve. It is clearly shown that the model-predicted product temperatures are on the conservative side. The result suggests that the commercial sterility value might not have been obtained if the input heating/cooling factors had been developed at a higher temperature in this case.

Figure 11.12 shows the effect of the come-up and cooling profiles on the NumeriCAL model-predicted results. The left curve shows a normal sterilization process with 4.5 min come-up time for developing NumeriCAL heating and cooling factors (*jh* = 1.79, *fh* = 44.79, *jc* = 1.56, *fc* = 50.70). This set of input

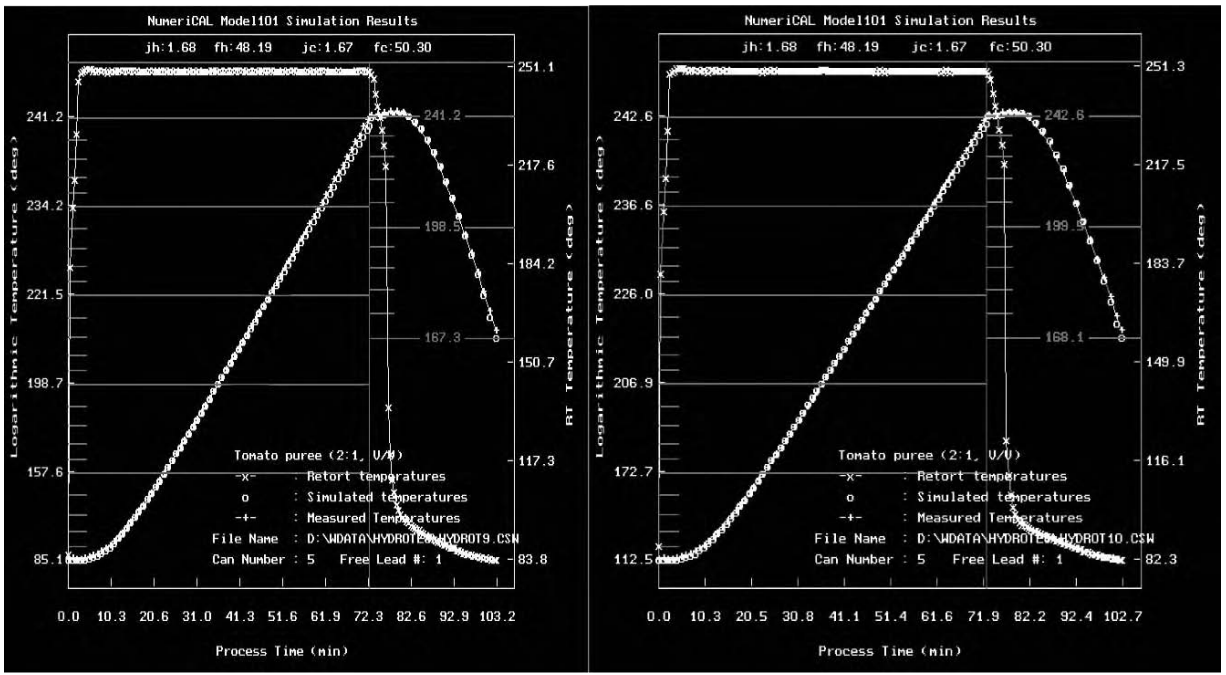

FIGURE 11.10 NumeriCAL simulated product temperatures (°F) under different initial product temperatures (IT) with 15.2°C difference (tomato puree, 2:1 v/v in 300 × 405 cans). Left: Modeling the heat penetration data with IT of 29.5°C (85.1°F). Right: Predicting product temperatures with IT of 44.72°C (112.5°F) ($jh = 1.68$, $fh = 48.19$, $jc = 1.67$, $fc = 50.30$).

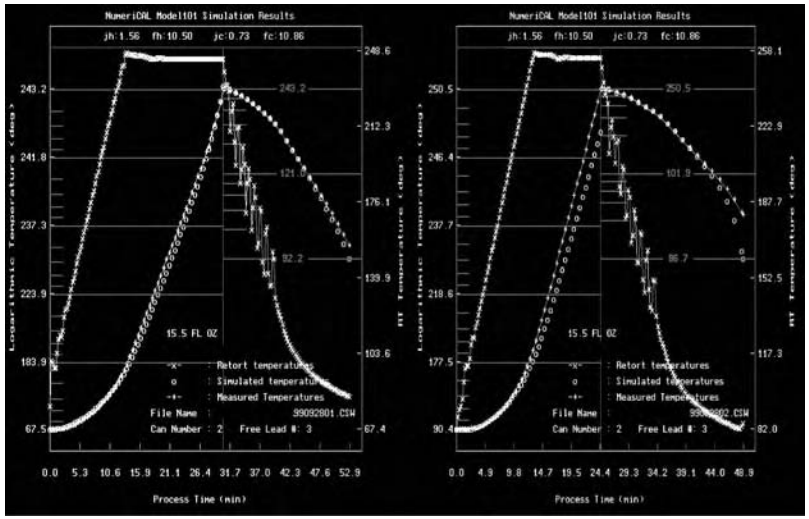

FIGURE 11.11 Chocolate drink in 15.5-fluid oz glass bottle processed at 119.4°C (246.9°F) and 125.6°C (258.0°F) retort temperatures (RT), respectively. Left: Modeling the heat penetration data with RT of 119.4°C (246.9°F). Right: Predicting the product temperatures with RT of 125.6°C (258.0°F) ($jh = 1.56$, $fh = 10.50$, $jc = 0.73$, fc = 10.86).

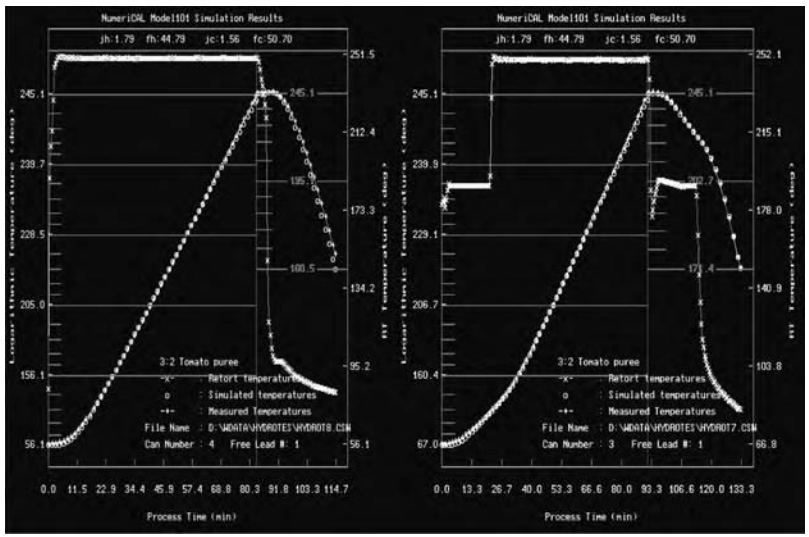

FIGURE 11.12 Effect of the come-up and cooling retort temperature profiles on the NumeriCAL modeling results (°F). Product: 300 × 405 canned condensed mushroom soup (2:1, v/v) processed in a hydrostatic sterilizer simulator. Left: Modeling the heat penetration data. Right: Predicting product temperatures with longer come-up and cooling profiles ($jh = 1.79$, $fh = 44.79$, $jc = 1.56$, $fc = 50.70$).

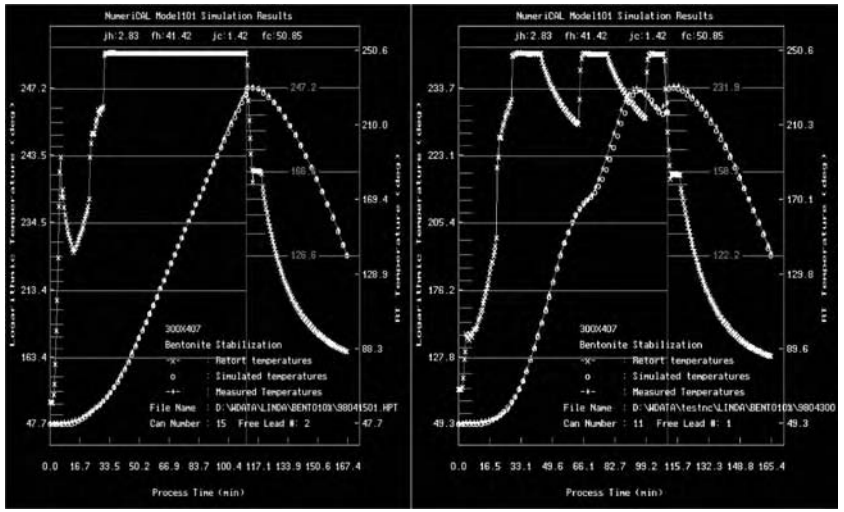

FIGURE 11.13 NumeriCAL simulation results (°F) under process deviation conditions. Product: 10% bentonite in 300 × 407 cans. Left: Normal heat penetration data modeling results. Right: Model-predicted time–temperature under multiple process temperature deviation conditions ($jh = 2.83$, $fh = 41.42$, $jc = 1.42$, $fc = 50.85$).

heating and cooling factors was then used to predict the product temperatures for the same product with longer come-up and cooling-down times (21.5 min for simulating hydrostatic sterilizer feed and discharge leg residence time). The results were plotted in the right curve and show that the model-predicted product temperatures agree well with the measurement data. The result suggests that the NumeriCAL heating and cooling factors used for the process design in this case are not affected by either the come-up profile or cooling-down profile.

Berry recognized that the come-up time and its profile have a profound effect on Ball's heating factors, particularly the *jh* value when using 42% come-up time correction.[35] If the heating factors were developed from the fastest come-up profile, it could cause food safety problems when these heating factors were used for the process development for a sterilizer actually having a longer come-up time. He recommended using a *true jh* value for the process development.

Table 11.2 shows various come-up time effects in a hydrostatic sterilizer simulator on both Ball's and NumeriCAL *jh* values. From feed leg time 4.5 to 21.5 min, we found that the Ball *jh* values ranged from 1.49 to 1.90, whereas the NumeriCAL obtained *jh* value was consistent, which was around 1.71. Since NumeriCAL uses actual come-up and cooling-down retort temperatures, the developed *jh* values reflect the true *jh* value, which has less effect on the come-up time profile.

Figure 11.13 shows the NumeriCAL simulation results under process deviation conditions (10% Bentonite in 300 × 407 cans), with the *jh* value larger than 2.0. The left curve shows the normal heat penetration data modeling results

TABLE 11.2
The Effect of Come-Up Time (CUT) on Ball *jh* and NumeriCAL *jh* Values

CUT (min)	Ball *jh*	Ball *fh*	NumeriCAL *jh*	NumeriCAL *fh*
4.5[a]	1.77 ± 0.05	44.85 ± 0.42	1.74 ± 0.03	46.77 ± 0.39
7.0[b]	1.90 ± 0.05	41.99 ± 0.56	1.71 ± 0.07	46.01 ± 0.15
21.5[b]	1.49 ± 0.05	45.30 ± 0.13	1.70 ± 0.02	47.09 ± 0.40

Note: The product is 300 × 405 can of condensed mushroom soup (2:1, v/v) processed in a hydrostatic sterilizer simulator at 121.1°C.

[a]Feed leg time simulation at 87.8°C.
[b]Normal come-up time (close to linear).

with NumeriCAL *jh* of 2.83, *fh* of 41.42 min, *jc* of 1.42, and *fc* of 50.85 min. This set of input heating and cooling factors was then used to predict the product temperatures for the same product with two process temperature deviations. The results were plotted in the right curve and demonstrated that the model-predicted product temperatures were in good agreement with physically measured product temperatures under process temperature deviation conditions. The results suggest that the model could be used in the computer-based real-time control for correcting the process temperature deviations.

11.4 INTELLIGENT THERMAL PROCESS CONTROL

To ensure that the optimized process is adequately delivered to the product, the critical control points used in the process calculation need to be satisfied and properly controlled. However, a sterilizer temperature deviation can often occur during a process due to steam supply interruption or failure. Figure 11.14 shows a typical industrial example of process temperature deviations (two times), which were recorded in a hydrostatic sterilizer. When the process temperature deviation occurs, the product might not be safe and could cause potential public health problems. For the low-acid or acidified canned food products in the U.S., a processor has to isolate all temperature deviation-affected products, which must be evaluated by a competent process authority for safety, as required by the FDA and USDA. Often, process downtime and product quality loss could cause a significant economic loss to the food processors. Therefore, developing a real-time lethality-based computer predictive model, which is able to predict and trace the lethality of the critical product during process temperature deviation, is of high interest to the food canning industry. The importance and benefits of using this technology have been recognized in commercial production.[19]

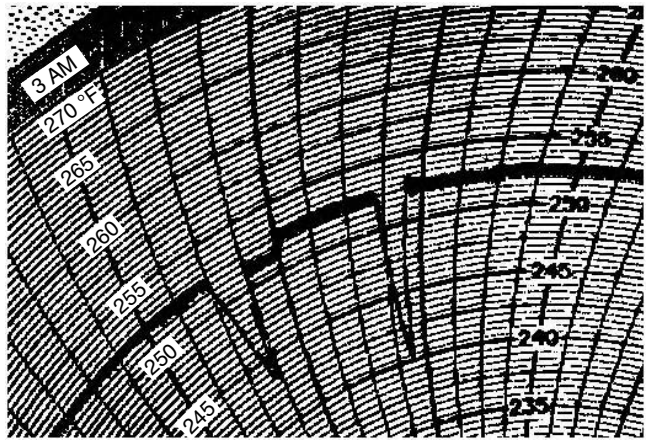

FIGURE 11.14 An industrial example of process temperature (°F) deviations in a hydrostatic sterilizer (two instance temperature deviations).

There are a number of methods that have been discussed and proposed for the real-time lethality-based computer control of thermal processes.[36–38] Lethality-based computer predictive control logic for a conduction-heating product processed in a batch sterilizer has been proposed.[39–41] The method can be used for online correction of retort process temperature deviations involving conduction-heating products. Weng[42–45] has further applied the lethality-based computer predictive control logic to the continuous sterilizer or pasteurizer systems. In this section, we are going to address the principles of lethality-based computer predictive control of the thermal process in batch and continuous sterilizers with the capability of real-time process temperature deviation correction.

11.4.1 Illustration of Mathematical Model

The goal of thermal process control is to deliver an adequate lethality to the product being *least* processed in the sterilizer under normal and deviated process conditions. Mathematically, this can be described in Equations 11.2 to 11.4:

$$\text{Min. } F^{z}_{Tref} - \text{value} = f(F^{z}_{Tref} - \text{value } (\theta))(\theta \in \Omega) \tag{11.2}$$

$$F^{z}_{Tref} - \text{value}(\theta) = \int_0^t 10^{(T-Tref)/z} dt \tag{11.3}$$

$$\text{Least } F^{z}_{Tref} - \text{value } (\theta_{\min}) \geq \text{Target } F^{z}_{Tref} - \text{value} \tag{11.4}$$

where θ is an individual container of product, Ω is the total containers affected by process deviation, and F^{z}_{Tref} value is the sterilization value for the microorganism

of concern. The product slowest-heating zone temperature, T, can be simulated by a well-known model, such as the NumeriCAL model, described above.

Equation 11.2 is used to find the least F^{z}_{Tref} value (or F_0 value for low-acid foods) container (or a group of containers), θ_{min}, which receives the minimum process among products (Ω) being processed. Equation 11.3 is used to calculate the total lethality or F^{z}_{Tref} value delivered to any container of product (θ) in the sterilizer. By knowing the least F^{z}_{Tref} value in the process, the model can then intelligently control the thermal process using the process time during heating in real time to meet the required food safety level (Equation 11.4).

11.4.2 Application to Batch Sterilizers

In batch sterilizers, the lethality delivered to each individual container of product is not uniform. A wide lethality distribution may be found in a processed batch of product, due to the temperature distribution in the sterilizer, as shown in Figure 11.15. The control strategy depicted in Equations 11.2 to 11.4 is to ensure that a commercial sterility for those containers located at the slowest-heating zone or the quickest-cooling zone of the sterilizer (least F^{z}_{Tref} value, Equation 11.2) is satisfied, whether or not a sterilizer temperature deviation occurred. Therefore, the least F^{z}_{Tref} value calculated from the containers located in the slowest-heating zone or the quickest-cooling zone in the sterilizer is used for the process control of the batch sterilizer system. When a process temperature deviation occurs, it is only necessary to validate or ensure the product safety for the worst-case container in the slowest-heating zone in the retort. The product safety affected by the process temperature deviation usually can be evaluated and controlled based on the retort temperature distribution

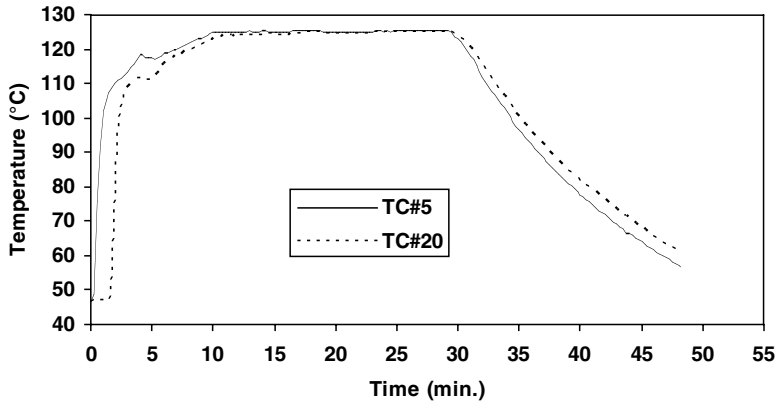

FIGURE 11.15 A typical example of the sterilizer temperature distribution in a water full-immersion four-basket batch sterilizer (TC 20 = slowest-heating zone, TC 5 = fastest-heating zone).

profile and the recorded temperature deviation profile.[42] An extended sterilization time is often needed to ensure the food safety.[39,42] Figure 11.13 (right) shows a typical example of using the NumeriCAL model for real-time correction of process temperature deviations in a batch retort. The industry benefit of using this technology in the batch retort was discussed and recognized.[19]

11.4.3 Application to the Continuous Sterilization System

In a continuous sterilizer system (e.g., hydrostatic sterilizer or reel-and-spiral rotary sterilizer), a uniform lethality can be delivered to the product for tightly controlled systems, since each product sees the same process time–temperature profile. However, in case of process temperature deviations, all deviation-affected carriers of containers (in hydrostatic sterilizer) or containers (in continuous rotary sterilizer) will have experienced different and unique heating time–temperature histories. As shown in Figure 11.16, for example, the entry product to the sterilization chamber first experiences the process temperature deviation and then the normal process temperature treatment. However, for the product that has already traveled to the middle of the chamber, it first experiences a normal process temperature, then the deviated temperature, and afterwards a normal process temperature again when the deviation is cleared. As a result, a wide spread of delivered lethality values to those deviation-affected products can be expected. The product that starts to significantly accumulate the lethality value upon deviation usually suffers most. The least F^{z}_{Tref} value containers (Equation 11.2) need to be identified for the process control purpose.[43–45]

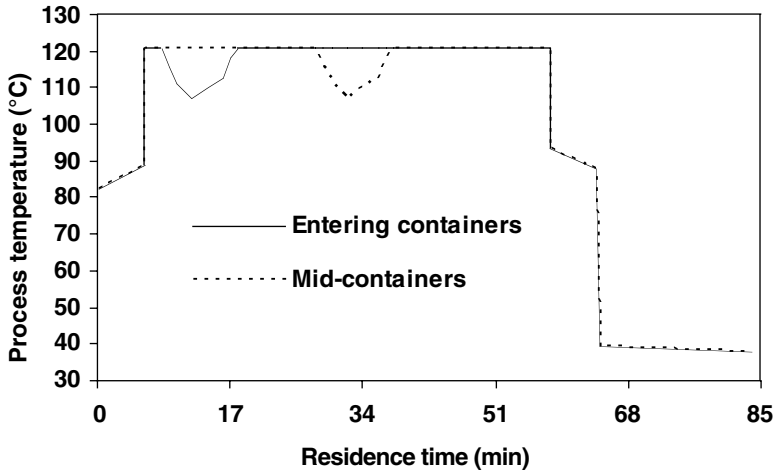

FIGURE 11.16 Two different time–temperature environmental histories for two carriers of products located at the beginning and middle positions, respectively, in a hydrostatic sterilizer steam dome when process temperature deviation occurred.

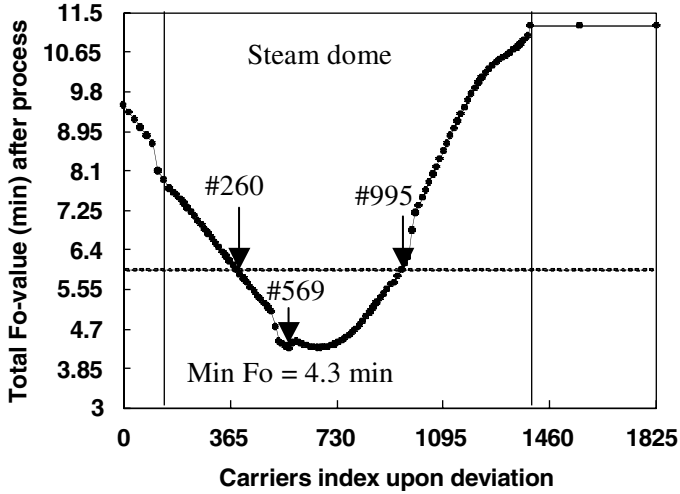

FIGURE 11.17 Total accumulated Fo value (min) distribution among carriers of product affected by steam dome process temperature deviation. (Steam dome temperature dropped from 121 to 112.8°C for 26 min, and the chain was not stopped upon deviation. Steam dome interface water level was raised by 0.508 m, and the water temperature was 90.6°C.)

Figure 11.17 shows the total F_0 value distribution among carriers of containers affected by the process temperature deviation for a hydrostatic sterilizer. It is noted that the carrier just entering the feed leg when the temperature deviation occurred was labeled zero (Figure 11.17 and Figure 11.18). The total sterilization value delivered to each carrier of product was calculated by using the NumeriCAL model based on its position during deviation. It was found that the total accumulated F_0 value for each deviation-affected carrier of containers was different, and its total F_0 value strongly depends on the carrier location when deviation occurs. The minimum F_0 value carrier was 569, with total F_0 value of 4.3 min. Those carriers of product from 260 to 995 were underprocessed, with a total F_0 value less than the scheduled commercial sterility value of 6.0 min in this case, which should be separated from the rest of the product.

Figure 11.18 shows a case study with two consecutive process temperature deviations in a continuous hydrostatic sterilizer. The steam dome temperature first dropped from 120 to 104.4°C for 10 min. After the process temperature was recovered for 5 min, another process temperature deviation occurred, with a process temperature drop to 110°C for another 10 min. During process temperature deviations, the sterilizer chain was properly stopped and the steam dome water interface was elevated for about 0.6 m. The total lethality value delivered to each carrier of product was calculated by using the NumeriCAL model based on the carrier position during deviations, and the results were plotted in Figure 11.18. As shown in Figure 11.18, the delivered total F_0 values for those carriers of

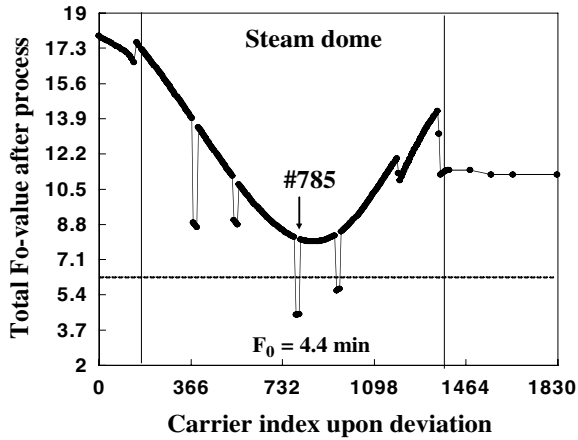

FIGURE 11.18 Total accumulated F_0 value (min) distribution among carriers of product affected by the multiple process temperature deviations. (The chain was properly stopped and the steam dome interface water level was raised by 0.6 m during deviations.)

product affected by the process temperature deviations were all different and followed a convex type of curve, with some low F_0 value pockets. The low F_0 value pockets were from products that were covered by the raised steam dome water due to the reduced steam dome pressure during the temperature deviations. The least F_0 value for all products affected by the temperature deviation was 4.4 min, with the carrier index number of 785. There are two sets of carriers of products (788 to 809 and 941 to 962), with the total delivered F_0 value less than the schedule commercial sterility F_0 value of 6.0 min in this case, which should be separated from the rest of the product.

Figure 11.17 and Figure 11.18 suggest that for the continuous sterilizer systems, the traditional incubation test for deviation-affected product should focus on sampling those containers that received the least sterilization value. Random sampling could miss the worst-case lethality value products. Failure to locate the true global least Fo value product could cause serious food safety issues during both offline and online process evaluations. Several methods have been proposed to identify and dynamically control the food safety for foods processed in a continuous sterilizer system.[43–45] One of methods proposed was to dynamically identify the underprocessed products at the exit of the continuous sterilizer system without stopping the chain (hydrostatic sterilizer), reel (reel-and-spiral rotary sterilizer), or belt (pasteurizer). The identified underprocessed product can be mechanically separated at the exit line. This method not only ensures the food safety, but also prevents potential incipient spoilage before processing and possible thermophilic spoilage in the warm water during cooling due to a long system stop time. The method could also be used to ensure the product quality by avoiding overprocessed products and prevent significant economic loss due to system stop downtime.

11.5 CONCLUSIONS

The thermal processing of canned foods continues to be advanced to meet the customer needs, particularly the convenience and quality aspects, and thermal sterilization systems are advancing to meet these challenges, such as for handling various convenience packages and geometry, and for increasing the production efficiency.

There is an increasing interest in the canning industry in using the new process modeling and calculation method for ensuring food safety and for optimizing product quality and process efficiency. The importance and benefits of using proper thermal processing software, such as the NumeriCAL model, have been more and more recognized in the food industry.

A process temperature deviation often occurs due to the failure of adequate supply of heating medium. The product affected could be underprocessed and could cause potential public health problems. Proper thermal process control with the capability of real-time process temperature deviation correction is one of the latest developments in thermal processing of canned foods. The lethality-based computer predictive control method has been discussed, and recently has been expanded to the continuous sterilizer systems, such as hydrostatic sterilizers and rotary reel-and-spiral sterilizers. It has been commercially applied to batch retort systems.

Lately we have experienced increasing interests in aseptic processing and packaging of low-acid foods with particles for both retail and institutional sizes. The major technical issues related to aseptic processing have been addressed.[46] A recognized mathematical modeling tool, such as *AseptiCAL*™,[47] and a bulk aseptic filler for packing low-acid foods in institutional sizes[48] are available. Perhaps the major challenge is how to increase the retail size aseptic packaging throughput, so that the quality of aseptically processed product can be recognized by the consumer and the cost can be comparable to that for canning operations.

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12 Thermal Processing of Ready Meals

Gary Tucker

CONTENTS

12.1 INTRODUCTION

This chapter considers thermal processing of ready meals in terms of the different types of meals on the market, their methods of manufacture, and the assurance of quality and safety of those meals. Temperature, referred to as thermal processing, is the most commonly used method to kill or control the numbers of microorganisms present within foods and on packaging material surfaces. Other methods for achieving

preservation, such as freezing and modified atmospheres, will be mentioned briefly in Section 12.2, but the priority is with thermal processing techniques.

Ready meals are multicomponent foods, typically composed of a meat or vegetable component and a rice, pasta, or potato component. These can be mixed together in one meal, for example, in a single canned product, or the components can be separated within a multicompartment tray. There are many types of ready meals, including traditional meals, such as cottage pie and roast beef with Yorkshire pudding, and oriental dishes with various accompaniments. The concept is that the product is a complete meal that requires minimal preparation by the consumer because the consumer receives it in a microbiologically safe condition. Thermal processing of ready meals to achieve such a safe condition is complicated because of the need to ensure that all parts are processed to minimum safety criteria. However, there will be differences in the rate of heating within the meal that must be controlled so that the level of processing is not detrimental to one or more of the parts. Ready meals sold for ambient storage will be thermally sterilized, whereas those intended for chilled or frozen storage will only receive pasteurization. The latter process has advantages in terms of product quality because of the milder process.

The commercial market for ready meals has grown significantly over the last few years. Table 12.1 presents commercial market data for all categories of foods that receive a thermal process, with market values scaled to 2003.[1,2] Thus, the total 2003 U.K. market value of thermally processed food products is £4402 million, with ready meals contributing £1535 million. These figures include ready meals that are stored under ambient, chilled, and frozen conditions; however, there is a requirement for all meals to receive a thermal process at some stage in the production.

TABLE 12.1
Commercial Information on the Market Size for Thermally Processed Foods

Product Category	Estimated 2003 Market (£ m)
Cooked poultry products	359.7
Cooked other meat products	231.7
Canned, bottled fruit	208.9
Processed fruit	143.4
Spreads, dressings, pickles, sauces	755.3
Canned meat products	120.3
Pet foods	953.3
Jams, jellies	94.7
Ready meals	1535.0
Total	4402.3

Note: 3% inflation assumed per year from 1996 to 2003.

Both retail and catering markets are important for ready meals and have seen tremendous growth recently as new processes such as *sous vide* increase in popularity. *Sous vide* is a technology that originated in France as a mild thermal process (e.g., 70°C for 40 min) for the manufacture of high-quality foods sold to the catering sectors.[3] More recent *sous vide* processes have targeted the psychrotrophic strains of *Clostridium botulinum* (e.g., 90°C for 10 min) that have required the process severity to be increased. Section 12.3 discusses microbiological targets and how thermal processes are validated.

Packaging formats vary significantly for ready meals and are linked with the methods of production, storage, and consumer preference. Paperboard, plastic, and aluminum trays are typical for chilled and frozen ready meals, where the thermal processes are most likely to be applied to the food components before they are packaged. These packaging formats often have multiple compartments in which the components, such as meat, vegetables, and rice, are placed separately, and each given a different thermal process. The processes given tend to be referred to as cooking steps, but there is a microbiological kill associated with these steps, and so it is correct to refer to this as thermal processing. The microorganism targets are discussed later in Section 12.3.

Production methods for single-component or multicomponent ready meals are varied, but can be categorized into those where the thermal processing step occurs prior to packaging (e.g., heat exchangers) or after packaging (e.g., retorts). The former method has the most variety in terms of the production methods, where factories making short-shelf-life meals can be divided into high and low care (or risk) areas. Methods of ready-meal manufacture are discussed in more detail in Section 12.2.

12.2 METHODS OF MANUFACTURE

In order to understand how thermal processing can be used to manufacture a complex food such as a ready meal, it is important to know how microorganisms behave. In the hazard analysis and critical control point (HACCP) context, food safety with respect to microorganisms is controlled by quantifying their introduction to the food, growth within that food, and survival through the production stages.[4] A factory HACCP plan will consider introduction, growth, and survival at all stages of manufacture.

There are categories of temperature sensitivity of microorganisms that help to define and position the thermal processes that are applied to ready meals:

- *Psychrotrophic* (cold tolerant), which can reproduce in chilled storage conditions, sometimes as low as 4°C. Having evolved to survive in extremes of cold, these are the easiest to destroy by heat.
- *Psychrophilic* (cold loving), which have an optimum growth temperature of 20°C.
- *Mesophilic* (medium range), which have an optimum growth temperature between 20 and 44°C. These are of greatest concern with ready meals.

- *Thermophilic* (heat loving), which have an optimum growth temperature between 45 and 60°C. In general, these organisms are only of concern with ready meals produced or stored in temperate climates.
- *Thermoduric* (heat enduring), which can survive above 70°C, but cannot reproduce at these temperatures.

The middle three categories are of greatest importance in ready-meal manufacture. Most of the pathogenic microorganisms fall within the mesophilic category, such as *Salmonella, Listeria,* and *Escherichia coli* O157, and so food production conditions will be designed to minimize their growth and survival during manufacture. The scheduled thermal processing conditions of hold temperature and time are designed specifically with the intended storage conditions that dictate microorganism growth. For example, it would be uneconomic to fully sterilize a chilled ready meal. Safe manufacture of a ready meal requires that the thermal processes are applied correctly and the intended storage and distribution conditions are maintained for the duration of the shelf life.[5]

There are four stages in bacterial growth, of which the first two, lag phase and log phase, are important during manufacture:

- *Lag phase*, during which the bacteria are acclimatizing to their environment, which can be several hours long.
- *Log phase*, during which reproduction occurs logarithmically for the first few hours. Conditions for growth are ideal during this period and toxin production is most common.
- *Stationary phase*, during which the bacteria's reproduction rate is cancelled by the death rate.
- *Mortality or decline phase*, during which exhausted nutrient levels or the level of toxic metabolites in the environment prevent reproduction, with the results that the bacteria gradually die off.

The lag phase is critical in ready-meal production because it allows the food manufacturer to complete the processing and assembly of the ready meal without surviving microorganisms germinating. Chilled ready-meal production is a good example of this, whereby the high-risk section is likely to be held at low temperatures (8 to 10°C) in order that microorganism germination and growth are controlled. Even the psychrophilic organisms require many hours to germinate at these temperatures.

The log phase is to be avoided at all costs, since this can result in microorganisms doubling in numbers in short periods (e.g., every 20 to 30 min if conditions permit). Toxin production is most likely to occur during the log phase.

12.2.1 Nonthermal Methods for Manufacturing Ready Meals

This chapter primarily considers thermal processing, but there are many other preservation methods that are used to manufacture ready meals.[6] For completeness, these methods are outlined in the subsections below.

12.2.1.1 Freezing

Freezing of food does not render the food sterile. Although the freezing process can reduce the levels of some susceptible microorganisms, this is not significant in the context of the overall microbial quality of the food. Thus, a frozen ready meal will have been subjected to a thermal process at some stage or stages in its manufacture. At commercial freezing temperatures (–18 to –24°C), all microbial activity is suspended and the length of time for which the food can be kept is dependent on quality factors. It is important to note, however, that once a frozen food is defrosted, those viable microorganisms present will grow and multiply.

12.2.1.2 Chilling

Chilling is the process that lowers the food temperature to a safe storage temperature of 0 to 5°C. Chilled foods can potentially present a greater risk to public safety than frozen foods. Keeping products at a low temperature reduces the rate of microbiological and chemical deterioration of the food. In most processed chilled foods, it is microbial growth that limits the shelf life; even the slow growth rates that occur under chilled conditions will eventually result in microbial levels that can affect the food or present a potential hazard (Table 12.2). This microbial growth can result in spoilage of the food (it may go putrid or cloudy or show the effects of fermentation), but pathogens, if present, may have the potential to grow and may show no noticeable signs of change in the food.

To reduce microbial effects to a minimum, chilled ready meals are usually given a thermal process, sufficient to eliminate a variety of pathogens, such as *Salmonella*, *Listeria*, and *E. coli* O157. A process equivalent to 70°C for 2 min is

TABLE 12.2
Minimum Growth Temperatures for Selected Pathogens

Pathogenic Microorganism	Minimum Growth Temperature (°C)
Bacillus cereus	4.0
C. botulinum (psychrotrophic)	3.3
E. coli O157 (and other VTEC)	7.0
Listeria monocytogenes	–0.4
Salmonella species	4.0
Staphylococcus aureus	6.7
Vibrio parahaemolyticus	5.0
Yersinia enterocolitica	–1.0

Source: Betts, G., Ed., *A Code of Practice for the Manufacture of Vacuum and Modified Atmosphere Packaged Chilled Foods with Particular Regard to the Risks of Botulism*, CCFRA Guideline 11, Campden & Chorleywood Food Research Association, Gloucestershire, U.K., 1996. With permission.

generally considered to be sufficient, but the exact process given will depend on the nature of the food. Application of hurdles to growth, such as pasteurization and chilling, can allow shelf lives of several days. If the pasteurization regime is more severe, for example, 90°C for 10 min,[8] it is possible to extend the shelf life to between 18 and 24 days or more. The exact length depends on the suitability of the food to support microbial growth, and it is common for a company to apply the same heat process to two different foods, yet the declared shelf life of one may be 14 days while the other may allow 20 days. Use of product ingredient(s) with low microbial count(s), ultraclean handling and filling conditions, in combination with sterilized packaging (i.e., near aseptic conditions) will serve to reduce initial microbial loading of the pasteurized product and thereby extend shelf life.

12.2.1.3 Drying and Water Activity Control

All microorganisms of public health significance need water to grow. Reducing the amount of water in a food that is available to the microorganism is one way of slowing or preventing growth. Thus, dried foods and ingredients, such as dried herbs and spices, will not support microbial growth, and provided they are stored under dry conditions, they can have an expected shelf life of many months, if not years. The shelf life of dried ready meals is usually limited by texture changes caused by moisture ingress through the packaging, with the food losing its crispness and becoming soft. Selection of suitable packaging materials is therefore critical in extending the shelf life of dried ready meals. Laminated paperboard with a plastic moisture barrier, such as polyethylene, is a common pack format for dried foods such as pot noodles.

12.2.1.4 Modifying the Atmosphere

This is a technique that is being increasingly used to extend the shelf life of fresh foods as well as bakery products, snack foods, and ready meals. Air in a package is replaced with a gas composition that will retard microbial growth and slow down the deterioration of the food. The exact composition of the gas used will depend entirely on the type of food being packaged and the biological process being controlled. Ready meals and other cook-chill products tend to use atmospheres containing 30% carbon dioxide and 70% nitrogen.[9] Modified atmosphere packaging (MAP) is generally used in combination with a mild thermal process and refrigeration to extend shelf life of ready meals toward the higher-quality end of the market.

An alternative to modifying the atmosphere is vacuum packaging, where all of the gas in the package is removed. This can be a very effective way of retarding chemical changes such as oxidative rancidity development, but care needs to be taken to prevent the growth of the pathogen *C. botulinum*, which grows under anaerobic conditions. A specific pasteurization process, referred to as the psychrotrophic botulinum process, is applied to the packaged food to reduce its numbers to commercially acceptable levels. By using vacuum packaging, mild heat, and chilled storage, greatly extended shelf lives have been achieved. This was the basis of *sous vide* cooking, described earlier in the chapter.

12.2.2 Preservation by Thermal Processing

Breakdown by microorganisms and enzymes is the major cause of undesirable changes in foodstuffs. Both are susceptible to heat, and appropriate heating regimes can be used to reduce, inhibit, or destroy microbial and enzymic activity. The degree of heat processing required to produce a ready meal of acceptable stability will depend on the nature of the food, its associated enzymes, the numbers and types of microorganisms, the conditions under which the processed food is stored, and other preservation techniques used.[5]

Manufacture of a thermally processed ready meal can be broken down into two basic processes:

1. The food is heated to reduce the numbers to an acceptably small statistical probability of pathogenic and spoilage organisms capable of growth under the intended storage conditions.
2. The food is sealed within a hermetic package to prevent reinfection. Preservation methods, such as traditional canning, seal the food in its package before the application of heat to the packaged food product, whereas other operations, such as aseptic, cook-chill, and cook-freeze, heat the food prior to dispensing into its pack.

Retorting and *canning* are terms that are still widely used in the food industry to describe a wide range of thermal processes where the food is heated within the pack to achieve a commercially sterile packaged food. The heating usually takes place in retorts that are basically batch type (Figure 12.1) or continuous hot water or steam-heated pressure cookers (Figure 12.2). The principal concept

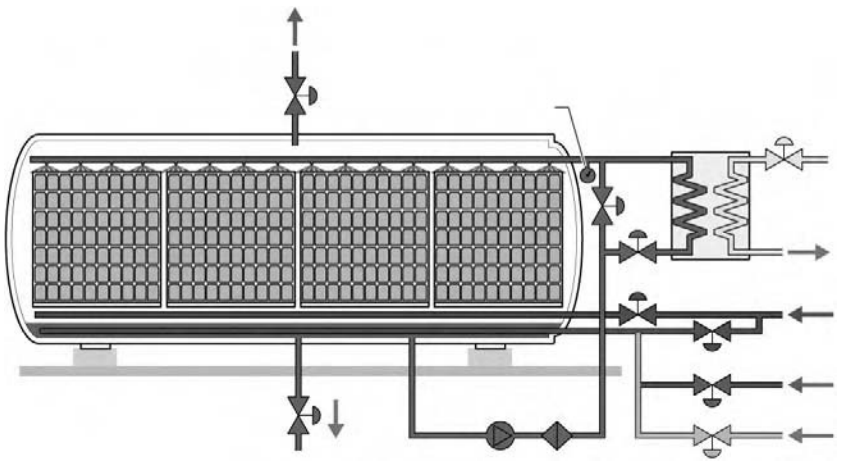

FIGURE 12.1 Example of a batch retort operating on the sprayed-water principle. (Courtesy of FMC Foodtech. With permission.)

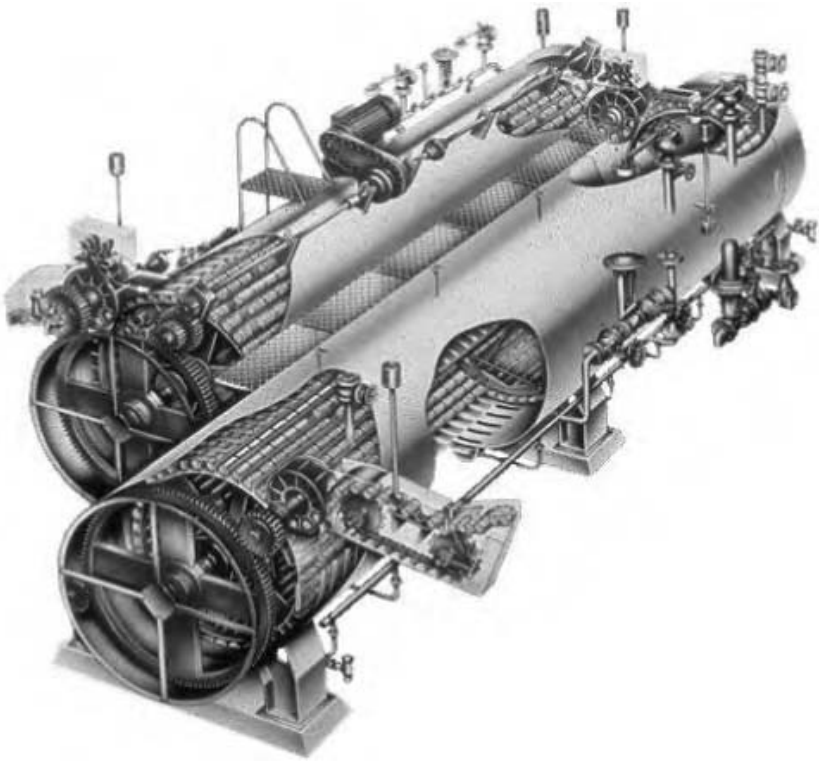

FIGURE 12.2 Reel-and-spiral cooker-cooler for processing cylindrical food cans. (Courtesy of FMC Foodtech. With permission.)

of food retorting is to heat a food in a hermetically sealed container so that it is commercially sterile at ambient temperatures (see Section 12.3). In other words, so that no microbial growth can occur in the food under normal storage conditions at ambient temperature until the package is opened.[5] Once the package is opened, the effects of retorting are lost, the food will need to be regarded as perishable, and its shelf life will depend on the nature of the food itself. Various packaging materials are suitable for use with retorted foods, which includes not only tin plate, but glass, plastic pots, trays, bottles and pouches, and aluminum cans.

The most heat resistant pathogen that might survive the retorting process of low-acid ready meals is *C. botulinum.* This bacterium can form heat-resistant spores under adverse conditions, which will germinate in the absence of oxygen and produce a highly potent toxin that causes a lethal condition known as botulism. This can cause death within 7 days. In practical terms, the sterilization process must reduce the probability of a single *C. botulinum* spore surviving in a pack of low-acid product to 1 in 1 million million (i.e., 1 in 10^{12}). This is called

a botulinum cook, and the standard process is 3 min equivalent at 121.1°C, referred to as F_0 3.[10–12] All retorting processes target this organism if no other effective hurdle to its growth is present. However, there is a growing trend to apply additional hurdles to microbial growth that allow the processor to use a milder heat treatment, referred to as pasteurization.

Milk is the most widely consumed pasteurized food in the U.K., and the process was first introduced commercially in the U.K. during the 1930s, when a treatment of 63°C for 30 min was used. Modern milk pasteurization uses an equivalent process of 72°C for 15 sec. Pasteurization is nowadays used extensively in the production of many different types of food, such as fruit products, pickled vegetables, jams, and ready meals.[13] Food may be pasteurized in a sealed container (analogous to a canned food) or in a continuous process analogous to an aseptic filling operation. It is important to note that pasteurized foods are not sterile and will usually rely on other preservative mechanisms to ensure their extended stability for the desired length of time.

Whereas thermally processed ready meals for ambient storage have shelf lives normally measured in years, cook-freeze meals typically have shelf lives measured in months and cook-chill foods in days.

12.2.3 In-Vessel Systems

The vessel acts in a way similar to that of a heat exchanger in that it raises the food temperature to that required for pasteurization. Sterilization processes are not normally applied within vessels because of the need to operate at pressures above atmospheric, and the benefits of sterilization are lost when the food is cooled and packaged. A typical vessel size is around 800 to 1000 kg and usually comprises a hemispherical steam-jacketed base with cylindrical sides (Figure 12.3). Direct steam injection can be used to effect a more rapid heating rate. A hinged lid is usually present to reduce heat loss and prevent foreign objects from falling into the food. With high-viscosity foods it is essential that the food is well mixed; otherwise, laminar boundary layers develop that reduce the thermal efficiencies and may assist burn-on to the heated surface. Horizontal agitators with scraped-surface blades offer the most effective mixing, although recirculating pumps and vertical mixing blades are alternatives.

Once pasteurized, the food can be filled either hot or cold into the containers. A hot-fill process will only require a short hold time at high temperature to ensure the inside container surfaces are pasteurized. This is usually achieved in a raining water tunnel pasteurizer, although it is possible to omit this step if:

1. The food's acidity is high (pH < 3.8)
2. The filling temperature is above 95°C
3. The containers are prewarmed or of low heat capacity

The shelf life of a sauce of low pH will be many months if hot filled, and determined by its chemistry and not by its microbiology. However, multicomponent

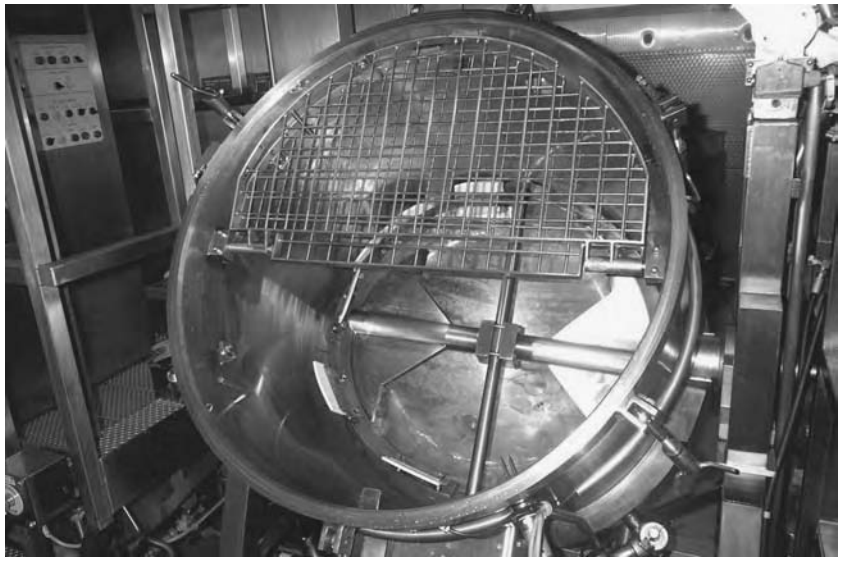

FIGURE 12.3 Jacketed vessel with horizontal scraped-surface agitation for the manufacture of medium- and high-viscosity foods with particulates. (Courtesy of T. Giusti Ltd.)

ready meals will be pH neutral unless they are packaged in multicompartment trays where one or more components is of low pH (e.g., a sweet-and-sour sauce).

A cold-fill process will not guarantee commercial sterility of the container, and as such requires far greater attention to hygiene in order to minimize the introduction of microbial contamination during filling. Most cold-filled products are sold chilled and have shelf lives up to 10 to 12 days. This is where the concept of low- and high-care factories becomes important, in that shelf-life extension beyond 10 to 12 days can be achieved. Many of the ready meals sold chilled or frozen are assembled in high-care areas, with their components having been manufactured in different factories and transported chilled to the assembly factory. Packaging formats for the components are varied. This method of manufacture is discussed in Section 12.4 on future trends.

12.2.4 Heat Exchangers

A heat exchanger offers the same type of thermal processing operation as a heated vessel in that the food is processed prior to packaging. Suitable heat exchangers for heating and cooling foods are plate packs for thin liquids, tubular heat exchangers for medium-viscosity foods, and scraped-surface heat exchangers for high-viscosity foods that may contain particulates. When establishing the processing times and temperatures, it is assumed that the thermal process is delivered solely within a holding section that is usually a long length of tube. This can give rise to excessive thermal processing because it does not take into account the

high-temperature periods at the end of heating and at the start of cooling. Sterilization or pasteurization values are calculated solely from the holding tube outlet temperature, and the residence time taken from the measured flow rate. Control of these parameters must be to high levels of accuracy because of the high temperatures and short times (HTST) used.

The term *UHT* (ultrahigh temperature or ultraheat treatment) is often used to describe food preservation by in-line continuous thermal processing followed by aseptic packing. Aseptic packing can be carried out with metal cans, plastic pots and bottles, flexible packaging, and foil-laminated paperboard cartons. In aseptic packing, the packaging operation takes place in a sterilized container within a sterilized environment. The major difference with retorting is that the package and food are sterilized separately and then brought together and closed in a sterile environment. One potential advantage that is often quoted for UHT processing is that of enhanced food quality.[14] This is because the problem of overcooking can be reduced at the typical temperatures and holding times in a UHT process (e.g., 140°C for a few seconds). At these elevated temperatures, the lethal kill to *C. botulinum* spores is substantial, whereas the rate of the cooking reactions is less significant; in effect, UHT allows extremely short process times with minimal detriment to quality.[12] This benefit is used in the production of sterilized milk and cream that would end up too brown (caramelized), with associated off-flavors, if it were processed in the pack. UHT technology for ready meals has been commercialized, but has not found widespread consumer acceptance, probably because the meal quality differs from that produced from conventional technology. One major drawback is that the meat and vegetable particulates heat by conduction, which is slow, and so the holding times have to be extended in order that the centers of the particulates are sterilized.

For ready meals that are processed as the complete meal, large particulates will almost certainly be present. This reduces the choice of conventional heat exchanger technology to two types:

1. Tubular heat exchangers with single product tubes (monotubes) large enough for the flow diameter to be of the order of four times the size of the largest particulate (Figure 12.4). The drawback with monotubes compared to smaller-diameter multitubes or concentric tubes is in the reduced thermal efficiency due to the thicker product layer. However, the particulates present in the ready meal will to some extent work as internal mixers and will hence promote heat transfer.[14]
2. If the food viscosity is high and there is a chance of product fouling the heated or cooled surfaces of a tubular heat exchanger, the scraped-surface heat exchanger must be employed (Figure 12.5). In principle, a scraped-surface heat exchanger is a monotube equipped with a rotating internal scraper. The scraper keeps the heating surface free from any deposits and also promotes turbulence. Drawbacks with scraped-surface heat exchangers are the shear damage to delicate particulates and high cost of the plant.

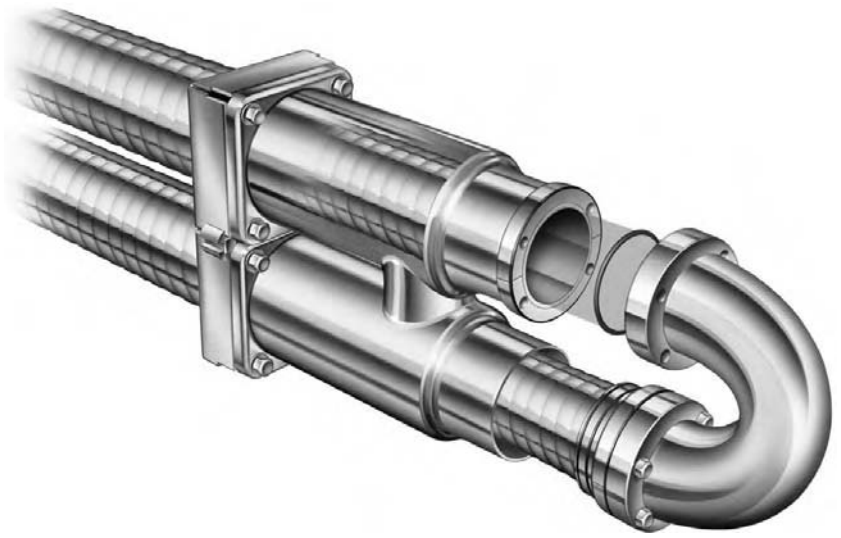

FIGURE 12.4 Monotube-type tubular heat exchanger suitable for continuous processing of foods with small particulates. (Courtesy of Tetra Pak.)

Alternate heat exchange techniques have been explored in the food industry for ready-meal production, with limited commercial succes.[15] *Ohmic heating* is a technology that was commercialized by APV Ltd. in the 1980s in which alternating electrical current is used to heat flowing foods to pasteurization and sterilization temperatures. Once cooled, the ready meals are aseptically filled into plastic trays or bags that can be stored in ambient conditions for many months. Ohmic heating is a volumetric method, and so a food of consistent electrical resistance will heat almost instantaneously and uniformly. By adjusting the carrier liquid conductivity, it is possible to heat particulates preferentially and, in doing so, thermally process a ready meal with great efficiency — that is, apart from cooling, which relies on conventional tubular heat exchangers. Ohmic heating has been used to sterilize ready meals for both catering and retail markets, but is no longer used in the U.K. for this application. Differences in the texture and flavor were the main consumer concerns with ohmically heated ready meals, and so the technology did not take off for this application and was mothballed. It is now used successfully for the pasteurization of fruit products with delicate particulates, in which the products are intermediates for assembly into yogurts and other dessert products.

12.2.5 In-Pack Retorting

One of the major advantages of retorting ready-meal packages is that both food and package are thermally processed together, which allows the filled packages to be commercially sterile. Low-acid ambient-stable ready meals are always

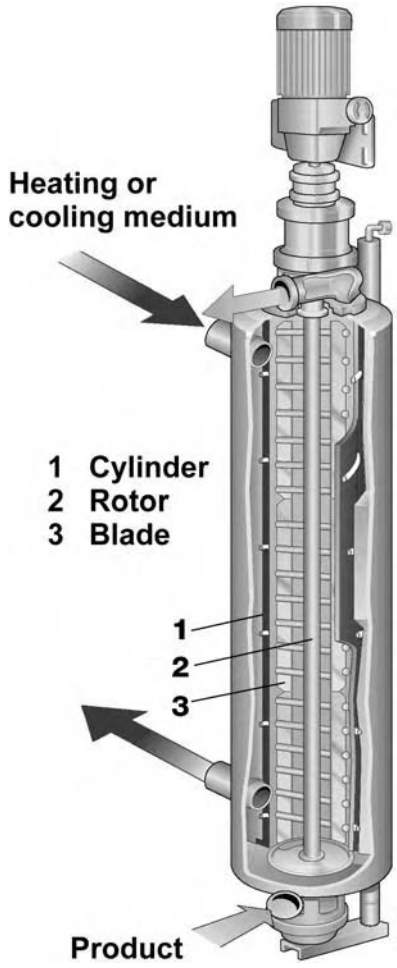

FIGURE 12.5 Scraped-surface heat exchanger for processing medium- and high-viscosity foods, including those with particulates. (Courtesy of Tetra Pak.)

retorted since they do not have any other preservation hurdle. However, retorting also has benefits for extending the shelf lives beyond the 10 to 12 days that are achieved with pasteurized and cold-filled ready meals for chilled storage. The disadvantages with retorting are that the containers need to be strong enough to withstand the high temperatures and the swings in pressure differential that can occur, and that the retorts are the production bottleneck in most factories. The former disadvantage incurs extra cost with the packaging.

The traditional retorted package is the metal can processed in a steam atmosphere, although glass jars, pouches, and flexible plastic or aluminum trays can now be successfully processed in steam or hot water. These containers require

an air overpressure to counteract the natural expansion of the gases present in the headspace and those released from the food as it rises in temperature. The desired effect is to push the lid or sides back to their original position, and therefore minimize the stress on the seals.

With almost all ready meals that are thermally processed by any technology, heat transfer from the media to the product thermal center is poor because of the viscous boundary layers that develop on the inside processing surfaces. The effect is to form an insulating layer that impairs heat transfer if there is no mixing inside the packages to remove the layers. This results in lengthy processing times to achieve commercial sterility, and so few companies will process ready meals without some form of agitation.

The first equipment (introduced by FMC Corporation in the 1930s) to increase heat transfer to canned foods was the reel-and-spiral cooker-cooler (Figure 12.2). This imposes a rotation of cans around their central axis and allows heating times to be reduced substantially (e.g., from 90 to 15 min in the steam chamber). Cans travel on a helical reel through the steam-heating and water-cooling sections and, in doing so, rotate at high speeds. The continuous operation of the cooker-cooler allows a high throughput to be achieved and favors high-volume production. Some canned ready meals are processed in reel-and-spiral cooker-coolers, although the high viscosity of the sauces and the high concentration of particulates (e.g., beans) reduce the heat transfer efficiency.

More recently, end-over-end (EOE) pack rotation has become popular, where the packages are constrained in baskets or crates that rotate. Being a batch system, this offers greater production flexibility and is not restricted to cylindrical metal cans (Figure 12.1). However, heat transfer enhancement is not as great as the cooker-cooler, and so the throughput is lower and operating costs higher. Ready meals in plastic pots and pouches are processed in steam/air or in water retorts where air overpressure is applied to maintain the package shape throughout the heating and cooling process. Expansion of the packages can put stresses on the heat seals of trays and pouches, which may lead to a failure in the *package integrity* and an increased chance of postprocess contamination. Low EOE rotation speeds (2 to 10 rpm) are often used to induce mixing, but without damaging the delicate packages or seals. Some of these packs can be multicompartment, and in these cases, the challenge is to design a thermal process that delivers a uniform level of microbial kill to all parts of the meal without overcooking any part of it.

12.3 ENSURING READY-MEAL SAFETY

Although pasteurization or sterilization of the food is the desired condition, the food is referred to as commercially sterile. By definition, *commercial sterility* or *appertization* of food is "the condition achieved by the application of heat which renders food free from viable micro-organisms, including those of known public health significance, capable of growing in the food at temperatures at which the food is likely to be held during distribution and storage."[5] In practice, however,

the food manufacturer makes a decision on the level of commercial risk with the applied thermal process because it is not possible to kill all of the microorganisms and produce a saleable product. A pasteurization process usually operates to 6 log reductions of the target organism,[8] and this differs from fully sterilized foods, where the intention is to achieve at least 12 log reductions in *C. botulinum* spores. The lower target log reductions for pasteurization are because of the reduced risks associated with the target microbial species when compared with the lethal botulinum toxin.

The following equation is used to calculate the target process or F value from heat resistance data on the likely pathogenic or spoilage organisms present. When the F value is divided by the decimal reduction time (D_T) for that organism, this gives the number of log reductions that will be achieved:

$$F = D_T (\log N_0/N) \tag{12.1}$$

where N is the final number of organisms after a specific time–temperature history, N_0 is the initial number of organisms, and D_T is the decimal reduction time at a fixed temperature (T) to reduce the number of organisms by a factor of 10 (minutes).

As the number and variety of ready meals increase, food companies are faced with the challenge of proving that these products are safely pasteurized or sterilized. This can sometimes be difficult if conventional temperature probe systems cannot be used and other more complex approaches need to be adopted. The categories that introduce these complexities include ready meals cooked in continuous ovens and meals with discrete particulates cooked in steam-jacketed agitated vessels or in heat exchangers. If an alternative to temperature probes is needed, the following approaches to validating microbiological process safety are the options available:

1. Microbiological methods can be used whereby cells or spores of a nonpathogenic organism, with similar temperature-induced death kinetics to the target pathogen, are embedded into an alginate bead.[16] The beads are made to mimic the food pieces in their thermal and physical behavior and so pass through the process with the food. Enumeration of the surviving organisms allows the log reduction and process value to be calculated. Section 12.3.2 deals with microbiological methods.
2. Simulated trials are carried out in a laboratory where the heat transfer conditions of the process are replicated and temperature measurement is feasible. This is more common with continuous particulate systems than with in-pack processes. Process models can then be developed that predict, for example, the temperature–time history of the critical food particulates as they travel through the heating, holding, and cooling zones of the process.
3. No validation is attempted, with the process safety being inferred from temperature probing of the bulk product or the environment. Substantial

overprocessing is allowed, in order that the thermal process delivered to the product thermal center is sufficient. Chilled or frozen storage is used for the ready meal, and end-product testing for microbiological activity is usual.

4. *Time–temperature integrators* (TTIs) can be applied to gather process data similar to those from microorganisms.[17,18] Section 12.3.3 discusses TTIs because this method is one of the most exciting to have emerged in recent years.

One of the core activities involved with establishing a thermal process is the selection of worst-case conditions likely to be experienced during normal production.[19–22] This is independent of the method chosen for process validation. The current methodology used by most food companies is to validate the microbiological process safety under worst-case conditions so that, by default, the process will be safe under normal production conditions.

To prove that the thermal process has achieved the target process value or F value during manufacture, it is necessary to conduct validation studies using an approved method. Various methods can be selected from the list above, and their choice depends on the costs and nature of the food and process type. Temperature measurements usually provide the cheapest method but are not appropriate for all foods.

12.3.1 Temperature Probe Systems

It has been stated above that the process validation study should be conducted using worst-case conditions. Therefore, by inference it should not be possible for a normal production batch to heat more slowly than the combination of factors evaluated as worst case. To determine the worst-case conditions it is necessary to first consider the product, process, and package separately, and second consider the influences of interactions. The following lists suggest the factors that should be addressed in a process validation study, although the lists are not intended to be exhaustive. This thought process, to arrive at the set of conditions that heat the slowest, is typical for in-pack processing, but is also appropriate for continuous processing.

Product factors:

- Formulation (weight variation in ingredients, e.g., high starch levels that could lead to increased viscosity)
- Fill weight (percent overfill of the key components, e.g., solids content)
- Consistency or viscosity of the liquid components (before and after processing)
- Solid components (size, shape, and weight before and after processing, potential for matting and clumping)
- Preparation methods (e.g., blanching)

- Rehydration of dried components (a complex area that should be avoided if possible)
- Heating mode (convection, conduction, mixed or broken heating)

Container factors:

- Type (metal cans, glass jars, pouches, semirigid containers)
- Nesting of low-profile containers (if processed in pack)
- Vacuum and headspace (residual gases with flexible containers, overpressure required to minimize stresses on pack seals)
- Orientation
- Fill method (initial temperature and the effects of delays in getting instrumented containers into the retort)
- Symmetry of pack rotation (end-over-end or axial)

Retort or processing system factors:

- Media type (steam, steam/air, water immersion, raining water; venting schedule if steam)
- Retort come-up time (should be as short as possible to minimize the quantity of heat absorbed by the product during this phase)
- Racking and dividing systems (flow of media)
- Rotation (slowest-heating position, usually along the retort axis)

The combination of conditions to arrive at the worst-case scenario should be determined by a competent individual, sometimes referred to as a thermal process authority. It does not matter which validation method is used (probes, microbes, or biochemical) or whether the process is continuous; the thought process for product, package, and process conditions and interaction should be the same.

For a high-viscosity sauce, typical of that in a ready meal, the position within a container that heats slowest is usually the geometric center. To validate a process for a food containing particulates, a large food chunk or piece is usually attached to the end of a temperature probe. While this will work for in-container processes, this method cannot be used for continuous processes, and so alternative methods are required.

12.3.2 Microbiological Methods for Process Validation

These are often referred to as direct methods, but they in fact rely on measuring the achieved log reductions for a process using a nonpathogenic organism and converting this to an F value using the same equation. The nonpathogenic or *marker organism* is put into the process in high numbers so that some will survive to be counted. If there are no surviving organisms, then it is only possible to conclude that the process achieved greater than, e.g., 6 log reductions for a 10^6 initial loading. In this situation, there will be uncertainty as to whether the organisms died as a result of the process, during transportation to or from the factory, or if the spores germinated during the come-up time, making them more susceptible to destruction at milder temperatures than the heat-resistant spores. Hence, controlling how these tests are performed is critical, and the expertise to

conduct a test using encapsulated spores or organisms tends to be restricted to a limited number of microbiology laboratories. A microbiological method can be conducted using organisms distributed evenly throughout a food product (inoculated pack) or concentrated in small beads (encapsulated organisms).

The inoculated pack method is also known as the *count reduction method* and involves inoculating the entire food with organisms of known heat resistance. For ease of handling, the organisms are usually in the spore form. It is essential that some organisms survive the heat process in order that the containers can be incubated and the surviving organisms counted. The average thermal process received by a container can be calculated using the equation for the F value. If the product is liquid, it is relatively easy to introduce the organisms, but for solid products, it is necessary to first mix the organisms in one of the ingredients to ensure that they are dispersed evenly throughout the container. Typical levels of the inoculum are between 10^3 and 10^5 organisms per container. An alternative is to use a gas-producing organism and estimate the severity of the process by the number of blown cans.

Encapsulating spores or organisms in an alginate bead allows the organisms to be placed at precise locations within a container or within the food particulates. The alginate bead can be made up with a high percentage of the food material so that the heating rate of the bead is similar to that of the food. This method has been used for continuous processes where the food contains particulates that require evaluation at their centers and conventional temperature sensing methods cannot be used. Large numbers of alginate beads are used to determine the distribution of F values that can occur in continuous processes as a result of the distribution of particle residence times. Estimating the exact number to use in a test is not straightforward because it depends on the F value distribution, which is not known until after the test is conducted and the results analyzed. The number of organisms used will be greater than that for an inoculated container test and can be on the order of 10^6 per bead. It is also important that not all are destroyed by the heat process; otherwise, it is not possible to estimate an F value.

12.3.3 Time–Temperature Integrators (TTIs)

These are an alternative means of process evaluation that does require live organisms to be deliberately taken into a food production environment.[17,18] A TTI can be an *enzyme* (e.g., amylase or peroxidase) that permanently denatures as it is heated. The reaction kinetics of the temperature-induced denaturation are designed to match those of the death kinetics for the target organism. F values for TTIs are calculated from the initial and final enzyme activities using an expression similar to that in Equation 12.1. Instead of using the initial and final number of organisms, the TTI F value uses enzyme activities. For the example where amylase is the TTI, the measurement of activity is a rate of color development when the amylase is reacted with a suitable reagent.

The breakthrough that enabled TTIs to be used for thermal process evaluation is in encapsulating the amylase solutions in silicone tubes.[17] When stored in

chilled water to minimize the rate of amylase degradation, the TTI tubes can be used for up to 14 days, therefore increasing the scope for applying TTIs to factories overseas. To further extend their usable shelf life, filled TTIs can be frozen in large numbers, and TTI tubes removed as and when required. Freezing has little impact on amylase structure or on the rate at which its structure degrades by heat. It is conceivable that several hundred TTIs could be made at one time, frozen individually, and used over a period of months. This would be an economical method for producing TTIs and would ensure that the kinetics for each tube would be similar.

12.4 FUTURE TRENDS

When processing a high-viscosity food such as a ready meal, the limits to heat transfer are to overcome the development of boundary layers that impair heat transfer rates at the heated surfaces. Some degree of agitation is advantageous irrespective of whether it is a continuous heat exchange process or one processed in a container. If particulates are introduced, then this imposes a further limitation to heat transfer rates because of the conduction within the particulates. Hence, most thermal process times will be considerably longer than those for foods without particulates. Traditional thermal processes may reduce the vitamin content of food and can affect its texture, flavor, and appearance.

Food manufacturers are continually looking for new ways to produce food with enhanced flavor and nutritional characteristics.[13] Much of this can be achieved by process optimization, but alternative methods are of interest. The development of new processes that are as effective as traditional thermal systems in reducing or eliminating microorganisms, but do not adversely affect the constituents of the food, is being actively researched.[6] In addition to those mentioned below, ultrasound, pulsed-light, electric field, and magnetic field systems are all being actively investigated. In the U.K., before any completely novel food, ingredient, or process can be marketed, it has to be considered by the Advisory Committee on Novel Foods and Processes (ACNFP). The primary function of the ACNFP is to investigate the safety of novel foods or processes and to advise the government of its findings. The European Union has also formulated novel foods legislation.

12.4.1 High-Pressure Processing

High-pressure processing (HPP) was originally considered in the 1890s, but it was not until the 1970s that Japanese food companies started to develop its commercial potential. Pressures of several thousand atmospheres (500 to 600 MPa) are used to kill microorganisms, but there is little evidence that high pressure is effective on spores or enzymes. Thus, chilled storage or high acidity are essential hurdles in preventing microbial growth. Jams were the first products to be produced in this way in Japan, and the process is now being investigated in Europe and the U.S. Sterilization of the package is not possible using high pressure, and without aseptic filling this may restrict its widespread use. There is some interest in HPP for ready meals.

12.4.2 Ohmic Heating

Ohmic heating achieves its preservation action via thermal effects, but instead of applying external heat to a food, as with in-pack or heat exchangers, an electric current is applied directly to the food. The electrical resistance of the food to the current causes it to heat up in a way similar to that of a light bulb filament. The advantage is that much shorter heating times can be applied than would otherwise be possible, and so the food will maintain more of its nutritional and flavor characteristics. The limitation is that ohmic cooling, or some other means of effecting rapid cooling, cannot be applied, and so cooling relies on traditional methods that are slow in comparison with ohmic heating. Foods containing large particulates are suited to ohmic heating because the electrical properties of the particulate and carrier liquid can be designed so that the particulate heats preferentially and instantaneously. The only commercial ohmic heater in operation in the U.K. (at the time of writing) is used to pasteurize fruit preparations, in which good particle definition is a key requirement. Prior to its use for fruit preparations, this ohmic heater was used for ready-meal sterilization. Meals were manufactured of a high quality, but they were not a commercial success for various reasons. One such reason was that their flavor was different from that of traditional processes because of the different rates of cooking reactions.

12.4.3 Microwave Processing

Microwave processing, like ohmic heating, destroys microorganisms via thermal effects. Frequencies of 950 and 2450 Hz are used to excite polar molecules, which produces thermal energy and increases temperature. On the continent, a small number of microwave pasteurization units are in operation, primarily manufacturing pasta products in transparent plastic trays. Some ready-meal production uses microwaves to effect the microbial kill step. Benefits of rapid heating can result in improved quality for foods that are sensitive to thermal degradation. The technology has not received widespread adoption because of the high capital costs of the equipment and the wide distribution in temperatures across a package. Heat generated by the microwaves pasteurizes the food and the package together, and the products are sold under chilled storage to achieve extended shelf lives. Microwave sterilization has not developed much because of the need for air overpressure to maintain the shape of the flexible packages during processing. This creates complications with continuous systems in that transfer valves are required between the chambers.

12.4.4 Irradiation

Irradiation has seen much wider applications in the U.S. than in the U.K., where public opinion has effectively sidelined it. In the U.K. there is a requirement to label food that has been irradiated or contains irradiated ingredients. In addition

to killing bacterial pathogens, such as *Salmonella* on poultry, it is especially effective at destroying the microorganisms present on fresh fruit, such as strawberries, and thus markedly extending their shelf life. Its biggest advantage is that it has so little effect on the food itself that it is very difficult to tell if the food has been irradiated. It also has some technical limitations, in that it is not suitable for foods that are high in fat, as it can lead to the generation of off-flavors. This restricts its use for sterilizing ready meals. The only commercial foods that are currently licensed for irradiation in the U.K. are dried herbs and spices, which are notoriously difficult to decontaminate by other techniques, without markedly reducing flavor. A major application for irradiation is in decontaminating packaging.

12.5 CONCLUSIONS

Changing lifestyles has ensured that consumer preference continues to be on the increase for ready meals as convenience foods. It is likely that thermal processing of ready meals will remain one of the key methods for their manufacture. Many thermal processing methods can be used for their production; however, two routes forward are gaining in popularity:

1. In-pack pasteurization in combination with chilled storage. This is being achieved through optimization of existing retort-based equipment and thermal processing regimes, which can be used to produce ready meals of high quality. Recent developments in overpressure retorts and packaging formats have allowed this ready-meal sector to advance at a rapid rate. Retorting has the advantage of pasteurizing both ready meal and packaging together, which can extend the shelf life under chilled storage.
2. Low-care and high-care factories (also known as low risk–high risk). Ready meals of the highest quality are being manufactured using mild or minimal heat processes for the components. The thermal processing steps take place in the low-care parts of a factory and are followed by packaging in high-care environments. Strict control of hygiene in the high-care areas is essential in order that microorganisms are not introduced to the food. Once packaged, there is no further preservation hurdle apart from chilled storage.

Neither of the above methods can be classified as traditional thermal processes. However, there is still a need to ensure that the thermal processing steps are applied correctly, which requires that the same methodology for establishing canning processes is followed. Both are pasteurization processes that require chilled storage. This is because the consumer trends are for higher-quality ready meals that can only be manufactured with mild thermal treatments and the additional preservation hurdle of chilled storage.

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13 Thermal Processing of Vegetables

Jasim Ahmed and U.S. Shivhare

CONTENTS

13.1 INTRODUCTION

Thermal processing is one of the major techniques that aims to produce commercially sterile packaged food of optimal quality. Commercial sterility of food has been considered the condition achieved by application of heat that renders the food free from viable microorganisms, including those of known public health significance, capable of growing in the food at temperatures at which the food is likely to be held during distribution and storage. The production and distribution of heat-treated food with respect to intrinsic and extrinsic factors can be divided into (1) mild heat treatment (pasteurization), and (2) severe heat treatment (sterilization) processes. The success of either process lies in destroying all viable microorganisms together with the nature of the food, environmental factors, hermetic packaging, and storage temperature. The choice of processing depends on the severity of the heat treatment and on the objectives to be accomplished.[1] Due to low acidity (pH > 6.0), vegetable products are subjected to severe heat treatment during processing in order to inactivate pathogenic microorganisms. The process is commonly termed *canning*. Sometimes, the canning process has been altered to treat the vegetables at lower temperatures in combination with other extrinsic factors (pH, preservatives, cooling, and packaging) to reduce microbial growth, and for safe handling during transportation and storage.

The ultimate objective of the production of thermal processed vegetables is to satisfy consumers. The quality of vegetable changes as it proceeds from harvest to consumer. Product quality is represented by the customers' satisfaction. Quality is a human construct additive parameter comprising many properties or characteristics.[2] The quality of thermally processed vegetables encompasses sensory properties (appearance, texture, aroma, and taste), nutritive value, chemical constituents, mechanical properties, functional properties, and defects. There has been an increasing public concern toward the quality of thermally processed vegetables. The major focus on thermal processing of vegetables now is to retain maximum nutritional and sensory quality with optimum process design, along with keeping the microorganisms at safe levels.

Since thermal processing is a heat-intensive process, significant loss of color and flavor of many vegetables results. Presently, extensive research is going on to incorporate nonthermal processing (high-pressure processing, pulse electric heating) into thermal processing to improve sensory quality and consumers' acceptability by reducing process temperature. It is now well established that high-pressure processing has a minimal effect on quality

attributes by retention of the covalent bond, and instant and uniform pressure distribution throughout a food system. Therefore, a combined preservation technology would help processors to produce safe and quality products with affordable prices.

The microbial pathogens and spoilage enzymes that would render the food unfit for consumption are inactivated during heat processing. On the other hand, concentration of heat-sensitive nutrients such as ascorbic acid and thiamine are greatly reduced and texture of thermally processed vegetables is excessively softened on many occasions. For example, canned vegetables may be too soft due to disintegration of cell wall materials. Fortunately, kinetics of microbial destruction and quality deterioration usually do not proceed at the same rate. Studies have shown that thermal death rates of bacteria generally proceed much faster with increased temperature (z values of 10 to 15°C) than simultaneous reactions that would lead to quality loss (z values of 30 to 35°C). It is therefore possible to apply the principles of the high-temperature short-time (HTST), ultra-high-temperature (UHT), and aseptic packaging processes for better quality retention.[3]

In order to balance the benefits of thermal processing without compromising safety, a good predictive model is required. Mathematical modeling is an essential tool to predict the impact of thermal processing on quality and safety of vegetables. The degradation kinetics of quality attributes and target microorganisms during thermal processing are complex. Mathematical models that accurately predict the progress of a chemical or biochemical reaction occurring in a homogenous liquid or semisolid phase during thermal processing and storage are useful in many engineering applications, including process optimization. Experimental studies and application of simplified models to predict and interpret kinetic parameters (reaction order, rate constant, and activation energy) have been utilized by the process industries to improve the process efficiency and quality. In thermal processing, it is possible to achieve different time–temperature combinations (TTCs) with the same lethal effect, but resulting in different quality losses.

The objective of this chapter is to provide an overview on quality changes during thermal processing, and quality assurance of thermally processed vegetables. Food safety principles and practices are integrated into activities identified within quality assurance or quality control programs, or within quality management systems; therefore, these programs and systems can address both food quality and safety simultaneously.[4]

13.2 CONSIDERATIONS IN THERMAL PROCESSING OF VEGETABLES

The primary objective of thermal processing of food is the destruction of microorganisms of public health concern as well as spoilage microorganisms and enzymes. The selection of thermal processing depends on various factors, like type of foods, chemical composition, type of microorganisms present in food, initial microbial

load, reaction kinetics of microbial death, and nutrient loss. Vegetables differ from fruits and other foods in chemical composition and therefore require different processing conditions. The acidity of vegetables is much lower than that of fruits, and they may contain more of the heat-resistant soil organisms than fruits.[5] Furthermore, vegetables require severe heat processing to produce better flavor and texture. Some of the important factors affecting thermal processing of vegetables are types of food, pH, nature of enzymes and microorganisms, thermal resistances of enzymes and microorganisms, mode of heat transfer, etc.

13.2.1 Thermal Processing and Reaction Kinetics

The rate at which a substrate disappears and new product forms is commonly represented by reaction kinetics. The rate can vary with temperature, pressure, moisture, acidity, amount of reactants/ingredients, and environmental conditions. It represents the extent of degradation or inactivation of nutritional and sensory factors or enzymatic and microbial activity in foods during processing. Some reactions result in quality loss, while others produce desired color or flavor, and therefore require optimization during processing.

The rate equation for the n^{th}-order reaction for inactivation or degradation of biological materials is given by

$$dC/dt = -kC^n \tag{13.1}$$

where C is the concentration of reactant at any time t, k is the reaction rate constant, with unit of (concentration)$^{1-n}$/(time), and n is the order of the reaction. The negative sign indicates decrease in concentration with time.

Equation 13.1 can be generalized in the following form for the n^{th} order of reaction:

$$C^{1-n} - C_o^{1-n} = (n-1)kt, \quad n > 1 \tag{13.2}$$

where C_o is the concentration of reactant at zero time.

The reaction rate is mostly described by either zero-, first-, or second-order reaction kinetics as follows:

$$\text{Zero order: } C - C_o = -kt \tag{13.3}$$

$$\text{First order: } \ln(C/C_o) = -kt \tag{13.4}$$

$$\text{Second order: } 1/C - 1/C_o = kt \tag{13.5}$$

where C is the measured concentration of microorganisms, enzymes, or quality attributes at time t, C_o is the initial concentration, and k is the reaction rate constant (1/min). In some cases, fractional reaction orders have been observed.[6] Care should

therefore be exercised to determine the order of reaction, which could be used for determining the effect of thermal processing on heat-labile compounds in food products.

Temperature dependence of the reaction rate constant is described by the Arrhenius equation:

$$\ln k = \ln A - E_a/RT \tag{13.6}$$

where A is a constant known as the preexponential factor (1/sec), E_a is the process activation energy (kJ/mol), T is the temperature of study (K), and R is the universal gas constant (8.314 J/(mol·K)). Activation energy is the minimum energy required to initiate a reaction at the molecular level and is computed from linear regression of ln(k) vs. the reciprocal of absolute temperature (1/T) (Figure 13.1). The magnitudes of A vary from 10^{14} to 10^{20} sec^{-1} for unimolecular and from 10^4 to 10^{11} sec^{-1} for bimolecular reactions, respectively. Reaction kinetic parameters of some selected vegetables are presented in Table 13.1.

13.2.2 Microbial Inactivation Kinetics

Inactivation kinetics of microorganisms is complex and has been well described in microbiology textbooks. Thermal death rate kinetics of test microorganisms must be studied to optimize time–temperature combinations during thermal processing. Earlier evidences support that the inactivation of microorganisms followed the first-order reaction kinetics (Equation 13.4), represented by the following form:

$$\ln(N/N_o) = -k.t \tag{13.7}$$

where N_o and N represent number of viable organisms at times zero and t, respectively.

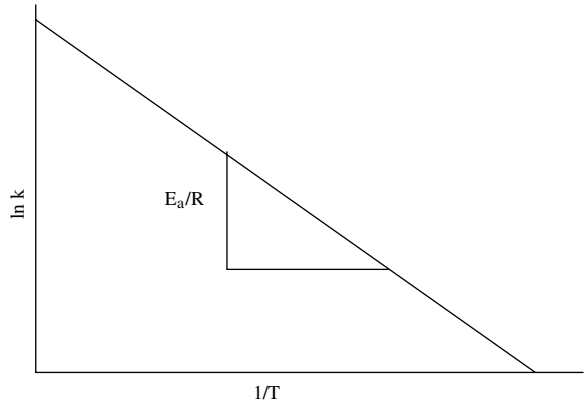

FIGURE 13.1 Temperature dependence of reaction rate constant.

TABLE 13.1
Reaction Kinetics Parameters of Selected Vegetables

Reaction Type	Vegetable	Order of Reaction	Temperature Range (°C)	Activation Energy (kJ/mol)	Reference
Thermal inactivation of peroxidase and lipoxygenase	Broccoli (floret)	Biphasic 1st	70–95	58	7
				43–53	7
	Green asparagus			83–86	7
	Carrot				
Chlorophyll degradation	Broccoli juice	1st	80–120	69.0	8
Green color degradation	Coriander leaves	1st	50–110	22.1–29.3	9
Texture degradation	Potato	1st	90–120	89.70	10
Texture softening	Potato	2nd	122	116–180	11
Overall sensory characteristics	Vegetable puree	1st	110–134	125–167	12
Ascorbic acid degradation	Mushroom	1st order with two degradation mechanisms	110–140	46.36–49.57	13

Applying Equation 13.6 for the thermal inactivation kinetics of microbial spores at reference temperature T_{ref}, and the corresponding reference reaction rate constant k_{ref}, the following equation can be found:

$$\ln k = \ln k_{ref} - [(E_a/R)(1/T - 1/T_{ref})] \tag{13.8}$$

The activation energy (E_a) for bacterial spores has been reported as 500 kJ/mol.[14] The excessive high magnitude of E_a has been explained in various ways by several researchers, and even a modified version of the Arrhenius equation has been proposed[15] to describe nonlinear forms of the inactivation curve. It considers that k is a function of the cell concentration.

13.2.3 Effect of Time–Temperature on Microbial Death

13.2.3.1 Decimal Reduction Time (*D Value*)

Equation 13.7 suggests a linear semilogarithmic plot of N vs. t. Equation 13.7 can be rewritten in common logarithmic form as

$$(\log N/N_o) = -kt/2.303 \tag{13.9a}$$

and

$$\log(N/N_o) = -t/D \tag{13.9b}$$

Equation 13.9 defines the decimal reduction time (D value), the time required to result in one decimal reduction in the survival cell population at a given temperature (Figure 13.2). In Equation 13.9, $D = 2.303/k$, the survival cell ($N < 1$) has been considered to be the probability of spoilage, while $N \geq 1$ implies certain spoilage.

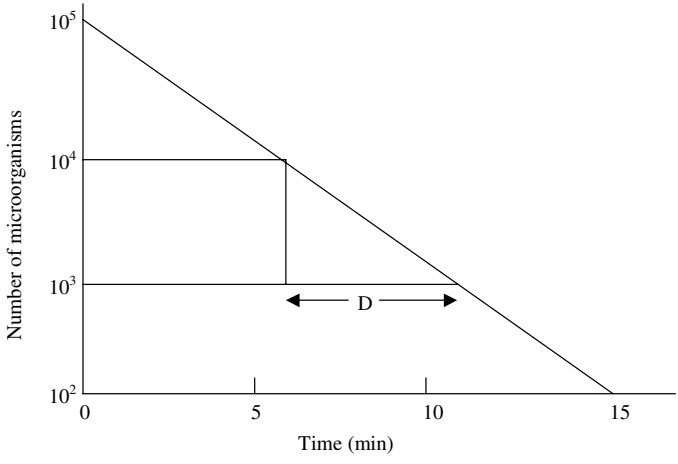

FIGURE 13.2 Graphical representation of decimal reduction time (D value).

13.2.3.2 Temperature Sensitivity and *z* Value

Temperature sensitivity of the D values is represented in terms of z value that indicates the influence of temperature on D values. The thermal resistance constant (z) is defined as the increase in temperature causing 90% reduction in D values (Figure 13.3). Different microorganisms have different z values, and even the z of the same microorganisms may vary with circumstances. Due to this reason, each food product must have its own temperature and time combinations (TTC) that are specific for the formulation, can size, and process parameters. Mathematically, z value is represented as

$$z = (T_2 - T_1)/[\log(D_1) - \log(D_2)] \tag{13.10}$$

where D_1 and D_2 represent decimal reduction times at temperatures T_1 and T_2, respectively.

13.2.4 Degradation Kinetics of Quality Attributes

Quality attributes of food are important for consumers' acceptability. The sensory attributes are perhaps the first criteria for acceptance or rejection. Appearance, color, and texture govern the initial acceptance of foods.[16] Thermal processing has significant effect on sensory attributes. However, information on the kinetic data on sensory evaluation and other properties is limited.

The kinetic parameters for degradation of a food component can be calculated by two procedures.[17] In the steady-state procedure, the thermal lag (heat-up or cool-down) time is considered insignificant compared to the overall processing time, and the reaction is considered to occur at constant temperature. In the

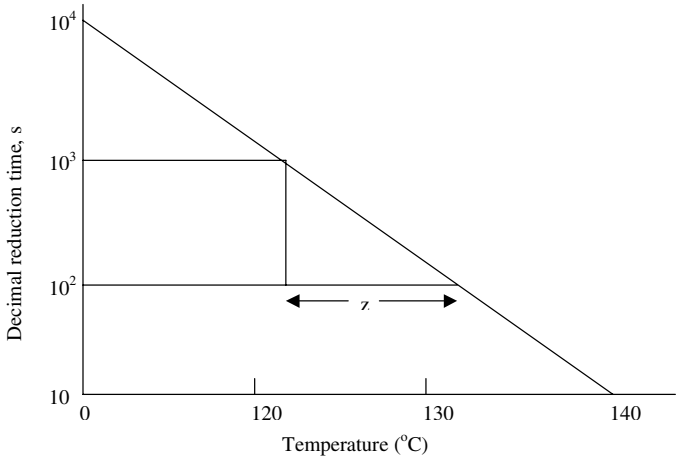

FIGURE 13.3 Graphical representation of thermal resistance constant (z value).

unsteady-state procedure, the reaction is considered to occur at a variable temperature and the data required are the concentration of the degraded component and the temperature profile of the sample during the heating–cooling process. Degradation of the component during the thermal lag is included in data analysis. Steady-state methods are used in most studies to estimate kinetic parameters, due to the difficulty of using temperature profile prediction models because of the natural complexity of foods.

It is evident from the work of many researchers that the kinetics of quality parameters follow the first-order reaction kinetics.[6] Equation 13.4 can be rewritten as

$$\ln(C_1/C_2) = k_c(t_2 - t_1) \tag{13.11}$$

where C_1 and C_2 are the concentrations or physical attributes (color, texture) at times t_1 and t_2, respectively, and k_c represents degradation rate constant for a chemical constituent or physical attribute.

The fractional conversion model has been recently used to describe quality loss during thermal processing. Fractional conversion is a convenient variable often used in place of concentration.[18] For irreversible first-order reaction kinetics, the rate constant at constant temperature can be determined through fractional conversion, f:

$$f = (C_o - C)/(C_o - C_\infty) \tag{13.12}$$

where C_∞ is the concentration at infinite time signifying that the reaction is completed. Considering fractional conversion, the first-order reaction kinetics model takes the form

$$\ln(1 - f)\ \ln[(C - C_\infty)/(C_o - C_\infty)] = -k_c t \tag{13.13}$$

The concept of D-z has been equally valid for heat-labile quality parameters. D_{ref} can generally be considered a D_c value at reference temperature T_{ref} and denotes 90% destruction of heat-labile components, the corresponding z value is designed z_c.[14] The following equation is used to determine D values for thermolabile components.

$$\log(D/D_{ref})_c = -(T - T_{ref})/z_c \tag{13.14}$$

where the subscript c refers to a chemical compound or physical attribute.

Modeling of the real food is difficult due to complexity of the nutrients and their interaction during processing. As a result, a model system under ideal conditions has been considered for mathematical treatment. A complex food exhibits a different rate of degradation and mechanism than an isolated nutrient system.

Working on thermal degradation of vegetables, most of the researchers have considered first-order reaction kinetics for simplicity. However, the degradation kinetics of real food are somewhat different from the first-order reaction kinetics used in the literature. The optimum temperature of a process can be affected if a first-order model, instead of real kinetics occurring in the product, is applied.[19] Therefore, more information is required to obtain consistent and reliable data on modeling of thermal processing.

13.3 APPLICATIONS OF THERMAL PROCESSING

Thermal processing has wide application in vegetable processing. These include blanching, cooking, evaporation, drying, extrusion, pasteurization, sterilization, microwave processing, etc. Due to limited scope and applicability to vegetables, the present discussion is limited to blanching, pasteurization, and sterilization only.

13.3.1 Blanching

Blanching is the treatment of vegetables in hot water or steam to inactivate oxidative enzymes. The process is extremely important if the vegetables are to be further processed by drying, freezing, or canning; otherwise, quality of the product will deteriorate during handling and storage. The thermal effect inactivates enzymes like polyphenol oxidase, catalase, peroxidase, lipoxygenase, and chlorophylase. Apart from enzyme inactivation, blanching helps to destroy microorganisms on the surface, cleans the dirt, and makes some vegetables like broccoli and spinach more compact. The process brightens the color, retards loss of vitamins, wilts vegetables, and facilitates packing.

Among the oxidative enzymes, it has been found that peroxidase (PO) is the most heat resistant and is considered an index of blanching adequacy. Blanching is carried out in many ways, like hot-water blanching, hot-lye blanching, steam blanching, microwave (MW) blanching, high-pressure blanching, and individual quick blanching. Hot-water and steam blanching are simple; however, the leaching of nutrients (vitamins and pigments) is excessive, and the process is energy intensive. It has been reported that microwave blanching reduces the nutrient loss[20]; however, the process may not be effective since some enzymes may not be inactivated. This could result in off-flavors and loss of texture and color. High-pressure blanching of vegetables has been designed on the concept of hot-water or steam blanching, but without the related leaching of nutrients, quality losses, and environmental effects.[21] However, the process could not achieve complete inactivation of polyphenol oxidase (PPO) enzymes. Moist hot gas and ohmic heating have rarely been used for blanching of vegetables.

Efficacy of blanching depends on the nature of the vegetable, geometry of the sample, residence time, water quality, heat transfer conditions, and indicator enzyme activity. The proportions of resistant and labile isoenzymes and kinetic parameters are important factors to predict and optimize blanching operations. Blanching time is crucial and varies with the vegetable and sample geometry.

Quality of water used to blanch vegetables may affect the texture of certain vegetables; for example, hard water could result in toughening of green beans. It is therefore advisable to check the quality of water to be used in blanching.

13.3.2 Pasteurization

Pasteurization is a relatively mild thermal treatment with less impact on product quality. The process has been applied to inactivate the enzymes and pathogenic microorganisms. *Mycobacterium tuberculosis* is the widely accepted target, but recently *Listeria monocytogenes* has been considered the test organism for pasteurization, especially for dairy products. Since the process is not severe enough to kill *C. botulinum*, the pasteurized foods require refrigeration immediately after processing. Thus, pasteurized products have limited shelf life in the distribution chain. The severity and duration of heat treatment depend on the nature of the product, pH, initial microbial load, type of heat processing, the nature of the resistive microorganism, etc. A plate-type heat exchanger (PHE) is commonly employed to pasteurize low-viscosity fluid (<5 Pa·sec). The cold fluid is pumped to the regeneration section of PHE followed by heating at a desired temperature (72 to 75°C), holding for a predefined residence time (15 to 30 sec), and finally cooling to a refrigeration temperature. Viscous products can be pasteurized using a scraped-surface heat exchanger whose inside surface in contact with the product is continuously scraped by molded plastic to prevent fouling. The scope of pasteurization for vegetable products is limited because of their high pH values (Table 13.2).

13.3.3 Sterilization

Theoretically, sterilization refers to the complete inactivation of all the microorganisms present in food. However, foods are generally commercially sterilized in retorts (enclosed vessel for canning) or a continuous-flow system. The primary objective of the process is to destroy *C. botulinum* and its spores, and to produce a safe, shelf-stable food. Success of the process depends upon not only inactivating microorganisms, but also considering other factors associated with the inactivation of spoilage and pathogenic microorganisms. These factors are the nature of foods (pH), environment (vacuum), hermetic package, and storage temperature.

13.3.3.1 Microbiological Considerations

Safety and quality retention are of major concern during thermal processing of vegetables. The process must be designed in such a way that the presence of survival microorganisms should be statistically insignificant, with no health risk to the consumer. There are three types of microorganisms present in foods: *yeast*, *mold*, and *bacteria*. Yeast and mold cannot withstand high temperatures, and therefore do not survive in thermally processed foods. However, bacteria and its spore can withstand high temperatures and are of major concern. *C. botulinum*, a heat-resistant, spore-forming, anaerobic toxin-producing bacteria, is of major

TABLE 13.2
pH Values of Selected Vegetables

Name of Vegetables	pH	Reference
Asparagus	5.4–5.8	5
Broccoli	5.2–6.5	5
Cabbage	5.2–6.3	5
Carrots[a]	4.9–5.5	a
Cauliflower	5.7–6.5	5
Celery	5.5–6.0	5
Coriander leaves[a]	6.0–6.25	9
Eggplant	5.3–5.8	5
Lettuce	6.0–6.4	5
Potato[a]	5.4–5.8	a
Peas	6.0–6.2	a
Rhubarb	3.1–3.4	5
Spinach[a]	5.2–6.2	a
Sweet potato[a]	5.3–5.6	a
Turnip[a]	5.2–5.6	5
Corn[a]	6.1–6.3	a
Capsicum (green)[a]	5.1–6.0	a
Jalapeno pepper	6.0–6.60	5
Wax beans	6.0–6.15	a

[a]Unpublished data of J. Ahmed.

safety concern in thermally processed vegetables. The spores of *C. botulinum* do not produce toxin, while the germinating vegetative cells are capable of producing deadly neurotoxin in low-acid vegetables. Other spoilage organisms are *Clostridium sporogenes, Bacillus stearothermophillus*, and related species.[22]

13.3.3.2 12D Concept

Since *D* values follow logarithmic destruction, mathematically it takes infinite time to destroy all the microorganisms present in the food. A statistical approach has been used to describe a number of survival microorganisms after thermal processing to provide a margin of safety. It has been established that the minimum safe heat process given to low-acid food should decrease the population by 12 logarithmic cycles, the basis of the 12D concept, or "bot cook." The process is found to be adequate even if the initial microbial load is too high. The *D* value for *C. botulinum* is estimated as 0.21 min at 121.1°C, with a z of 10°C. In this case, application of the 12D process (equivalent to 12×0.21 min) resulting in a heating period of 2.52 min at 121°C is known as minimum process lethality (F_o). Many low-acid foods are processed beyond the minimum value, and an F_o value of 5 min is frequently used for vegetables. The 12D process has been considered a minimum safe standard for vegetables.[23]

13.3.3.3 pH

The microbial growth depends on the pH of the medium, and hence it is an important factor in determining the degree of thermal treatment. Foods are divided into two categories based on pH: acidic food (pH < 4.5) and nonacidic food (pH > 4.5). It has been established that *C. botulinum* cannot grow or produce toxin at a pH below 4.6. Most vegetables are nonacidic in nature (Table 13.2), and spores of *C. botulinum* are the primary concern for vegetable processing. Therefore, it is necessary to apply the time–temperature combination sufficient to inactivate spores of *C. botulinum.* The pH can affect the *D* value of microorganisms in different ways. Lowering of pH reduces the heat resistance of the spores and process severity. Furthermore, the pH adjustment of the food could inhibit microbial growth, especially during storage. This is considered an extra safety measure for thermally processed foods.

13.3.3.4 Heat Transfer

Penetration of heat into the cold spot of food is confronted by convective resistance from the heating medium to the outer surface of the container and from the inner surface to the product, as well as the resistance of the packaging material and food product. The internal resistance depends on the thermophysical properties, geometry, and product dimensions.[24] The mechanism of heat transfer through the container wall is by conduction. For metallic containers of normal thickness and thermal conductivity, there is no appreciable resistance to heat transfer. With regard to the heat transfer from the container wall into the product, the mechanism largely depends on the viscosity of the food. Liquid and semiliquid foods are mainly heated by convection, while solid foods are heated by conduction. However, an increase in *viscosity* and the presence of solid particles in semiliquids affect the rate of heat transfer and make the process more complex.

Foods are heterogeneous in nature and vary from liquid to semisolid to solid. This heterogeneity has considerable implications in the characteristics and behavioral properties of thermally processed foods. As such, when semiliquid and solid foods are processed in still retorts, various problems are encountered. In general, still retorting is associated with a slow rate of heat transfer, resulting in considerable loss of quality attributes. Numerous thermal processing techniques have been developed. The improved methods involve carefully engineered processes, such as application of the high-temperature short-time principle in aseptic and agitating processing.

13.3.3.5 Sterilizers

Sterilization of vegetables is generally carried out in both batch and continuous retorts. A batch retort is suitable for a small-scale operation and is available in horizontal and vertical types. The cans are stacked in crates and can be placed on the retorts by hydraulics. Product characteristics govern the choice of retorts.

Many vegetable products have high-viscosity components (vegetable stews, beans in tomato sauce, sauce with hydrocolloids), and therefore require agitation to ensure better heat transfer and sterilization temperature at the center of the can. Container agitation in rotary retorts during processing provides several advantages over still-retort processing. The advantages are improved quality and reduced process time as a result of increased rate of heat penetration.[25] These involve axial or end-over-end agitation, and special retorts or modified retorts are used. For adequate sterilization of vegetables, it is important to control the headspace of the can, solid–liquid ratio, consistency, rotational speed of retort, process time, temperature, pressure, and operating cycles.[14]

For continuous operation, hydrostatic pressure cookers are used. A typical hydrostatic cooker contains a preheat leg, a steam sterilizing chamber, and a cooling leg. These arrangements can be modified with product nature and heat treatment requirement. Saturated steam and a steam–air mixture are used as heating sources for the sterilization of vegetables.

13.3.3.6 Aseptic Processing

The process involves filling commercially sterilized food into a presterilized container, which is hermetically sealed under aseptic conditions. The technique is based on the principle of the HTST process, which is claimed to have several advantages over conventional processing. The advantages include shorter processing time and a better-quality end product. In addition, it reduces energy consumption, suitable for new packaging and designing, and is readily adaptable to automatic control.[26] Development of new container materials, such as polymer plastics and polymer-coated paper containers, have a remarkable influence on the increased interest and attention devoted to aseptic processing and packaging of low-acid foods.

13.4 THERMAL PROCESSING AND QUALITY ATTRIBUTES OF VEGETABLES

13.4.1 Quality and Quality Attributes

Quality is defined as the degree of excellence. Kramer and Twigg[27] defined quality as "the composite of those characteristics that differentiate individual units of a product, and have significance in determining the degree of acceptability by the buyer." *Food quality* embraces both sensory attributes that are readily perceived by the human sense and hidden attributes, such as safety and nutrition, that require sophisticated instrumentation to measure.[28] The quality of vegetables is based on some predefined quality parameters. These parameters have been set for product safety and reproducibility. On the one hand, it governs manufacture of the food according to public health significance, and on the other, it makes a consistent product to acquire a good market share. The processed vegetable loses some quality during processing, while some quality loss occurs during storage. The major quality

attributes of thermally processed vegetables are color, aroma, taste, and texture, while hidden quality attributes like nutritional values and safety (chemical and microbiological) remain the most challenging concern in processed vegetables.

Color plays an important role in appearance, processing, and acceptability of vegetables. When a vegetable is exposed to light, about 4% of the incident light is reflected at the outer surface, causing specular reflectance or gloss, and the remaining 96% of incident energy is transmitted through the surface into the cellular structure of the product, where it is scattered by the small interfaces within the tissue or absorbed by cellular constituents.[29] Recently, imaging technology has been introduced for more precise color measurement of fruits and vegetables, and multi- or hyperspectral cameras permit rapid acquisition of images at many wavelengths.[2] This type of imaging provides information about the spatial distribution of constituents (pigment, sugar, moisture) in vegetables near the surface of the product.

Rheology, the study of the deformation and flow of matter, has been extensively applied to vegetables in an effort to understand the relationship between structure, texture, and changes taking place during processing. The mechanical properties of vegetables have been widely studied following the same technique applied for nonbiological materials. It helps to understand the mechanical behavior of vegetables to some extent; however, vegetables as a biological material differ from nonbiological materials in many respects. Various researchers have defined the term *texture* of vegetables in different ways.[30] Sensory analysis of vegetable texture in combination with mechanical measurement could represent the vegetable texture more precisely.

The application of the principle of hazard analysis and critical control points (HACCPs) has done much to focus and formulize the process of demonstrating the safety of processed vegetables. It is generally agreed that verification processes are necessary to assess the effectiveness of the HACCP plan and to confirm that the food safety system, once implemented, adheres to the HACCP plan. An optimum time–temperature combination (TTC) is an important critical control point (CCP) that has to be controlled in order to guarantee the microbiological safety of processed vegetables. The safety of the sterilization process can be evaluated according to the lethality achieved and the microbiological risk alteration[31] of the target microorganisms that survive the thermal treatment.

13.4.2 Effect of Blanching on Quality of Vegetables

13.4.2.1 Enzymes

Peroxidase (PO) is considered to be the most heat stable enzyme in vegetables and is therefore used as the indicator of blanching efficiency. The Food and Drug Administration (FDA) recommends its inactivation to reduce quality loss during storage of processed foods.[32] Thermal inactivation of PO depends on the nature, thickness, and geometry of the vegetables, and the applied time–temperature combination. Heating times can be significantly reduced if an individual quick blanching process is followed. The first-order reaction kinetics can adequately describe PO inactivation.[33]

The PO inactivation of savoy beet, amaranth, and fenugreek was reduced to a negligible amount in 1 min in hot water (95 ± 3°C),[34] while the same was achieved at 85°C in 30 sec or 95°C for 15 sec for spinach[35] and 99°C for 2 min for fenugreek leaves.[36] Microwave blanching (2 min) of artichokes inactivated PO completely without any losses of ascorbic acid, while boiling water (8 min) and steam blanching (6 min) exhibited 16.7 and 28.9% loss of ascorbic acid with inactivation.[37]

There are evidences that the quality of blanched and processed food is superior if some PO activity is left at the end of the blanching process.[38,39] One of the problems associated with complete inactivation of PO is the presence of 1 to 10% more heat stable isoenzymes of PO in most vegetables. The complete inactivation of PO indicated overblanching of the process.[40]

Though PO has been considered as an indicator for the blanching process, low correlations between residual PO activity and the keeping quality of frozen foods have been reported.[38] Inactivation of residual PO results in overblanching, which can lead to reduced quality in frozen food and thus cause economic losses. Various researchers have advocated for consideration of other enzymes as a blanching indicator instead of PO. Lipoxygenase (LPO) is widely distributed in vegetables and is involved in off-flavor development and color loss.[41] Several authors recommended that analysis of LPO activity, rather than PO, may be a more appropriate index of blanching adequacy.[41,42] Inactivation of LPO requires less heat treatment, resulting in improved color, flavor, and nutritive values.[33] A time–temperature relationship based on an 80% reduction of LPO has been recently reported,[43] and the inactivation followed a first-order kinetic model.

Polyphenol oxidase (PPO) has been used as an indicator in blanching of the potato. Polyphenol oxidase is a generic term for the group of enzymes catalyzing the oxidation of phenolic compounds to produce the brown pigment on the cut surface of fruits and vegetables. Due to PPO, certain phenols, especially mono-, di-, and polyphenols, are hydroxylated in the o-position adjacent to an existing –OH group, further oxidized to o-benzoquinones, and then nonenzymatically polymerized to melanins.[44] The PPO activity is related with color changes due to the formation of colored polymers. Therefore, color measurements could be considered an indirect index of PPO activity, and samples that did not show browning or other analogous colors were reasonably PPO-free.[44]

Thermal resistance of enzymes is greatly affected by pH. *Bacillus licheniformis* -amylase exhibited a higher thermal resistance between pH 6.5 and 9, while below pH 5 or above pH 11 thermal inactivation was significantly faster.[45,46] It was also noted that the stability of this enzyme at different pH values was enhanced by the addition of calcium chloride and that the optimum pH for enzyme stability was found to be 8.5.[47] Thermal stability of LPO from asparagus was found to be independent of pH in the range 4.0 to 7.0.[48] Likewise, thermal resistance of PPO from mushroom did not change significantly with pH from 5.5 to 7.5, although a slight decrease of the z value with pH was observed.[49] For horseradish, a maximum stability at pH 7 (in the range 4 to 10) has been reported. A study carried out on PO from asparagus revealed that the thermostability of the enzyme was affected by changes in pH (from 4.0 to 7.0), but the highest stability was observed at pH 6.[47]

However, a continuous decrease in the stability with an increase of pH was reported,[50] thereby suggesting a maximum stability at mild acidic conditions.

13.4.2.2 Color and Pigment

Generally visual color degradation *of* vegetables is expressed in terms of tristimulus color values (*L*, *a*, and *b*) individually or its combination, chroma, hue, or total color difference value. Color degradation of vegetables depends on blanching temperature, medium, and duration. While working on blanching of artichoke in three types of medium (steam for 6 min, boiling water for 8 min, and microwave (MW) for 2 min), it was found that boiling water and MW-blanched samples retained maximum *L* and *–a* values.[37] Though boiling water and MW blanching exhibited similar results for color values, boiling water treatment retained maximum chlorophyllous pigment.

Loss of color during blanching of green beans and broccoli at 40 to 96°C has been modeled by using *–a/b* color values.[51] Initially the color increased during processing but decreased later on. Color change was modeled by a simplified mechanism of two consecutive reactions: one that sets color and one that degrades color. Formation and degradation of visible color in vegetables is governed by processes related to the coloring compounds (like chlorophyll and chlorophyllides), irrespective of the vegetable under study.[51] The color ratio (*a/b*) has also been used as a quality parameter for vegetables during blanching.[52] This change has been associated with change of green color to yellow due to conversion of chlorophyll to pheophytin and further to pyropheophytin.

Blanching at high temperatures (80 to 100°C) degraded greenness (*–a* value) of vegetables faster than that at low temperatures.[53,54] Both temperature and blanching time had a significant effect on the *–a* value but did not affect *L* and *b*. Chlorophyll a and b decreased after blanching.

The conventional perceived color is associated with *hue* ($\tan^{-1}b/a$) and is represented by yellow for an angle of 90°; objects with a higher *hue angle* are more green; lower hue angles are more orange-red.[55,56] The blanching process reduces the hue angle for vegetables, while MW blanching of artichokes exhibited a maximum hue, compared to steam or water blanching.[37] Chroma [$(a^2 + b^2)^{0.5}$] decreased during blanching; however, there was no significant difference in chroma of boiling water and MW-blanched artichokes.[37] Steam blanching significantly reduced chroma.

Chlorophyll is lost during the blanching process. There was a 40% chlorophyll loss in the savoy beet,[34] while 10 to 15% losses have been reported in fenugreek leaves and amaranth.

13.4.2.3 Texture

Blanching affects the texture of vegetables. For some vegetables, texture softening is desirable, but for others, it is undesirable, e.g., for sweet potato, carrot, and jalapeno. Low-temperature blanching has been found to be effective for some

vegetables[54,57–59] and is being practiced commercially for canned snap beans and canned cauliflower, tomato, potato, and carrot.[60,61] Maximum firming effects of these vegetables could be obtained by blanching at 55 to 80°C for times ranging from several minutes to several hours. For sweet potato, blanching at 62°C for 90 min resulted in maximum firmness,[59] while high-temperature blanching disrupted cell integrity and cell adhesion, and reduced tissue rigidity. Blanching at 55°C for an hour produced maximum firmness of jalapeno.[54]

Several researchers have emphasized the benefits of HTST blanching. Carrot tissues subjected to high temperature for a short time (HTST) (100°C, 0.58 min) retained a firmer texture than those subjected to a low temperature for a long time (LTLT) (70°C, 71.10 min).[43] Galacturonic acid and sugar content of pectin extract during blanching of carrots were determined, and immunocytochemistry experiments elucidated changes in the cell membrane. Blanching decreased galacturonic acid and total sugar contents for all treatments. Carrots subjected to HTST blanching contained higher galacturonic acid and sugars in pectins than carrots blanched by the LTLT process.

Two-stage blanching was found to be effective to maintain firmer texture of green beans. Instead of single blanching at 93°C, preliminary blanching at 70°C followed by high-temperature blanching resulted in firmer texture of green beans. During low-temperature blanching, pectinase enzymes partially demethylate the pectins. This leaves –OH sites free on the pectin chain to cross-link with other pectin molecules via a calcium bridge, resulting in a firmer texture.[62,63] The beans are given high-temperature blanching in a second stage, which inactivates the enzymes.

Several researchers have investigated the changes in pectic substances of processed vegetables.[64–67] Results indicated that cooking-associated texture loss is often related to the dissolution of pectins. Cooking or blanching has also been found to activate enzymes.[68–70] The demethoxylation and depolymerization of pectic substances were catalyzed by *pectin methylesterase* (PME) or pectin polygalacturonase in blanched carrots. At 50 to 80°C, PME hydrolyzed the ester bond to yield free carboxyl groups and to release methoxyl groups. These free carboxyl groups were then cross-linked by salt bridges with calcium ions that were present in the tissue. The cross-linking bridges were often found to result in a firmer texture of fruits and vegetables.[70] The demethoxylation of pectins in blanched vegetables can also be caused by chemical saponification.[70] Chemical saponification or enzymatic deesterification produces a random deesterification of pectic polymers.[70,71]

13.4.2.4 Sensory and Nutritional Quality

Ascorbic acid is one of the most heat labile nutrients and easily oxidizable by the naturally occurring enzyme system, ascorbic acid oxidase. Retention of ascorbic acid decreases with increased temperature and duration of blanching. In the case of the potato, significant differences in respect to ascorbic acid retention were observed during blanching at 80 and 93°C.[72] Boiling water treatment and microwave blanching of frozen beans showed the same reduction of ascorbic acid

content. MW-blanched broccoli retained the greatest amount of ascorbic acid compared to steam blanching.

Leaching losses are prominent during blanching. Blanching in hot water (95 ± 3°C for 1 min) followed by potassium metabisulfite (KMS) treatment reduced leaching loss.[33] The maximum leaching loss was observed in savoy beet where 53% of -carotene and 80% ascorbic acid (dry-weight basis) were lost during blanching.

Blanching of vegetable soybeans at different TTCs (80°C for 30 min, 90°C for 20 min, and 100°C for 10 min) resulted in nutrient losses, including sugar and vitamins B_1, B_2, and C, while the loss was minimum at 100°C for 10 min.[55] Howard et al.[73] studied the effect of steam blanching on nutritional qualities of broccoli, carrot, and green beans. The maximum loss (30%) of ascorbic acid was observed in broccoli, while green beans exhibited the least. The loss in carrot was about 14%. Steam blanching is thought to result in little or no loss in carotene content.[74,75]

13.4.3 Effect of Pasteurization on Quality of Vegetables

Since vegetables are low-acid foods, the scope of pasteurization is limited. Little information is available on the literature on pasteurization of vegetable products. Few reports are available on pureed foods and vegetable juices where the pH is lowered to approximately 4.0 to carry out pasteurization to retain sensory quality.[76,77] However, acidification degraded the color and pigment significantly, while no significant changes were found in the texture or flavor of these products.

13.4.4 Effect of Sterilization on Quality of Vegetables

Commercial sterilization is extensively used to process vegetables, which causes loss of quality during thermal processing.

13.4.4.1 Pigment and Color

The time–temperature combination used in the canning process has a substantial effect on pigments. Chlorophyll, carotenoids, lycopen, and xanthophyll are the predominant pigments present in vegetables. Chlorophyll is responsible for the color of green vegetables. Chlorophyll pigments have been the subject of enormous research because of their prominent function in plant physiology. Both chlorophyll *a* and *b* are the derivatives of dihydroporphyrin chelated with a centrally located magnesium atom, and they occur in an approximate ratio of 3:1.[78] Structurally, the only difference between chlorophyll *a* and *b* is in the C-3 atom, where the former contains a methyl group and the latter contains a formyl group. Both of these pigments differ in perceived color and thermal stability. Furthermore, the chlorophylls contain an isocyclic ring. It is believed that chlorophyll is present in the chloroplasts, forming a complex with protein; however, the binding nature is not clear.[79] The central magnesium atom is easily replaced by hydrogen, thus forming pheophytins under various conditions. The chlorophyll

degradation involves the loss of phytol to form chlorophyllide, loss of Mg^{2+} to form pheophytin, loss of Mg^{2+} and phytol to form pheophorbide, and loss of Mg^{2+} and the carbomethoxy group to form pyropheophytin.[80] The conversion is enhanced by extended heat treatment, acidity, and storage.[81] The most common change that occurs in green vegetables during thermal processing is the conversion of chlorophyll to pheophytins, causing a color change from bright green to olive-brown, which is undesirable for consumer acceptability.[34,82–84]

Various methods to retain green color have been proposed. Controlling pH, followed by HTST processing, showed better retention of the green color of vegetables.[85–88] Color retention was superior in most of these processes immediately after thermal processing, but the retained chlorophyll degraded rapidly during storage. Greater stability of chlorophyll in blanched spinach puree was found when surfactants were added. However, the protective effect of surfactants was lost at or above 100°C, indicating its unsuitability for heat-sterilized food products.

The tristumulus *L* value described the color change of mushroom,[89] while the *a* value represented the pigment content of many vegetables during thermal processing. The total pigment content of sweet potato and squash correlated well with the tristimulus *a* value.[90–92] The color ratio (*a/b*) is measured routinely as the quality index in tomato, orange, and red pepper processing industries.[93]

13.4.4.2 Kinetics of Color Degradation of Vegetables during Thermal Processing

The color degradation kinetics of vegetables is complex, and dependable models to predict experimental color change are limited. Kinetics of pigment and color degradation of vegetables during thermal processing has been studied by numerous researchers.[8,84,93–96] The major finding of these studies is that both pigment and color degradation during thermal processing follow first-order reaction kinetics.

Chlorophyll a degrades faster than chlorophyll *b*.[85] Degradation of chlorophyll a is 2.5 times faster than chlorophyll *b* at 37°C and a water activity of 0.32. Thermal degradation of chlorophylls and chlorophyllides in spinach puree was studied at 100 to 145°C for a retention time of 2 to 25 min and 80 to 115°C for 2.5 to 39 min. Reaction kinetics revealed that both chlorophyll a and chlorophyllide a degraded more rapidly than the corresponding b form.[97]

The tristimulus color ratio (*a/b*) has been used to determine reaction kinetic parameters for the discoloration of some vegetables.[98] The process activation energies for change in visual green color using rate constants were determined at various temperatures. The activation energy values were found to be in the range from 33.14 to 43.38 kJ/mol for asparagus, green beans, and green peas, respectively.

Since the color *a* value represents only major pigment, it therefore does not represent the total color change of vegetables during thermal processing. In practice, any change in the *a* value is associated with a simultaneous change in *L* and *b*. Representation of quality in terms of total color may therefore be

more relevant from the processing viewpoint.[9,99,100] Different combinations of tristimulus L, a, and b values were therefore selected to represent the color change in green vegetable.[96,100] *La/b* was found to be the optimum combination to describe the total color degradation of pea puree,[96] while a combination of $L \times a \times b$ was found to adequately describe color changes of many pureed foods (green chili, red chili, garlic, coriander leaves).[9,76,77,99]

A fractional conversion model is currently practiced by researchers to describe the color loss of vegetables during processing. The technique was exploited by many researchers[8,9,84,99–101] to study the kinetic parameters of the visual green color loss of vegetables. They considered the $-a$ value a physical property that represented loss of visual green color, and therefore Equation 13.13 can be rearranged in the following form:

$$\ln[(-a)-(-a_\infty)]/[(-a_o)-(-a_\infty)] = -kt \tag{13.15}$$

where $-a_o$ is the $-a$ value at zero time, t_o; $-a$ is the $-a$ value at any time, t; and a_∞ is the $-a$ value at infinite time, signifying complete degradation of the chlorophyll to pheophytin. Color degradation of many green vegetables (peas, green peppers, coriander leaves, and spinach) followed first-order kinetics, while color degradation of broccoli juice followed two-step reaction kinetics (first degradation step for pheophytinization of the total chlorophyll, followed by subsequent decomposition of pheophytin in second step).[52]

Degradation of both green and total color of green chili and a mixed green leafy vegetable puree (mustard:spinach:fenugree $k = 1{:}0.75{:}0.25$) was studied using the fractional conversion concept to determine the kinetic parameters.[77,100] Degradation of both green and total color followed the first-order reaction kinetics. The green color was represented by the $-a$ value, while $L \times a \times b$ was found to adequately represent the changes of total color. Dependence of the rate constant during heat treatment obeyed the Arrhenius relationship. The activation energy values for green and total color degradation of green chili were 23.04 and 25.02 kJ/mol, respectively, while the corresponding values for mixed leafy vegetables were 19.71 and 41.64 kJ/mol, respectively.

Table 13.3 reports the major findings of various researchers to relate color of vegetables with tristimulus L, a, and b values during thermal processing.

Color changes of many foods during processing have been transformed into a single variable, which would correlate with visual judgment and color degradation as a quality control parameter. A numerical total color difference (ΔE) technique, commonly applied in the paint and textile industries, has been used to represent the color of food products during processing and storage.[103–105] Total color difference is the square root of the sum of the squares of the differences in each axis and is represented as

$$\Delta E = \sqrt{(L - L_{ref})^2 + (a - a_{ref})^2 + (b - b_{ref})^2} \tag{13.16}$$

TABLE 13.3
Tristimulus *L*, *a*, and *b* Values Used in Thermal Processing of Vegetables

Product	Color Value Used	Major Finding	Reference
Broccoli juice	*a*	Color degradation was best represented using $-a$ value; fraction conversion technique was used	8
Coriander leaf puree	*L*, *a*, *b*	Combination of ($L \times a \times b$) was found to represent color degradation	9
Jalpeno pepper	*L*, *a*, *b*	Color parameter $-a$ well correlated with process temperature to optimize blanching process of jalapeño pepper	54
Garlic	*L*, *a*, *b*	Combination of ($L \times a \times b$) represented well the change of color during thermal processing	76
Pea puree	*a*	Green color degradation was best correlated by $-a$ value; fractional conversion technique was used	84
Mushroom	*L*	*L* value adequately represented thermal color degradation	89
Sweet potato	*a*, *b*	*a* was correlated well with pigment concentration	90, 92
Green peas	*a*, *b*	$-a/b$ was correlated with degree of conversion of chlorophyll	93
Pea puree	*L*, *a*, *b*	Combination $-(La/b)$ described well the color degradation of pea puree during thermal processing	96
Asparagus and green beans	*a*, *b*	*a/b* was considered to represent color degradation	98
Red chili (pepper)	*L*, *a*, *b*	Fraction conversion model of color combination ($L \times a \times b$) adequately described color degradation of red chili	99
Green peas	*a*	Color degradation was described in terms of $-a$ value; fractional conversion model was applied to represent color of green peas	101
Tomato	*L*, *a*, *b*	Color combination ($L \times b/a$) exhibited high correlation with visual score of processed tomato products	102

The effect of thermal processing on color values has also been assessed by ΔE. Some researchers[105] advocated that ΔE values of 1 or less be regarded as satisfactory for the best product, while a value greater than 3 was considered unsatisfactory. The ΔE has successfully been applied to the kinetic study of red chili puree during thermal processing, along with the fractional conversion technique.[99] However, failure of ΔE to represent the color of pea and carrot puree was reported by Little[106] to be primarily due to large chromaticity differences.

13.4.4.3 Texture and Rheology

Textural changes occur in food during thermal processing. Softening of the tissues due to physical and chemical changes may render the food unacceptable to the consumers.[107] Thermal processing should therefore ensure a desirable texture in the product.[3]

Kinetics of texture degradation optimizes the process to yield the best-quality product with minimal textural degradation. Recently, numerous studies have been reported in the literature on thermal softening and texture degradation kinetics of vegetables. Texture degradation kinetics is complex, and different approaches have been proposed to analyze experimental data of texture degradation during thermal processing of vegetables. The literature suggests that thermal degradation kinetics of vegetables is well described by first-order reaction kinetics. Kinetic data are available on a variety of vegetables.[107–109]

An alternative approach of the dual-mechanism first-order kinetics model has been reported while vegetables are being processed for longer periods. In this concept, it is assumed that two substrates (say S_1 and S_2) participate in the textural degradation reaction consecutively, resulting in two different kinetic parameters. Huang and Bourne[108] reported that the rate of thermal softening followed a biphasic behavior in which it was assumed that there was a labile component and a resistant component, and the labile component was degraded during the first heating stage. Biphasic models have been successfully applied to other vegetables, like asparagus, peas, knoll-khol, and carrots.[20,109] However, the mechanism for texture changes at high temperatures may differ from the mechanism at low temperatures.[107] Thermal softening of white beans heated between 90 and 122°C exhibited a biphasic behavior, but at temperatures of 110°C the first phase of thermal softening was not seen.[110] It was pointed out that a main defect in many studies of softening has been the lack of thermal lag correction.[107] An iterative thermal lag correction procedure was proposed in which the temperature history for the center of a cylindrical container could be used to estimate the transient temperature distribution.[98]

Two-step mechanisms of texture degradation have some limitations, especially in the second step, where the degradation reached equilibrium in the softening stage and the calculated activation energy became negative. To overcome those limitations, the fractional conversion technique has been employed to describe thermal softening of vegetables,[10,111] and it was inferred that the first-order reaction kinetics was appropriate to describe texture degradation during

thermal processing. Fractional conversion takes into account the nonzero texture property during prolonged heating, and therefore Equation 13.13 can be rearranged for texture degradation into the following forms:

$$\ln[(TP - TP_\infty)/(TP_o - TP_\infty)] = -kt \tag{13.17}$$

$$TP = TP_\infty + (TP_o - TP_\infty)\exp(-kt) \tag{13.18}$$

where TP_o is the texture property at zero time; equilibrium texture property (TP_∞) is determined using the average of all measurements when the heating time is greater than 2 d to a constant TP. However, it is extremely difficult to obtain TP for all the experiment runs, as the fluctuation from sample to sample is significant. One of the biggest advantages of applying the fractional conversion technique in data reduction is that there is no longer a need to standardize the experimental protocol.[111]

The geometry (size, shape, and thickness) of the sample does not significantly affect the kinetic parameters of vegetable texture.[112,113] Using the potato as a model food, various researchers[114,115] studied the texture parameters using different instruments and concluded that kinetics of texture degradation were independent of testing parameters. However, contradictory reports are available in the literature while testing parameters were applied to measure food texture using various techniques. The process activation energies during thermal softening of potato[112,116,117] and texture degradation of carrots varied significantly.[108,113] The variation was explained on the basis of sample size.

The correct kinetic models of thermal degradation of vegetables' texture depend on the setup of the experimental procedures — whether it is steady state (isothermal heating) or unsteady state (nonisothermal heating). The kinetic parameters obtained by these processes are significantly different. Most of the studies were carried out at steady-state conditions to avoid complexity of modeling. An unsteady-state method was employed for estimating texture degradation during heating–cooling of green asparagus spears.[118] The method used a mathematical model of heat transmission for time–temperature history estimation, and a nonlinear regression of texture measurements of asparagus spears to estimate the kinetic parameters. The mathematical model and the kinetic parameters estimated could be used to design and evaluate thermal processes for green asparagus and other similar products, like cucumber or corn on the cob.

Texture softening is caused by the hydrolysis of pectic substances, gelatinization of starches, and partial solublization of hemicelluloses combined with loss of cell turgor of vegetables. Heat processing will also result in changes of the cell walls, particularly the middle lamella, and gelatinization of starch. The final texture will therefore depend on the relative importance of each factor contributing to texture and the degree to which that factor has been changed by the processing method used.

Reports on low-temperature blanching (LTB) are available in the literature.[59–61] LTB followed by canning of vegetables resulted in higher fracturability

and hardness of texture. The LTB also caused increase in gumminess and springness of canned sweet potato.[59]

Many vegetables are washed, blanched, comminuted, and converted to puree or paste. The puree/paste is considered a minimally processed food, as the product is sometimes acidified (approximate pH = 4.0) and pasteurized. These products retain color and flavor comparable to the fresh produce and are convenient to use. The rheological characteristics of these products change during thermal processing. Rheological parameters are significantly affected by process temperature. Pureed food behaves as a non-Newtonian fluid with yield stress and is pseudoplastic in nature.[119] The consistency index decreased with temperature, while the flow behavior index increased. Rheological parameters obtained from a controlled rate rheometer of some strained vegetable pureed foods during thermal processing are presented in Table 13.4. Among various rheological models, the Hershel–Bulkley model (Equation 13.19) adequately describes shear stress–shear rate data of vegetable purees. The presence of yield stress ($_o$) of pureed food indicates application of minimum force to initiate the flow of the product. Temperature has a significant effect on $_o$, and the yield stress decreased with temperature:[119]

$$\tau = \tau_o + K(\dot{\gamma})^n \tag{13.19}$$

TABLE 13.4
Rheological Characteristics of Strained Vegetable Puree

Vegetable Type	Temperature Range (°C)	Yield Stress (Pa)	Consistency Index (Pa·sec^n)	Flow Behavior Index (–)	Apparent Viscosity at 100 sec^{-1} (Pa·sec)
Carrot puree (7.4°Brix and pH 4.88)	20–80	1.65–3.72	5.44–11.53	0.27–0.35	0.24–0.42
Pea puree (7°Brix and pH 5.92)	20–80	1.25–1.83	1.12–1.35	0.36–0.44	0.11–0.14
Corn puree (14°Brix and pH 6.46)	20–80	0.43–1.18	0.58–2.06	0.26–0.30	0.02–0.05
Sweet potato puree (11.2° and pH 5.27)	20–80	1.46–2.66	0.77–1.20	0.38–0.43	0.06–0.09
Wax bean puree (5.1°Brix and pH 5.05)	20–80	5.10–5.23	0.22–1.86	0.48–1.0	0.23–0.26

Source: Unpublished work of J. Ahmed and H.S. Ramaswamy.

where τ and τ_o are shear stress and yield stress, respectively (Pa), $\dot{\gamma}$ is the shear rate (sec^{-1}), K is the consistency index ($Pa \cdot sec^n$), and n is the flow behavior index (dimensionless).

13.4.4.4 Sensory and Nutritional Quality

Nutrient losses during the canning processing are significant.[120] Differences among cultivars of vegetables have been noted for most nutrients. Vitamin losses occur during commercial sterilization of vegetables. Vitamin A is comparatively stable, as it is heat stable and insoluble in water and survives during the canning process. However, 30% losses during thermal processing have been reported.[73] Thiamin is heat labile and lost during the sterilization process. The losses could be reduced by the HTST process. Ascorbic acid is most susceptible to losses during processing due to its solubility in water and highly oxidized nature. Canning resulted in a significant loss of ascorbic acid.[73] Information on degradation of nutrients during thermal processing is available in the literature.[121] There are about 85% losses of the heat-sensitive nutrients during thermal processing. In processed foods, most significant losses occur as a result of chemical degradation. Several researchers have studied the mechanism of ascorbic acid loss and reported that it obeys the first-order reaction kinetics.[122,123]

13.4.4.5 Quality Optimization

Quality optimization during thermal processing involves optimum balance between inactivation of spoilage microorganisms and retention of quality parameters. The rate of heat transfer inside a can depends upon the consistency, nature of vegetables, and can size. For convection heating of vegetables, the internal mixing produces uniform cooking. However, for conduction heating, cooking starts from the outside surface to the inside of the can. This produces overcooking of the surfaces, resulting in brown color and loss of overall acceptability. A slow heat transfer rate to the coldest region limits the applicability of the HTST process. For theses situations, however, it is possible to ascertain an optimum condition of TTC, leading to microbiologically safe food and minimized quality losses.[124] Quality optimization of thermally processed food has been well described by Holdsworth.[14]

13.4.4.6 Food Safety

Food safety principles and practices have been applied to foods, starting with farm produce, processed food products, ingredients, processing aids, contact surfaces, and packaging materials that are used in manufacturing the foods. Government agencies all over the world have enacted laws and regulations designed to ensure that processed foods are safe for the consumers and keep strict vigil on food safety rules. The safety of foods in international trade is governed by the World Trade Organization (WTO)/Sanitary and Phytosanitary (SPS)

Agreement, which recognizes that governments have the right to reject imported foods when the health of the population is endangered. The criteria used to determine whether a food should be considered safe should be clearly conveyed to the exporting country and should be scientifically justifiable.[125]

Application of HACCP to the thermal processing industries makes it convenient to identify the critical control points (CCPs) in the process line. Each step has to pass through CCPs and is well monitored. It provides ample opportunity to reduce chances of food hazards or contamination, which could be physical, chemical, or microbiological in nature. For example, the reaching of temperature at the coldest point of canned food is the most important CCP, as it provides the vital information of survival of the most heat resistant spores.

Each CCP reduces end-of-line sampling. This is not always possible for microbiological techniques, which take time to deliver the results. The monitoring system has always been recorded and takes corrective action. Verification of the CCPs would further reduce chances of contamination or mechanical fault during processing and ensure product safety more precisely.

The worldwide acceptance of the Codex Alimentarius model has resulted in a consistent format (12 steps) for developing and implementing HACCP plans in food establishments around the world and has contributed to the recognition of HACCP systems to address food safety issues in bilateral and international trade.[4]

During the last few years, many thermal processing industries have implemented a number of quality assurance (QA) systems, including good manufacturing practices (GMP), HACCP, International Organization of Standardization (ISO), and a total quality management (TQM) program, in order to introduce new quality systems and to produce high-quality products. However, mixed responses are available from the industries. Introduction of QA and TQM does not produce the desired performance in quality. These implementation failures and the context of the organization require continuous adjustments of quality management activities, which should be based on assessment of quality performance.[126]

13.5 CONCLUSIONS

The vegetable processing industry has undergone significant changes during the last few years in response to changing consumer demand for safe and quality products. However, canning is a traditional technology that remains the means of choice for bringing processed vegetables to the marketplace, and the trend will continue because of the consumers' demand for high-quality safe food, which can only be manufactured by minimal thermal processes. The use of more advanced mathematical models to evaluate and predict thermal processing operation and quality retention will provide benefits to producers and customers. Thermal processing in combination with nonthermal processing technologies would produce food with better-quality retention and consumer satisfaction. Introduction of TQM would ensure more product safety and smooth operation in the food processing industry.

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NOMENCLATURE

a	Tristimulus color value at time t measures redness and greenness
a_o	Tristimulus color value at time zero measures redness and greenness
a_∞	Tristimulus color value at infinite time measures redness and greenness
a_{ref}	Tristimulus color value measures of redness and greenness considered as reference
A	Preexponential factor (1/sec)
b	Tristimulus color value at time t measures yellowness and blueness
b_o	Tristimulus color value at time zero measures yellowness and blueness
b_∞	Tristimulus color value at infinite time measures yellowness and blueness
b_{ref}	Tristimulus color value measures of yellowness and blueness considered as reference
C	Concentration of reactant/microorganisms, enzymes, or quality attributes at time t
C_o	Concentration of reactant/microorganisms, enzymes, or quality attributes at time zero
C_∞	Concentration of reactant/microorganisms, enzymes, or quality attributes at infinite time
C_1	Concentration or physical attributes (color, texture) at times t_1
C_2	Concentration or physical attributes (color, texture) at times t_2
CCP	Critical control point
D	Decimal reduction time (min)
D_1	Decimal reduction time at temperatures T_1 (min)
D_2	Decimal reduction time at temperatures T_2 (min)
D_{ref}	Decimal reduction time at reference temperature (min)
E_a	Process activation energy, kJ/mol
ΔE	Total color difference value
f	Fractional conversion
F_o	Process lethality (min)
FDA	Food and Drug Administration
GMP	Good manufacturing practices
HACCP	Hazard analysis and critical control points

HTST	High temperature for shorttime
ISO	International Organization of Standardization
k	Reaction rate constant, (concentration)$^{1-n}$/(time)
k_c	Degradation rate constant for a chemical constituent or physical attribute
k_{ref}	Reaction rate constant at reference temperature (concentration)$^{1-n}$/(time)
K	Consistency index (Pa·sec^n)
L	Tristimulus color value at time t measures lightness
L_o	Tristimulus color value at time zero measures lightness
L	Tristimulus color value at infinite time measures lightness
L_{ref}	Tristimulus color value measures of lightness considered as reference
LPO	Lipoxygenase
LTLT	Low temperature for long time
MW	Microwave
n	Flow behavior index
N	Number of viable microorganisms at time t
N_o	Number of viable microorganisms at time zero
PHE	Plate heat exchanger
PO	Peroxidase
PPO	Polyphenol oxidase
QA	Quality assurance
R	Universal gas constant (8.314 J/(mol·K))
t	Time (sec)
T	Temperature of study (K)
T_1, T_2	Temperature (K)
T_{ref}	Reference temperature (K)
TP_o	Texture property at zero time
TP	Texture property at infinite time
TP	Texture property at zero time
TQM	Total quality management
TTC	Time–temperature combinations
UHT	Ultraheat treatment
z	Thermal resistance constant (°C)
z_c	Thermal resistance at reference temperature (°C)

Greek

τ	Shear stress (Pa)
τ_o	Yield stress (Pa)
$\dot{\gamma}$	Shear rate (sec^{-1})

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Part III

Innovations In Thermal Food Processes

14 Ohmic Heating for Food Processing

António Augusto Vicente, Inês de Castro, and José António Teixeira

CONTENTS

14.1 INTRODUCTION

Ohmic heating (OH) (also called Joule heating, electrical resistance heating, direct electrical resistance heating, electroheating, or electroconductive heating) is defined as a process where electric currents are passed through foods to heat them (Figure 14.1). Heat is internally generated due to electrical resistance.[1] OH is distinguished from other electrical heating methods by (1) the presence of electrodes contacting the foods (if microwave and inductive heating electrodes are absent), (2) the frequency applied (unrestricted, except for the specially assigned radio or microwave frequency range), and (3) waveform (also unrestricted, although typically sinusoidal).

The OH concept is well known, and various attempts have been made to use it in food processing. A successful application of electricity in food processing was developed in the 19th century to pasteurize milk.[2] This pasteurization method was called the electropure process, and by 1938, it was used in approximately 50 milk pasteurizers in five U.S. states and served about 50,000 consumers.[3] This application was abandoned apparently due to high processing costs.[1] Also, other applications were abandoned because of the short supply of inert materials needed for the electrodes, although electroconductive thawing was an exception.[4]

However, research on ohmic applications in fruits, vegetables, meat products, and surimi has been undertaken by several authors more recently.[5–8]

Aseptic processing is considerably developed in the food industry, especially for liquid foods, which are processed predominantly by heat exchangers. Food technologists and the food industry are interested in extending this technology to more complex foods, such as highly viscous, low-acid, and particulate-containing foods. In fact, most of the technologies actually used rely on conductive, convective, and radiative heat transfer. Their application to particulate foods is limited by the time required to ensure the sterilization of the center of larger particles, often causing overcooking of the surrounding volume. Consequently, product safety is achieved at the expense of quality.

In order to maximize food quality, high-temperature short-time (HTST) processes have been used. This process is based on reactions that reduce the level

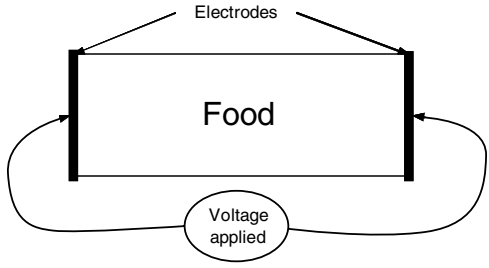

FIGURE 14.1 The principle of ohmic heating.

of bacterial spores with lower activation energy than the ones responsible for the loss of quality (e.g., reduction in vitamins and color degradation).

OH technology has gained interest recently because the products are of a superior quality to those processed by conventional technologies.[8–10] Moreover, the ohmic heater assembly can be incorporated into a complete product sterilization or cooking process. Among the advantages claimed for this technology are uniformity of heating and improvements in quality, with minimal structural, nutritional, or organoleptic changes.[11] The potential applications are very wide and include blanching, evaporation, dehydration, fermentation,[12] pasteurization, and sterilization.

OH is currently used in Europe, Asia, and North America to produce a variety of high-quality, low- and high-acid products containing particulates. A large number of additional applications are being developed for this technology, as shall be seen further in this chapter.

A consortium of 25 partners from industry (food processors, equipment manufacturers, and ingredient suppliers), academia (food science, engineering, microbiology, and economics), and government was formed in 1992 in the U.S. in order to overcome the challenges still remaining about regulatory evaluation and formula optimization. A 5-kW pilot-scale continuous-flow ohmic system (APV Baker Ltd., Crawley, U.K.) was evaluated and a wide variety of shelf-stable (low- and high-acid) products were developed. These included broccoli and cheese (broccoli florets in cheddar cheese sauce), shrimp gumbo (shrimp, okra, and tomatoes in a savory sauce), strawberries in glaze, oriental chicken (chicken, water chestnuts, corn, peapods, bamboo shoots, mushrooms, carrots, and red peppers in Savoy sauce), and pasta primavera (shrimp, surimi, carrots, green beans, and mushrooms in alfredo sauce). These products were found to have equal or higher texture, color, and nutrient retention than those processed by traditional methods, such as freezing, retorting, and aseptic processing. The consortium concluded that the technology was technically and economically viable.[9]

The OH system allows for the production of new, high-added-value, shelf-stable products with a quality previously unattainable with alternative sterilization techniques, especially for particulate foods. Its major advantages are:[9]

- Continuous production without heat transfer surfaces
- Rapid and uniform treatment of liquid and solid phases with minimal heat damages and nutrient losses (e.g., unlike microwave heating, which has a finite penetration depth into solid materials)
- Ideal process for shear-sensitive products because of low flow velocity
- Optimization of capital investment and product safety as a result of high solids loading
- Reduced fouling when compared to conventional heating
- Better and simpler process control with reduced maintenance costs
- Environmentally friendly system

Some of the disadvantages accounting for OH are the higher initial operational costs and the lack of information or validation procedures for this technology.

The following sections will introduce several aspects of the OH technology, with emphasis on modeling and the application to industrial processes.

14.2 MODELING OHMIC HEATING

The main objective of OH is to increase the temperature of food materials to a point at which the food is considered adequately processed. Also, the so-called cold spot must be identified. The most effective manner requires the exact measurement of the temperature profile in the food material when heating is applied. Models describing the effect of the main operating parameters on temperature of food materials (and especially of the system's cold spot) are required.

The models are mathematical representations of physical and chemical phenomena such as the laws of conservation of mass, energy, and momentum. They can be applied to generate the results of virtual experiments. This saves time and money and can be the only way to obtain the relevant data. The more complex a model, in terms of structure and the equations used, the more accurate the results. Other equations may be required to express particular observations or conditions, or simply to establish boundary conditions. It is not possible to consider all the phenomena involved in the process to be modeled. Instead, assumptions are usually made to simplify the set of equations needed to solve the problems without oversimplifications. Another important issue is the parameters of the model. These must be evaluated as accurately as possible to avoid jeopardizing all the modeling efforts. In fact, even if a model is correctly built, the solutions obtained from it can be very far from reality if the parameters involved are not properly determined.

In order to model the OH process (Section 14.2.4), all of the above — equations, parameters, and assumptions — have to be taken into account, which will be discussed in the following sections.

14.2.1 Basic Equations

14.2.1.1 Electric Field

In order to generate heat in an OH system, an electric field must be applied to the food. The electric field (voltage distribution) is a function of the electrode and system geometry, electrical conductivity, and the applied voltage.[1] The electric field is determined by the solution of Laplace's equation:

$$\nabla(\sigma \cdot \nabla V) = 0 \tag{14.1}$$

where σ is the electrical conductivity, and ∇V is the voltage gradient. This equation has been obtained combining Ohm's law with the continuity equation for electric current,[13] and differs from the usual form of Laplace's equation:

$$\nabla^2 V = 0 \tag{14.2}$$

because σ is a function of both position and temperature.

In order to solve Equation 14.1, boundary conditions specific for each case must be established. The solution has been obtained by de Alwis and Fryer[1] for a static ohmic heater containing a single particle, using as boundary conditions: (1) a uniform voltage on the electrodes, or (2) no current flux across the boundary elsewhere. For a more general case of many different particles flowing in a fluid composed of several liquid phases (e.g., vegetable soup, where different vegetable solid pieces are dipped in a fluid broth with at least an aqueous and a lipid phase), the mathematical solution for Equation 14.1 is, to our knowledge, still unknown. In these cases, the prediction of the electric field has been based on semiempirical models (see, for example, Sastry and Palaniappan[14] or Sastry[15]).

The determination of the electric field is one of the most challenging subjects of the modeling effort in OH technology.

14.2.1.2 Heat Generation

In order to ohmically heat a food, it is necessary to pass electrical current through it. The heat generated in the food by that current ($\dot{Q}$) is proportional to the square of its intensity (I), the proportionality constant being the electrical resistance (R), thus yielding

$$\dot{Q} = R \cdot I^2 \tag{14.3}$$

Alternatively, if both electrical conductivity (σ) and voltage gradient (∇V) are known, it is possible to write

$$\dot{Q} = |\nabla V|^2 \cdot \sigma \tag{14.4}$$

where σ is a function of position and temperature. The dependence of position is because foods are not necessarily homogeneous materials, the limiting scenarios being foods containing particles (e.g., vegetables soup) and that of a reasonably homogeneous liquid (e.g., orange juice). The relation of σ with temperature is usually well described by a straight line of the type[5]

$$\sigma_T = \sigma_{ref} \cdot [1 + m \cdot (T - T_{ref})] \tag{14.5}$$

where σ_T is the electrical conductivity at temperature T, σ_{ref} is the electrical conductivity at a reference temperature, T_{ref}, and m is the temperature coefficient.

14.2.1.3 Energy Balance

The next step for the model is to determine the temperature distribution of the fluid and the solid phases (if present). This is done by establishing an energy balance for the fluid phase and solid phase.[16] Both equations for the fluid and solid phases are established based on the knowledge of the predominant energy (mainly heat) transfer phenomena occurring during OH. These are schematically outlined in Figure 14.2, together with the relevant mass and momentum transfer phenomena, along z and r, which are the axial and radial coordinates, respectively.

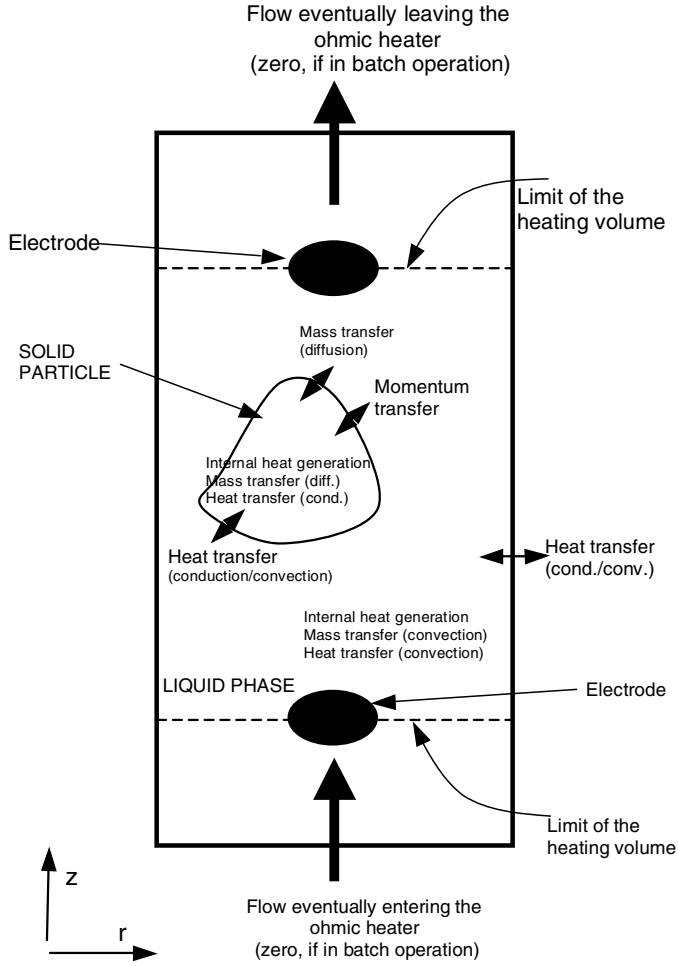

FIGURE 14.2 Main heat, mass, and momentum transfer phenomena occurring during OH. The presence (continuous) or absence (batch) of a mass flow through the heater will alter the hydrodynamic conditions, and thus the relative importance of the phenomena.

According to Figure 14.2, for a continuous process (the more general case) and for the fluid phase (the system considered here is a tubular heater — which is the most common geometry — where the electrodes are placed along the heater, thus creating a longitudinal voltage field; in any case, the application of the following equation to the case of a radial voltage field — i.e., where the electrodes are placed on the walls of the tube — should be straightforward), the energy balance is

$$\rho_f \cdot C_{pf} \cdot \overline{v}_z \cdot \varepsilon_f \cdot \frac{\partial T_f}{\partial z} = \beta(\varepsilon_f) \cdot \nabla(k_f \cdot \nabla T_f) - \frac{n_p \cdot A_p \cdot h_{fp}}{V_{sys}} \cdot (T_f - T_{ps}) + \frac{\dot{Q}_f}{V_{sys}} \tag{14.6}$$

where ρ_f is the fluid density, C_{pf} is the fluid specific heat, $\overline{v}_z$ is the mean fluid velocity profile in the axial direction, ε_f is the fluid volume fraction in the heater, T_f is the fluid temperature, k_f is the fluid thermal conductivity, n_p is the number of solid particles in the considered volume, A_p is the area of each solid particle, h_{fp} is the fluid–particle heat transfer coefficient, V_{sys} is the volume of the system between the electrodes, and T_{ps} is the temperature at the surface of the solid particle, being also

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2} \tag{14.7}$$

where r and z are the radial and axial coordinates, respectively, and $\dot{Q}_f$ is the heat generated in the fluid, given by the combination of Equations 14.4 and 14.5, yielding

$$\dot{Q}_f = |\nabla V|^2 \cdot \sigma_{0f} \cdot (1 + m_f \cdot T_f) \tag{14.8}$$

where σ_{0f} is the electrical conductivity of the fluid before the heating takes place (initial value of σ_f), and m_f is the temperature coefficient of the fluid. Still, in Equation 14.6, $\beta(\varepsilon_f)$ represents the fraction of heat transfer by conduction through the mixture in the fluid phase. The exact form of $\beta(\varepsilon_f)$ is unknown, but based on the Kopelman model,[17] its expression can be given by

$$\beta(\varepsilon_f) = 1 - (1 - \varepsilon_f)^{2/3} \tag{14.9}$$

In any case, Orangi et al.[16] noted that the influence of this term on the result is marginal, as the conduction term is very small relative to other terms in Equation 14.6. Also in this equation, the axial conduction term $(\partial^2/\partial z^2)$ is normally considered small when compared with the radial conduction term (this situation corresponds to a large Peclet number) and can be neglected.

For Equation 14.6, if no solids are present, then n_p equals zero, thus cancelling the term $n_p \cdot A_p \cdot h_{fp} \cdot (T_f - T_{ps})$.

Also for Equation 14.6, the value of $\overline{v}_z$ (the mean fluid velocity profile in the axial direction) can be obtained assuming plug flow (an assumption generally valid for high solids concentration) or considering the more general case of a flow with a velocity gradient (assuming a power law fluid behavior), which can be given by[16]

$$v_z = \left(\frac{3n+1}{n+1}\right) \cdot \overline{v}_z \cdot \left[1 - \left(\frac{r}{R}\right)^{n+1/n}\right] \tag{14.10}$$

where n is the flow behavior index. In this case, v_z will replace $\overline{v}_z$ in Equation 14.6.

In order to obtain the solution of Equation 14.6, initial and boundary conditions must now be established. For the initial condition, the following applies:

$$T_f = T_0 \quad \text{at} \quad z = 0 \tag{14.11}$$

For the boundary condition at $r = R$ (R being the radius of the heater tube), it is necessary to consider the balance between conductive and convective heat transfer on the outer surface of the tube:

$$-k_f \cdot \nabla T_f \cdot \vec{n}\big|_w = U \cdot (T_f - T_{air})\big|_w \tag{14.12}$$

where $\vec{n}$ is the unit vector normal to the surface of the tube's wall (w), U the overall heat transfer coefficient, and T_{air} the temperature of the air surrounding the walls of the heater. This balance must then be applied to Equation 14.6 to obtain the boundary condition at $r = R$.

Another boundary condition must be established on the axis ($r = 0$), which can be obtained by applying Equation 14.6 when $r \rightarrow 0$.

The energy balance for the solid phase is (assuming spherical particles, Figure 14.2)

$$\rho_p \cdot C_{pp} \cdot \frac{\partial T_p}{\partial t} = \nabla(k_p \cdot \nabla T_p) + \frac{\dot{Q}_p}{V_p} \tag{14.13}$$

where ρ_p is the particle density, C_{pp} is the particle specific heat, T_p is the particle temperature, t is the time, k_p is the particle thermal conductivity, V_p is the volume of the particle, T_{ps} is the temperature at the surface of the solid particle, and $\dot{Q}_p$ is the heat generated in the particle, given by the combination of Equations 14.4 and 14.5, yielding

$$\dot{Q}_p = |\nabla V|^2 \cdot \sigma_{0p} \cdot (1 + m_p \cdot T_p) \tag{14.14}$$

where σ_{0p} is the *electrical conductivity* of the particle before the heating takes place (initial value of σ_p), and m_p is the temperature coefficient of the particle.

Similarly to what has been made with Equation 14.6, initial and boundary conditions must now be established for Equation 14.13. For the initial condition, the following holds:

$$T_p = T_{0p} \quad \text{at} \quad t = 0 \tag{14.15}$$

where T_{0p} is the initial temperature of the particle.

The boundary condition is established at the surface (s) of the particle, where it is again necessary to consider the balance between conductive and convective heat transfer, given by

$$-k_p \cdot \nabla T_p \cdot \vec{n}\,|_s = h_{fp} \cdot (T_{ps} - T_f|_s) \tag{14.16}$$

If there is more than one solid phase present, this energy balance must be applied to each of them.

14.2.1.4 Mass and Momentum Balance

In order to completely describe the system, it is necessary to solve *mass and momentum balance* equations in three dimensions. This includes the solutions of those balances for both the solid phase (or phases, if several are present) and the liquid phase (or phases, if several are present) and constitutes substantial modeling and computational efforts.[1,16,18] The hydrodynamics of the overall system (batch or continuous) must be well characterized in order to define fully the velocity field of all phases present in the ohmic heater. This is related to the determination of the quickest particle (or portion of fluid) and is crucial in determining the safety of the heat treatment. There are commercial software programs, based on computational fluid dynamics, that are able to address these issues. These are being used to obtain the flow field in a continuous ohmic heater to obtain the temperature distribution of the solid and liquid phases in a two-phase flow (Castro et al., unpublished results). However, these are trials and alternatives have been used.

The equations described above will form the basis for the development of models to predict the heating rate of fluids and fluid-containing solid particles. According to de Alwis et al.,[19] the heating rate is a function of (1) electrical conductivity of the food constituents (of both fluid and solid phases), (2) particle geometry and size, (3) particle orientation, and (4) thermal variation of physical properties. Sastry and Palaniappan[14] added a particle's volume fraction to this list. While the particle's size, geometry, orientation, and volume fraction are parameters relatively easy to measure and control, and there are extensive data available on the temperature dependence of the main physical properties, electrical conductivity (especially a particle's electrical conductivity) is a critical point.[15]

14.2.2 Main Parameter: Electrical Conductivity

Probably the most important parameter in OH modeling is σ.[20] Some of the characteristics of this property are summarized below:

- σ can be anisotropic (varies in different directions).
- Changes in the value of σ reflect changes in the matrix structure, e.g., during starch gelatinization or cell lysis.
- The value of σ of a material that is not suitable for ohmic processing, can be suitably modified, e.g., by blanching.

However, perhaps the most striking feature of σ is its dependence on temperature, as it has been shown to increase with increasing T. This observation is due to a variable opposition (drag force) to the movement of the ions responsible for conducting the electricity in food materials: for higher temperatures, that opposition is less important than for lower temperatures.[21]

For most solid foods, σ increases sharply with temperature at around 60°C, and this has been attributed to the breakdown of cell wall materials,[22] releasing ionic compounds to the bulk medium. Figure 14.3a represents this dependence for several electric field (F) strength values, demonstrating that the relationship between σ and T becomes linear for increasing values of F (the lower limit of F — i.e., $F = 0\ \mathrm{V \cdot m^{-1}}$ — represents conventional heating). This effect has been demonstrated by, among others, Palaniappan and Sastry,[5] who suggested that it

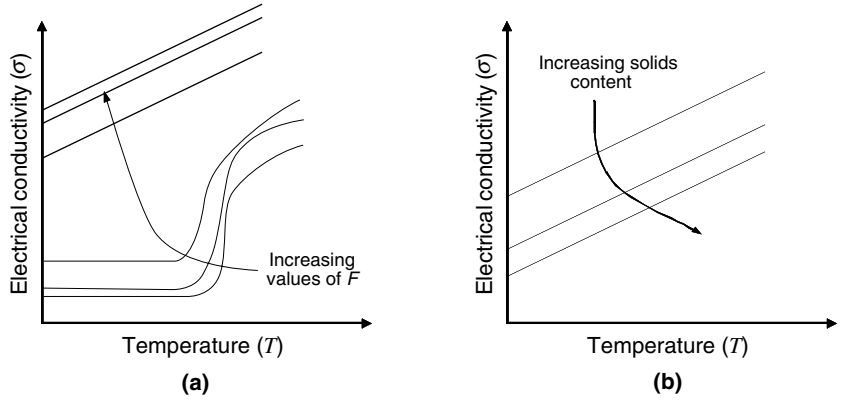

FIGURE 14.3 (a) Variation of σ with T for solids and for several electric field strength values (F), showing that the relationship between σ and T becomes linear for increasing values of F (the lower limit of F, i.e., $F = 0\ \mathrm{V \cdot m^{-1}}$, represents conventional heating). (b) Variation of σ with T for liquids, showing that σ always has a linear relationship with T, with the value of σ decreasing for increasing concentration of nonpolar (thus nonconductive) constituents (e.g., soluble solids). (Adapted from Sastry, S.K. and Palaniappan, S., *Food Technol.*, 45, 64–67, 1992.)

may be due to electro-osmotic effects, which could increase the effective conductivity at low temperatures. This means that for normal OH conditions, the relationship between σ and T can be represented by Equation 14.5.

For liquid foods, σ always has a linear relationship with T; however, the value of σ decreases if nonpolar (thus nonconductive) constituents are present (Figure 14.3b). If those constituents are generally regarded as the solid content of the liquid (e.g., the pulp content of juice), it is possible to write, e.g., for tomato and orange juices[6]

$$\sigma_T = \sigma_{ref} \cdot [1 + K_1 \cdot (T - T_{ref})] - K_2 \cdot S \tag{14.17}$$

where K_1 and K_2 are constants, and S is the dissolved solids content.

A similar influence of solids concentration on σ has also been reported by other authors,[8,23] but in these cases the solids were particles of significant sizes suspended in a fluid. This situation differs from the above because the value of σ is not that of the fluid, but a combined value for the mixture fluid + particles, the so-called effective electrical conductivity (σ_{eff}). In fact, not only solid content but also solid size will influence the mixture σ_{eff}.

Another major factor affecting σ is the ionic content of the food: the higher the ionic content, the higher the value of σ.[24] This has been demonstrated by several authors.[5,25–27]

σ is also a function of the frequency at which it is measured,[28] and evidence shows that the value of σ of a food heated electrically is different from that cooked by conventional heating.[20] In fact, Wang and Sastry[7] demonstrated that samples preheated by either conventional or OH had a higher heating rate due to increased σ, and that the values found for σ were different in each case.

It was mentioned that σ vs. T is usually a linear relationship. However, this is not always the case. Several examples exist where the curve became nonlinear.[27,29] This nonlinearity has been attributed to the equilibration of solutes within the samples during heating, thus altering the value of the observed σ_{eff}.

14.2.3 Other Parameters: Particle Orientation, Geometry, Size, and Concentration — the Effective Electrical Conductivity

Other parameters have been found to influence the values of OH rate of the constituents of a food, as mentioned before. When more than one phase is present, these parameters can exert their influence via the effective conductivity of the mixture (σ_{eff}), which is the case of particle size and concentration, or they can directly influence the heating rate of the different constituents, which is the case of particle orientation and geometry.

Particle geometry was demonstrated to be of importance only when the aspect ratio of the solid particle is far from unity.[30] If this is the case, for a static OH system containing a fluid and a single elongated particle with a lower conductivity than the fluid, de Alwis et al.[19] showed that when the particle was placed with

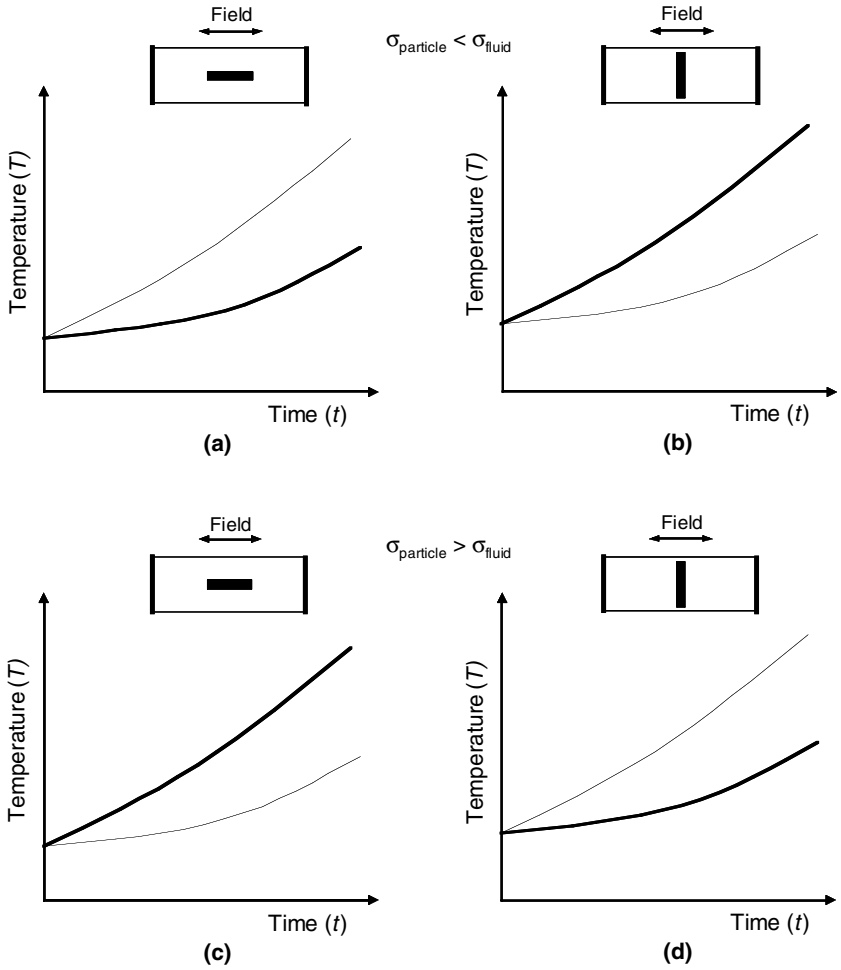

FIGURE 14.4 Heating curves of a single solid particle suspended in a fluid contained in a static ohmic heater (▬, particle; —, fluid) when the particle has a lower electrical conductivity than the fluid and its longer axis is parallel to the electric field (a) or perpendicular to the electric field (b), and when the particle has a higher electrical conductivity than the fluid and its longer axis is parallel to the electric field (c) or perpendicular to the electric field (d).

its longer axis parallel to the electric field (Figure 14.4a), it would heat slower than the fluid. However, if such a particle would be placed with its longer axis perpendicular to the electric field (Figure 14.4b), then the particle would heat faster than the fluid. Exactly the reverse would occur if the particle had a higher conductivity than the fluid (Figure 14.4c and d). This has been confirmed by mathematics.[1,31] The cases documented by Figure 14.4a and d are referred to by Sastry and Salengke[32] as worst-case scenarios. The particle will be underheated

compared to the fluid, and it may be underprocessed. In the case of Figure 14.4a, underheating may result from the major part of the current bypassing the particle, thus heating more the surrounding fluid. Alternatively (Figure 14.4d), underheating may result from the particle transmitting most of the current, thus creating a low field gradient within the particle and low current densities in its vicinity. A similar situation will be that of a cluster of particles (more conductive than the fluid) blocking the cross section of the heater. However, the authors conclude that both the latter cases are avoidable in an industrial application (e.g., controlling particle size or online sensing the σ of the product to divert possible particle clumps from the product stream prior to heating), the former one causing the greater concern. In practice, if a single low-conductivity particle enters the system, there is potential for underprocessing that particle, because its cold spot would have a significantly lower temperature than that of the fluid.[15] Such a particle might be a fat globule that, if carrying a microbial load, could present a serious risk for the safety of the product being processed.

Most of the conclusions presented above have been drawn for a static ohmic heater. What happens then in a continuous-flow ohmic heater? In this case, the fluid will be agitated, and therefore the fluid–particle heat transfer will be higher than in the static situation. Sastry and Salengke[32] have shown that the static situation is not always related to the worst-case scenario. In fact, when the solid is less conductive than the fluid. the worst situation will be that of a mixed fluid (continuous situation). Nevertheless, if the solid is more conductive than the fluid, then the worst case will be that of a static fluid (static situation). Evidently, the rheological properties of the fluid have great influence, and viscous fluids tend to make a continuous system behave as a static system.[33]

The concentration and size of the particles are also responsible for alterations of the heating rate of particle/fluid mixtures (Figure 14.5a and b). In fact, the values of σ of orange and tomato juices decreased with solids content.[6] The same observation has been made by other authors using other food systems (e.g., Zareifard et al.[23] used carrot puree or cubes immersed in a starch solution and Castro et al.[8] used strawberry cubes immersed in strawberry pulp (Figure 14.9a)). A possible explanation for this finding is given by Palaniappan and Sastry,[6] who establish a comparison with the case of a fluid without particles. In this case (as mentioned in the beginning of this section), the increase of σ with T is due to the reduced opposition (drag force) to the movement of ions. At constant T, this opposition is increased when solid particles are present (e.g., due to the increased tortuosity of the path that the ions have to follow, among other effects), and this may be the reason for the observed decreasing trend of σ with increasing particles content (Figure 14.5a), which is in line with what happened with dissolved solids concentration (see Figure 14.3b). This same explanation may be applied to justify the decreasing of σ when particle size increases (Figure 14.5b). This effect has been observed by several authors in various systems.[6,8,23]

If a solid particle with a lower σ than the fluid, in which the particle is immersed, is subjected to OH, it will heat slower than the fluid (assuming a particle with an aspect ratio close to unity or aligned as in Figure 14.4a). However, if a number of

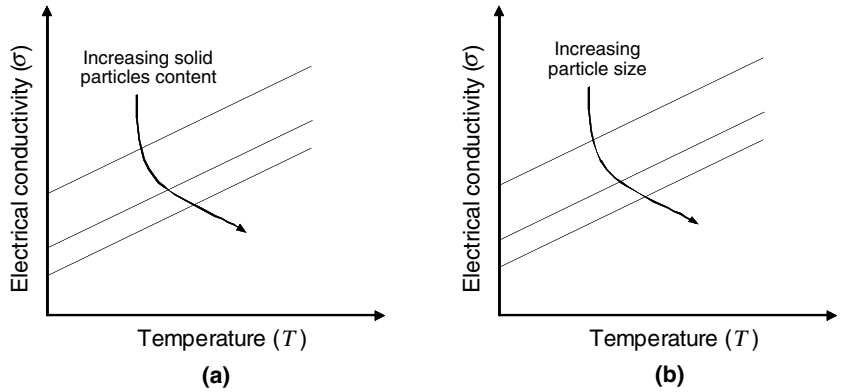

FIGURE 14.5 (a) Variation of σ with T for various particle contents, showing that σ always has a linear relationship with T, with the value of σ decreasing for increasing particle volume fractions. (b) Variation of σ with T for various particles sizes, showing that in this case σ also always has a linear relationship with T, with the value of σ decreasing for increasing particles size. (Adapted from Zareifard, M.R. et al., *Innovative Food Sci. Emerging Technol.*, 4, 45–55, 2003.)

such particles are present, simulations have shown and experiments have confirmed[14] that although the heating rate of the particles is initially lower than that of the fluid, it overtakes that of the fluid (Figure 14.6a). This can be explained in light of what has been represented in Figure 14.4b, where a particle with a lower σ blocking the current conduction would heat faster than the fluid; similarly, as the particles'

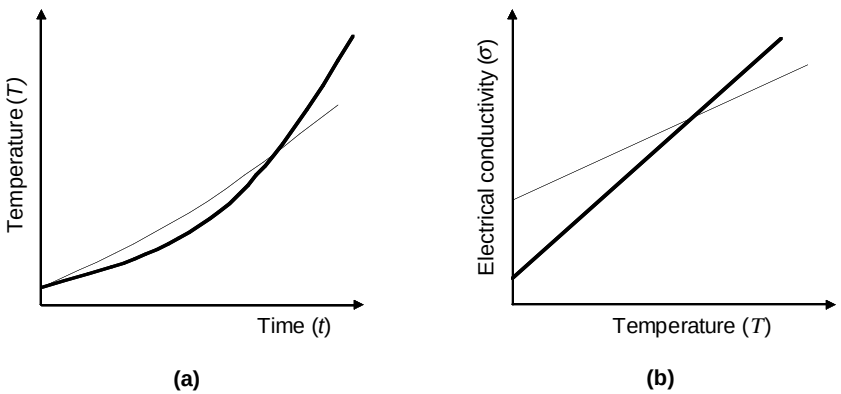

FIGURE 14.6 Behavior of a mixture of a fluid with a high concentration of particles (these having a value of σ lower than that of the fluid) (- particles;- fluid); (a) heating of particles and fluid (adapted from Sastry, S. K. and Palaniappan, S., *Journal of Food Engineering* 15: 241–261, 1992), and (b) corresponding variation of σ with T (Adapted from Zareifard, M. R. et al., *Innovative Food Sci. Emerging Technol.* 4: 45–55, 2003).

concentration increases, they will increasingly block the conduction paths, forcing a greater proportion of the total current to flow through them, thus showing higher heat generation rates than those of the fluid. This means that the particles' σ, although lower than the fluid's σ at low temperatures, will increase faster (Figure 14.6b), overtaking the latter for higher temperatures and therefore justifying the shape of the heating curves in Figure 14.6a.

Attempts have been made to determine the (overall) σ_{eff} of particle–fluid mixtures, which is a function of the conductivity and solids fraction of the component phases. The first relation was determined by Maxwell, as quoted by Fryer and Li[20] and is valid for a dilute dispersion of spheres with a volume fraction ε_p and electrical conductivity σ_p immersed in a fluid with electrical conductivity σ_f:

$$\sigma_{eff} = \sigma_f \cdot \frac{1 - 2 \cdot \Phi \cdot \varepsilon_p}{1 + \Phi \cdot \varepsilon_p} \tag{14.18}$$

where $\Phi = \frac{\sigma_f - \sigma_p}{2 \cdot \sigma_f - \sigma_p}$.

Modifications of this equation have been proposed, and there are a number of different models for σ_{eff}.[26] However, the main problem persists because σ_{eff} will vary with the position and orientation of the particles in the mixture. Kopelman[17] proposed the following model:

$$\sigma_{eff} = \frac{\sigma_f \cdot (1 - C)}{(1 - C) \cdot \left(1 - \varepsilon_p^{1/3}\right)} \tag{14.19}$$

where $C = \varepsilon_p^{2/3} \cdot \left(1 - \frac{\sigma_p}{\sigma_f}\right)$.

These models (of which Equation 14.19 is an example) can be of use if they are representative of the conditions under which they are to be applied. If this is the case, then it is possible to use σ_{eff} to estimate the temperature increase of a mixture when it is subjected to OH by a very simple calculation.

14.2.4 Models

The models described in the following sections are either the ones that are most quoted in the literature or those that, in our opinion, constitute important landmarks in the modeling effort in OH. Generally speaking, all assume that the physical properties of the phases present in a food are constant with respect to the temperature, with the obvious exception being electrical conductivity. Considering the coexistence of several solid particles immersed in a fluid, it is also generally assumed that the particles have short interaction times with the surrounding particles and with the walls of the heater.

14.2.4.1 Model for a Single Particle in a Static Heater Containing a Fluid

A model for a single solid particle in a static heater containing a fluid was developed initially by de Alwis and Fryer[1] and further enhanced by de Alwis and Fryer[34] for a two-dimensional system. The main purpose of the model is to predict the sterilization effect in a practical situation, where complex food shapes are heated. It is a finite-element model that has been designed to simulate three types of situations:

- *Zero convection*: This is the case of highly viscous and gel-forming foods, where convective processes are less significant.
- *Enhanced conduction*: When convection cannot be neglected, one of the convenient ways of treating the problem is to consider the existence of an *effective* conductivity value (σ_{eff}), which can be determined empirically and approximately to replace the effects of both convection and conduction.
- *Well-stirred liquid*: In previous work,[19] where an unstirred fluid was used, no hot spots were noticed when very low viscosity mixtures were heated, indicating that rapid convective mixing was taking place. In this case, a well-stirred liquid condition can be applied.

To obtain the electric field distribution, Equation 14.1 was written for a two-dimensional situation, yielding

$$\frac{\partial}{\partial x}\left(\sigma_x \cdot \frac{\partial V}{dx}\right) + \frac{\partial}{\partial y}\left(\sigma_y \cdot \frac{\partial V}{dy}\right) = 0 \tag{14.20}$$

where x and y are the space coordinates of the system and σ_x and σ_y the values of σ in the x and y directions, respectively. The solution of this equation was obtained using boundary conditions of (1) a uniform voltage on the electrodes, or (2) no current flux elsewhere across the boundary.

For heat generation, a network theory approach was used in which each triangular element was considered an isolated network, with nodal voltages known by solution of Equation 14.20. Heat generation in the particle was thus found by

$$\dot{Q} = \sum_{i=1}^{i=3} V_i \cdot I_i \tag{14.21}$$

where i is the node number.

Finally, the temperature distribution has been found by means of an energy balance, similar to that presented in Equation 14.13:

$$\rho \cdot C_p \cdot \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k_x \cdot \frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left(k_y \cdot \frac{\partial T}{\partial y}\right) + \frac{\dot{Q}}{V_{sys}} \tag{14.22}$$

where k_x and k_y are the values for the thermal conductivity in the x and y directions, respectively, and V_{sys} is the volume of the relevant part of the system (either solid or liquid).

The model was validated by comparing the results of the simulations to those from pieces of lamb. The model has also been used to simulate the heating of particles with different shapes and under different orientations, the results of which have been presented previously.

Later on, Zhang and Fryer[35] extended the work subsequently by using commercial software to simulate the behavior of a two-phase system containing different numbers of particles. A review article is available.[20] The same commercial software was also used by Fu and Hsieh[31] to simulate the temperature distribution in a two-dimensional OH system. The simulation results were compared with experiments made in an ohmic heater that was especially designed to meet the main assumptions of the model (a two-dimensional heating system containing a fluid and a single solid particle). They concluded that the boundary conditions and physical property values were crucial to obtain a reliable simulation.

14.2.4.2 Model for Multiparticle Mixtures in a Static Heater Containing a Fluid

The case of a mixture of particles in a static heater containing a fluid was studied.[14] This is a three-dimensional finite-element model aiming at predicting the temperature of the mixture of a liquid in which various particles are suspended. The most accurate solution has to be obtained considering the existence of a particle size distribution, having the heat transfer problem solved for each particle. Such a solution is unlikely to be applied in practice due to the extreme computational effort needed. Instead, an average size particle can be assumed, with cubic geometry.

Again, the electric field problem has to be solved. A solution for Equation 14.1 would be difficult for a mixture of several particles, since one would need knowledge of the location and properties of every particle at all points in time; instead, the authors obtained an estimation of the electric field distribution using a circuit theory-based approach. The following two cases were analyzed.

14.2.4.2.1 Mixtures of Several Particles Involving Large Particle Populations

Such a mixture is considered to be composed of a continuous (fluid) and a discrete (particles) phase. The equivalent electrical circuit is that of parallel fluid (R_{fP}) and particle (R_{pP}) resistances, in series with a liquid resistance (R_{fS}); therefore, the total resistance (R) is

$$R = R_{fS} + \frac{R_{fP} \cdot R_{pP}}{R_{fP} + R_{pP}} \tag{14.23}$$

and

$$R_{fS} = \frac{l_{fS}}{A_{fS} \cdot \sigma_f} \tag{14.24}$$

$$R_{pP} = \frac{l_{pP}}{A_{pP} \cdot \sigma_p} \tag{14.25}$$

$$R_{fP} = \frac{l_{fP}}{A_{fP} \cdot \sigma_f} \tag{14.26}$$

where l_{fS}, l_{fP}, and l_{pP} are the lengths of each phase, respectively, which are related to the length of the heater (l) and to each other by

$$l = l_{fS} + l_{fP} \tag{14.27}$$

and by

$$l_{pP} = l_{fP} \tag{14.28}$$

For A_{fS}, A_{fP}, and A_{pP} (the cross-sectional areas of each phase), they are related to the cross-sectional area of the heater (A) and to each other by

$$A = A_{fS} = A_{pP} + A_{fP} \tag{14.29}$$

In a similar way to Kopelman,[17] it was assumed that the cross-sectional area and length of the discrete phase (particles) could be estimated from the volume fraction of that phase (ε_p) by

$$A_{pP} = A \cdot \varepsilon_p^{2/3} \tag{14.30}$$

and

$$l_{pP} = l \cdot \varepsilon_p^{1/3} \tag{14.31}$$

Finally, the electric field was calculated using

$$V = I \cdot R(x) \tag{14.32}$$

where $R(x)$ is the resistance as calculated by Equation 14.23 up to position x, where the voltage (V) is to be calculated.

14.2.4.2.2 Mixtures with Relatively Small Numbers of Particles

In this situation the orientation and location of the particles are easily known; thus, the equivalent resistance can be calculated separately for zones with or without particles. For the former, the equivalent resistance (R) can be calculated as in Equation 14.23, while for the latter, the equivalent resistance simply equals R_{fS}, as in Equation 14.24. The electric field can then be calculated using Equation 14.32.

The next problem is the one of heat generation. This has been solved for this model as explained previously by using Equations 14.3 to 14.5.

Finally, the energy balance must be established for the fluid phase and the particles, to allow the determination of temperatures of each phase during the heating process. For the fluid phase, Equation 14.6 was slightly modified (Equation 14.6 is valid for the more general case of a continuous ohmic heater) for usage in a static (batch) ohmic heater, which yields

$$\rho_f \cdot V_f \cdot C_{pf} \cdot \frac{T_f^{n+1} - T_f^n}{\Delta t} = -U \cdot A_w \cdot (\bar{T}_f - \bar{T}_{air}) - n_p \cdot A_p \cdot h_{fp} \cdot (\bar{T}_f - \bar{T}_{ps}) + \dot{Q}_f \tag{14.33}$$

where V_f is the volume of the fluid, n is the time step index, $\bar{T}_{air}$ is the average temperature of the air surrounding the heater, and

$$\bar{T}_f = \frac{T_f^{n+1} - T_f^n}{2} \tag{14.34}$$

$$\bar{T}_{ps} = \frac{T_{ps}^{n+1} - T_{ps}^n}{2} \tag{14.35}$$

For the particles, Equation 14.13 holds with Equation 14.16 as the boundary condition.

The simulations were carried out and compared to the experimental results obtained with potato cubes of various sizes heated in a static ohmic heater containing phosphate solutions of various concentrations to simulate fluid phases with different electrical conductivities. This mathematical model was considered to be in agreement with the experiments. Critical parameters were found to be the (1) conductivities of liquid and solid phases, and (2) volume fraction of each phase. This model has been compared with the one presented in the previous section in terms of its capability of predicting the behavior of the static ohmic heater in a worst-case scenario.[32] The assessment of which model is more conservative depends on whether the particles are more or less conductive than the fluid.

14.2.4.3 Model for Multiparticle Mixtures in a Continuous-Flow Heater Containing a Fluid

The model described in the previous section for a static heater has been extended to the situation of a continuous-flow heater by Sastry.[15] Equations and assumptions were essentially the same (Equations 14.23 to 14.35) in the introduction of fluid and particle flow in and out of the system. Both fluid and particles will increase in temperature (and thus conductivity) during their path through the heater, and therefore the voltage drop must be calculated not for the whole heater, but separately for each of the incremental sections into which the heater must be divided for the calculations. As a consequence of this, Equations 14.23 to 14.32 have to be applied separately for each of those sections, in order to determine the electric field. Subsequently, Equations 14.3 to 14.5 need to be applied for the heat generation, and finally Equations 14.33 to 14.35 are applied to resolve the thermal problem.

The simulations performed with this model allowed several important aspects of continuous processing with OH technology to be emphasized:

- Although when a multiparticle mixture of low conductivity is present these particles tend to heat faster than the fluid, if an isolated low-conductivity particle crosses the system, it can be underprocessed.
- The residence time distribution and the fluid–particle heat transfer coefficient are crucial aspects to consider when designing a continuous heater.

These results were confirmed and extended by Orangi et al.,[16] who studied a similar problem when investigating the continuous-flow sterilization of solid–liquid food mixtures by OH.

14.2.4.4 Other Models

Other models of the behavior of particle–fluid mixtures subjected to OH have been developed. Benabderrahmane and Pain[36] presented a model based on the principle of a mean slip velocity between the fluid and the particles in plug flow (the slip phase model). The existence of a difference between the velocity of the fluid and that of the particles has been demonstrated by Lareo et al.,[37] Lareo,[38] Liu et al.,[39] Fairhurst,[40] and Fairhurst and Pain,[41] and therefore is considered in this model. It also takes into consideration internal heat generation, convective heat transfer, and heat conduction within the solid particles, thus following closely the scheme outlined in Figure 14.2, although the heater walls are assumed to be adiabatic. One of the main contributions of this model is that it demonstrates the importance of the temperature gradient inside the particles. It also confirmed results obtained earlier by other authors (see, e.g., Sastry[15]), showing that for a mixture of particles in a fluid, the process critical point is situated in the fluid and not in the particles. For conventional heating processes, the critical point is in the particles.

Other in-depth problems have been addressed that arose during the modeling effort during the previous two decades. Lacey[42,43] and Lacey et al.[44] studied the problem of thermal runaway while modeling OH, first by considering only heat transfer by conduction and second by including heat convection, which was found to dominate heat conduction.[45] In the same line, a diffusion–convection problem was addressed by Kavallaris and Tzanetis,[46] with the Heaviside function representing the food resistivity (which is the inverse of the conductivity).

14.3 THERMAL AND NONTHERMAL EFFECTS OF OH

This section reveals the research efforts to determine the effects of OH, both thermal and nonthermal, on microbes and on food constituents such as enzymes and vitamins. The information on proteins is limited to the studies made with *surimi* and its gel-forming ability due to the presence of the myosin heavy chain (see, e.g., Yongsawatdigul et al.[47,48]).

14.3.1 Microbial Kinetics

Microbial inactivation in foodstuffs is predominantly carried out by thermal processes, and the thermal inactivation kinetics of most of the target microorganisms is well studied. The need to reduce processing time and the increasing interest in using OH as an alternative heating technology to conventional heat transfer during commercial processes of sterilization or pasteurization were the impetus for the study of nonthermal mechanisms of microbial inactivation.

The destruction of microorganisms by nonthermal effects such as electricity is still not well understood and generates some controversy. Little work has been done in this field. Moreover, most of the published results do not refer to the sample temperature, or cannot eliminate temperature as a variable parameter.

The application of OH in the fermentation by *Lactobacillus acidophilus*, a lactic acid bacterium used in the dairy industry and with human health implications,[12] was studied. The lid of the fermentation vessel was equipped with ports for the thermocouple, pH probe, inoculation, water circulation coil, medium circulation, and two stainless steel plate electrodes. Metal surfaces were coated with epoxylite for electrical insulation and inertness. Temperature control was carried out under either conventional heating (by continuous water circulation) or OH (a constant voltage of 15 V, low voltage, or 40 V, high voltage, was applied), at different temperatures (30, 35, and 40°C). The results indicated that the lag phase for fermentations at 30°C was significantly lower (18-fold) under low-voltage ohmic conditions, which was also the lowest lag period of all the conditions tested. Although additional investigation is needed to explain the shortening of lag phase, this may be due to the improvement of absorption of nutrients and minimization of the inhibitory action of fresh medium. The application of an electrical field may induce pore formation in membranes (similar to the electroporation mechanism used to transform cells in molecular biology studies), allowing a faster

and efficient transport of the nutrients into the cells, thus decreasing lag phase. The minimum generation time for *L. acidophilus* was not affected by the heating method. Small differences in the final pH of the fermentation between the two methods were also reported. The consumption of glucose and the release of lactic acid were not significantly affected by the heating method. On the other hand, the production of lacidin A, an antimicrobial protein (bacteriocin) by the bacterium, decreased when fermentation occurred under ohmic conditions. The electrical current measurements follow approximately the changes in growth of *L. acidophilus* during the fermentation, and these changes in σ could, perhaps, be used to monitor fermentations. This study provides evidence that OH in the food industry may be useful to shorten the time for processing yogurt and cheese,[12] among other applications.

The kinetics of inactivation of *Bacillus subtilis* spores by continuous or intermittent ohmic and conventional heating were studied by Cho et al.[49] to determine if electricity had an additional effect on the killing of this microorganism at single- and double-stage heating treatments. Experiments were conducted in an ohmic fermentor for temperatures ranging from 88 to 97°C (Table 14.1). Spores heated at 92.3°C had significantly lower decimal reduction time (D) values when using ohmic rather than conventional heating. These results indicate that electricity has an additional killing effect against bacterial spores. The dependence on temperature of the D (z value) and the activation energy (E_a) were not significantly affected, indicating that electricity affects the death rate but not the temperature dependency of the spore inactivation process.

Palaniappan et al.[50] indicated that electricity did not influence inactivation kinetics, but the application of a nonlethal electric field reduces the intensity of the subsequent thermal treatment. This implies that the electric field lowers the

TABLE 14.1
Kinetic Constants and Thermal Inactivation Parameters for *Bacillus subtilis* Spores under Conventional and Ohmic Heating

Temperature (°C)	D_{conv} (min^{-1})	D_{oh} (min^{-1})	k_{0conv} (sec^{-1})	k_{0oh} (sec^{-1})
88.0	32.8	30.2	0.00117	0.001271
92.3	9.87	8.55	0.003889	0.004489
95.0	5.06	—	0.007586	—
95.5	—	4.38	—	0.008763
97.0	3.05	—	0.012585	—
99.1	—	1.76	—	0.021809
z (°C)	8.74	9.16	—	—
E_a (kJ·mol^{-1})	—	—	292.88	282.42

Source: Adapted from Cho, H.Y. et al., *Biotechnol. Bioeng.*, 62, 368–372, 1999.

TABLE 14.2
Kinetic Constants and Thermal Inactivation Parameters for *Zygosaccharomyces bailii* under Conventional and Ohmic Heating

Temperature (°C)	D_{conv} (min^{-1})	D_{oh} (min^{-1})	k_{0conv} (sec^{-1})	k_{0oh} (sec^{-1})
49.8	294.6	274.0	0.008	0.009
52.3	149.7	113.0	0.016	0.021
55.8	47.21	43.11	0.049	0.054
58.8	16.88	17.84	0.137	0.130
z (°C)	7.19	7.68	—	—
E_a (kJ·mol^{-1})	—	—	123.97	116.19

Source: Adapted from Palaniappan, S. et al., *Biotechnol. Bioeng.*, 39, 225–232, 1992.

heat resistance of microorganisms. Microbial death during OH was mainly attributed to thermal effects, while the nonthermal effects were insignificant (Table 14.2).

The effect of an electric field on the thermal inactivation kinetics of a highly heat resistant microorganism, *Byssochlamys fulva*, has been studied. This is a thermotolerant, ascospore-producing, filamentous fungus and was investigated by Castro et al. (personal communication, 2003). It can also produce the important mycotoxin patulin. *B. fulva* death kinetics were determined in an industrial strawberry pulp (14.5°Brix, pH = 4.0). The experimental D values for *B. fulva* obtained under OH (D_{oh}) conditions were half the ones obtained for conventional heating (D_{conv}) (T = 85°C, D_{conv} = 7.23, D_{oh} = 3.27). Unsurprisingly, these results are not consistent with those obtained for *B. subtilis* and *Zygosacharomyces bailii (*a bacterium and yeast, respectively), and the nonthermal inactivation mechanism needs to be studied in more detail, in terms of the effect of the electric field on the membrane/wall integrity of ascospores and enzymes participating in ascospores' activation. Finally, the effect of OH on patulin production in food by *B. fulva* and degradation of patulin requires investigation.

Data on nonthermal effects are scarce and more studies are needed to determine, for example, the effect of electricity on the physiological characteristics of microbes, changes in glycosylation degree of proteins and lipids, and other elements that can affect the heat resistance of microorganisms. The differences between microorganisms such as bacteria, filamentous fungi, and yeast need to be fully recognized.

The effects of OH on fermentations using immobilized cells or high-cell-density systems should also be further investigated, namely, in terms of substrate/metabolite diffusional limitations, lag phase duration, and efficiency of metabolite production. The effect on toxic metabolite production by microorganisms and degradation in food requires investigation in general.

14.3.2 Enzyme Degradation Kinetics

The industrial application of the OH technology is fully dependent on its validation with experimental data in order to evaluate the effects of the electric field on microorganisms, enzyme toxins, and biological tissues.

Enzymes are used in the food industry for (1) improving food quality (e.g., texture and flavor), (2) recovery of by-products, and (3) achieving higher yields of extraction.[51,52] Enzymes may also have negative effects on food quality, such as production of off-odors, tastes, and altering texture. Control is required in many food processing steps to promote/inhibit enzymatic activity during processing. Studies on the degradation kinetics of enzymes have been conducted to determine the effects of novel processing technologies, such as pulse electric fields[53–56] and high hydrostatic pressure[57,58] on enzyme inactivation kinetics.

The effects of OH on enzyme activity have not been investigated extensively. However, the sensitivity of several related enzymes toward OH has been studied by the authors (Castro et al., personal communication): lipoxygenase (LOX), polyphenoloxidase (PPO), pectinase (PEC), alkaline phosphatase (ALP), and β-galactosidase (β-GAL), which are summarized in Table 14.3, including the origins of the

TABLE 14.3
Overview of Enzymatic Systems Tested, Media Used, and Activity Determination Methods

Enzyme	Origin	Medium	Activity Measurement
Lipoxygenase (LOX)	Soybean (sigma)	Tris-HCl buffer (pH 9)	Spectrophotometric at 234 nm and 25°C Substrate: linoleic acid
Polyphenoloxidase (PPO)	Apples (cv. golden delicious)	Phosphate buffer (pH 6)	Spectrophotometric at 395 nm and 30°C Substrate: catechol
Pectinase (PEC)	Fermentation (Novo enzymes)	Citrate buffer (pH 4.5)	Spectrophotometric at 276 nm and 40°C Substrate: polygalaturonic acid
Alkaline phosphatase (ALP)	Raw milk	Milk	Spectrophotometric at 410 nm and 37°C Substrate: p-nitropheny lphosphate
β-galactosidase (β-GAL)	Genetically modified *Saccharomyces cerevisiae* with β-galactosidase gene of *Aspergillus niger*	Fermentation broth	Spectrophotometric at 405 nm and 65°C Substrate: p-nitrophenylgalactopi ranosyde (pNPG)

selected enzymes, the media used for the enzyme activity assays, and the methods for those assays. For both ohmic and conventional processes, and for similar samples' thermal histories, the corresponding D values were determined, leading to the calculation of the z value, the activation energy (E_a), and the preexponential factor (k_0) of the Arrhenius equation for each enzyme (Equations 14.36 to 14.38):

$$\frac{\log C_A - \log C_{Ao}}{t} = \frac{1}{D} \tag{14.36}$$

$$\frac{\log D_2 - \log D_1}{T_2 - T_1} = \frac{1}{Z} \tag{14.37}$$

$$k(t) = k_0 \exp^{\left(-\frac{E_a}{RT}\right)} \tag{14.38}$$

Lipoxygenases (LOX) are nonheme but iron-containing dioxygenases that catalyze the dioxygenation of polyunsaturated fatty acids containing a cis,cis-1,4-pentadiene-conjugated double-bond system, such as linoleate and linolenate, to yield hydroperoxides. Garotte et al.[59] evaluated the sensory characteristics of blanched vegetable purees to which isolated enzymes had been added and found that LOX was the most active enzyme in aroma deterioration in English green peas and green beans. LOX is distributed widely in vegetables, and evidence is accumulating to support its involvement in off-flavor development and color loss.[59] To optimize the blanching process of vegetables, it is essential to establish the kinetic model for the inactivation of this indicator enzyme. LOX is also important in the baking industry because it interacts with a gluten side chain in dough, making the gluten more hydrophobic and subsequently stronger. With stronger gluten, the dough has better gas retention properties and increased tolerance to mixing.

Table 14.4 presents the kinetic parameters obtained for the thermal degradation of LOX.[60] This demonstrates that the electric field has an additional effect on the LOX inactivation with much lower D values. This means that for the same inactivation degree, the time required for thermal treatment is much lower, thus reducing negative thermal effects in the other food components.

Pectinase (PEC) hydrolyzes the linkages that bind the small building blocks of galacturonic acid together in pectic substances, producing smaller molecules. Its main functions in foods are (1) to clarify juices and wines, (2) to reduce viscosity, (3) to accelerate the rate of filtration, (4) to prevent pectin gel formation of fruit juice from the fruit, and (5) to improve color extraction, e.g., from grape skin.[51]

The kinetic parameters for PEC inactivation are presented in Table 14.5, and it is clear that the electric field does not have any influence in the inactivation kinetics. Both conventional and ohmic processing D and z values are identical.

The enzyme responsible for enzymatic browning, ortho-diphenol oxygen oxidoreductase, is also known as catecholase, tyrosinase, phenolase, and

TABLE 14.4
Kinetic Constants and Thermal Inactivation Parameters for the Thermal Degradation of LOX

Temperature (°C)	*D* Value (min)		*Z* value (°C)		Pre-Exponential Factor (k_0) (s^{-1})		Activation Energy (E_a) ($\times 10^{-3}$ J·mol^{-1})	
	Conv.	Ohmic	Conv.	Ohmic	Conv.	Ohmic	Conv.	Ohmic
60	117.8	6.92						
62	20.44	5.38						
65	10.03	—						
68	5.43	1.57	10.83	14.75	0.997	0.997	0.757	0.969
70	3.76	—						
75	0.99	0.58						
78	0.77	0.47						

Source: Adapted from Castro, I. et al., The Influence of the Presence of an Electric Field on Lipoxygenase and β-Galactosidase Inactivation Kinetics, paper presented at Proceedings of NFIF 2003: New Functional Ingredients and Foods: Safety, Health and Convenience, Copenhagen, Denmark, 2003.

polyphenoloxidase (PPO).[51,61] PPO is present in most foods and participates only in the beginning phase of oxidation, as it catalyzes the change of monophenols to diphenols, which are then changed to highly reactive colored *o*-quinones. These then react with other *o*-quinones, amino acids, reducing sugars, etc., to form polymers that precipitate, resulting in the appearance of a dark color.[61] There are various phenols present in fruits and vegetables that are simultaneously used as substrates for PPO. Oxidative browning occurs only when the tissues are disrupted or destroyed and the compounds come into contact with air and with each other. The browning

TABLE 14.5
Kinetic Constants and Thermal Inactivation Parameters for the Thermal Degradation of PEC

Temperature (°C)	*D* Value (min)		*z* Value (°C)		Pre-Exponential Factor (k_0) (s^{-1})		Activation Energy (E_a) ($\times 10^{-3}$ J·mol^{-1})	
	Conv.	Ohmic	Conv.	Ohmic	Conv.	Ohmic	Conv.	Ohmic
60	14.00	15.00						
62	9.79	8.70						
65	3.41	3.57						
68	1.56	1.67	8.11	7.75	0.997	0.997	0.782	0.560
70	0.75	0.83						
75	—	0.52						

TABLE 14.6
Kinetic Constants and Thermal Inactivation Parameters for the Thermal Degradation of PPO

Temperature (°C)	*D* Value (min)		*z* Value (°C)		Pre-Exponential Factor (k_0) (s^{-1})		Activation Energy (E_a) ($\times 10^{-3}$ J·mol^{-1})	
	Conv.	Ohmic	Conv.	Ohmic	Conv.	Ohmic	Conv.	Ohmic
70	193.0	—	11.85	12.77	0.997	0.997	0.777	0.815
75	61.61	19.37						
80	23.74	6.79						
85	10.30	3.52						
90	3.15	0.92						
95	1.51	0.58						

of fruits and vegetables is undesirable, and so careful handling is required to avoid tissue injury. However, browning is important to flavor and color development (e.g., cocoa and tea), and so the tissues of these plants are deliberately damaged.

The effects of the electric field on the thermal inactivation kinetics of PPO (Table 14.6) are similar to the ones described for LOX. An enhanced enzyme inactivation is obtained when an electric field is present, thus reducing inactivation time.

Alkaline phosphatase (ALP) is an enzyme used as an indicator of the effectiveness of the milk thermal processing. For this enzyme conventional and ohmic inactivation mechanisms are similar, and the results obtained do not demonstrate a clear additional effect of the electric field on the enzyme inactivation (Table 14.7).

The use of the enzyme *β-galactosidase* (β-GAL) in lactose-containing foodstuffs may be an area of interest. It may be useful for people who are lactose

TABLE 14.7
Kinetic Constants and Thermal Inactivation Parameters for the Thermal Degradation of ALP

Temperature (°C)	*D* Value (min)		*z* Value (°C)		Pre-Exponential Factor (k_0) (s^{-1})		Activation Energy (E_a) ($\times 10^{-3}$ J·mol^{-1})	
	Conv.	Ohmic	Conv.	Ohmic	Conv.	Ohmic	Conv.	Ohmic
55	35.46	31.75	9.00	9.34	0.997	0.997	0.649	0.675
60	19.00	11.00						
62	4.41	4.06						
65	3.54	2.89						
67	1.96	1.28						
70	0.91	0.89						

TABLE 14.8
Kinetic Constants and Thermal Inactivation Parameters for the Thermal Degradation of β-GAL

Temperature (°C)	*D* Value (min)		*z* Value (°C)		Pre-Exponential Factor (k_0) (s^{-1})		Activation Energy (E_a) ($\times 10^{-3}$ J·mol^{-1})	
	Conv.	Ohmic	Conv.	Ohmic	Conv.	Ohmic	Conv.	Ohmic
65	182.00	—	5.12	5.13	0.997	0.997	0.370	0.350
70	33.90	12.24						
72	12.89	9.70						
75	2.99	2.77						
78	0.52	0.64						
80	0.50	0.28						

Source: Adapted from Castro, I. et al., The Influence of the Presence of an Electric Field on Lipoxygenase and β-Galactosidase Inactivation Kinetics, paper presented at Proceedings of NFIF 2003: New Functional Ingredients and Foods: Safety, Health and Convenience, Copenhagen, Denmark, 2003.

intolerant and cannot eat milk and dairy products. When the intestine produces little or no lactase, lactose (the milk sugar) is not digested and moves into the colon, where bacteria ferment it, producing hydrogen, carbon dioxide, and organic acids. The results of this fermentation are diarrhea, flatulence (gas), and abdominal discomfort. However, conventional and ohmic inactivation mechanisms are similar, and the results obtained (Table 14.8) do not show a clear additional effect of the electric field on the enzyme inactivation.[60]

In summary, no general behavior or trends are observed, and the effect of ohmic heating is dependent on the enzyme and probably also on the food system. The electric field reduces the *D* values for LOX and PPO, while *z* and E_a values are not greatly affected. For the other enzymes tested, the effect of the electric field is unclear.

14.3.3 Ascorbic Acid Degradation Kinetics under OH

Ascorbic acid (vitamin C) is frequently used as a food preservative or a vitamin supplement. Industrially, its main function is to prevent browning and discoloration, thus enhancing the shelf life of several products. Ascorbic acid is, for example, an effective inhibitor of peroxidase in fruits such as kiwi.

It is known to be thermolabile, and its degradation mechanism is specific to the particular system in which it is integrated. Degradation depends on whether aerobic or anaerobic pathways are employed.[62] The aerobic degradation pathway is related to the presence of oxygen (either in the headspace or dissolved).[63] The anaerobic pathway is mainly driven by the storage temperature, with lower temperature storage being the only way to minimize the degradation rate.[64] When oxygen

is present, the contribution of anaerobic degradation to the total vitamin C loss is small compared to aerobic degradation.[65] Several studies have been made to determine the kinetic parameters of thermal degradation of ascorbic acid in food systems under conventional and OH conditions (Table 14.9). It must be stressed that thermal degradation kinetics are variable and depend on the products being processed. In summary, from the limited amount of data available comparing the degradation of ascorbic acid by conventional heating and OH, no statistically significant differences have been demonstrated.

Castro et al.[29] studied ascorbic acid degradation kinetics in industrial strawberry pulps, concluding that degradation followed first-order kinetics for conventional and OH treatments. The obtained kinetic parameters were identical, for the temperature range of 60 to 97°C and for the two types of heating processes. This led to the conclusion that the presence of lower values of the electric field strength (<20 $V \cdot cm^{-1}$) do not affect the ascorbic acid degradation. Lima[69] drew similar conclusions for orange juice systems.

The OH technology will be extremely useful in minimizing thermal gradients (and thus overprocessed volumes), and consequently minimizing ascorbic acid degradation (and other thermolabile compounds). The final products obtained are expected to be of higher nutritional and organoleptic quality. This may be extremely important in producing functional foods.

14.4 BASIC OHMIC HEATER CONFIGURATIONS

This section presents the basic configurations for ohmic heaters, but it does not imply that these are the only ones available. In fact, other possibilities exist, including some under development, which are not considered here. The fundamental requirements for OH equipment for food processing are a pair of electrodes, a container for the food to be processed, and an alternating power supply.

The ohmic heater can be integrated into a *batch* or *continuous process*. The most typical configuration for the ohmic heater is that of a horizontal cylinder with one electrode placed in each extremity for a batch process (Figure 14.7a). For a continuous process, the design of the ohmic heater can be more variable, depending on the manufacturer. It can range from a simple tube with pairs of opposing electrodes mounted on the tube walls opposite to each other (Figure 14.7b), to coaxial tubes acting as electrodes with the food flowing between them (Figure 14.7c), or a vertical tube with the electrodes embodied at regular intervals (Figure 14.7d). Because the electric field is perpendicular to the food flow for the equipment represented in Figure 14.7b and c, these configurations are often called *cross-field*. If the electric field is parallel to the food flow (Figure 14.7d), the configuration obtained is termed *in-field*.

Ideally, it is possible to consider that in the cross-field configuration the electric field strength is constant. For the in-field configuration, σ will increase, and therefore the field strength experienced by the product will increase as it approaches the outlet because the product will heat during its path through the heater. To minimize this effect, when multiple electrodes are used in series (Figure 14.7d),

TABLE 14.9
Kinetic Constants and Thermal Inactivation Parameters for the Degradation of Ascorbic Acid in Several Fruits

Product	Temperature Range (°C)	pH	°Brix	E_a (kJ·mol^{-1})	k_0 (sec^{-1})	z (°C)	$D_{75°C}$(min)	Source
Strawberry pulp	60–97 (conventional heating)	4.0	14.5	21.36	0.15	46.7	175	29
Strawberry pulp	60–97 (OH)	4.0	14.5	21.05	0.14	46.7	169	29
Grapefruit juice	61.0–96.0 (conventional heating)	3.05	11.2	21.0	3.90×10^{-2}	49.3	1354	66
Grapefruit juice	60.0–91.0 (conventional heating)	3.05	31.2	22.0	6.10×10^{-2}	45.0	1228	66
Lime	20.0–92.0 (conventional heating)	5.92	6.3	58.1	1.55×10^{4}	35.8	1186	67
Lemon	20.0–92.0 (conventional heating)	2.94	6.0	46.5	3.59×10^{2}	44.6	949	67
Tangerine	20.0–92.0 (conventional heating)	4.10	13.4	44.6	2.25×10^{2}	46.5	771	67
Grapefruit	20.0–92.0 (conventional heating)	3.54	11.2	56.9	9.29×10^{3}	36.5	1276	67
Orange juice	70.3–97.6 (conventional heating)	3.60	12.5	128.3	3.23×10^{13}	19.0	24110	68
Orange juice	70.3–97.6 (conventional heating)	3.60	36.7	97.4	1.62×10^{9}	24.9	10447	68
Orange juice	65–90 (conventional heating)	Not reported	Not reported	12.6	3.30×10^{4}	Not reported	Not reported	69
Orange juice	65–90 (OH)	Not reported	Not reported	12.5	3.26×10^{4}	Not reported	Not reported	69

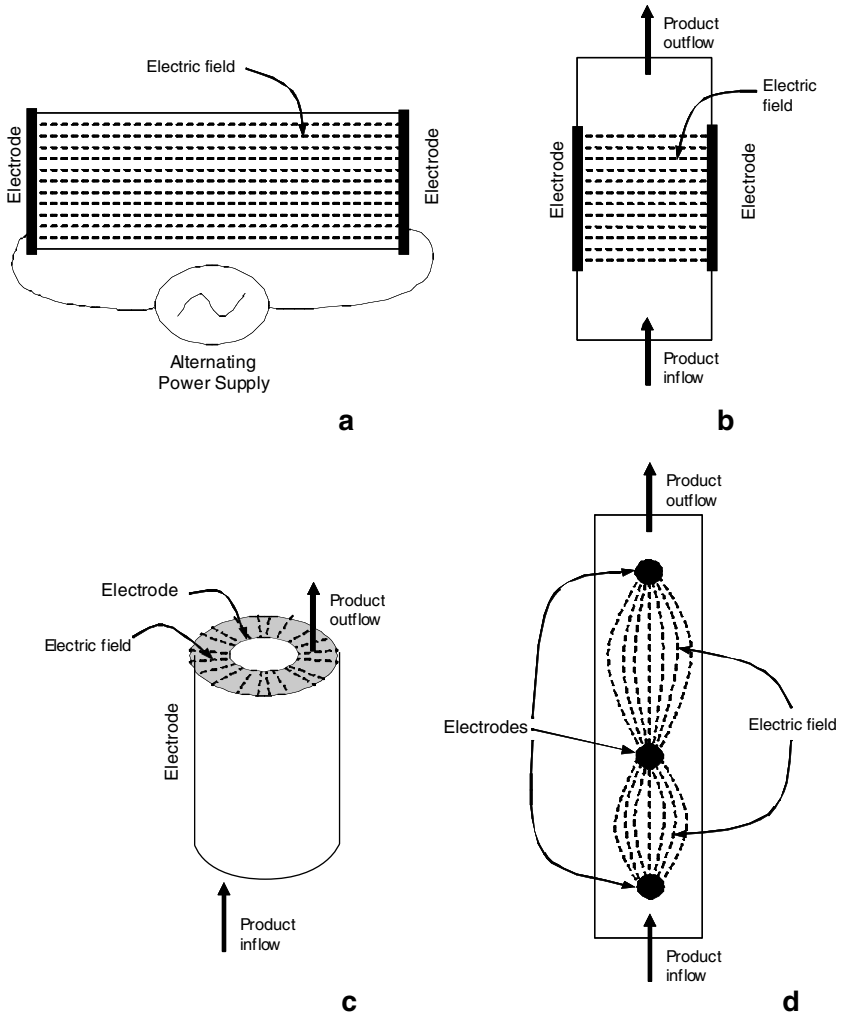

FIGURE 14.7 Basic configurations for ohmic heaters: (a) batch, (b–d) continuous. Panels (b) and (c) correspond to the cross-field configuration, while panel (d) corresponds to the in-field configuration, depending on if the electric field lines are perpendicular or parallel to the direction of the flow of the food, respectively.

they are spaced to account for the increase of σ with temperature. Therefore, as the product approaches the outlet of the heater, a lower value of the electric field strength is needed, and this is accomplished by increasing the spacing between each pair of electrodes.

The choice of the best configuration will obviously depend on the food being processed and the objectives of the process (e.g., cooking, pasteurization, sterilization).

Batch processes are typically used to cook, e.g., meat products,[70] while continuous processes are more appropriate for viscous fluids or fluids with particulates.

14.5 APPLICATIONS

The OH technology provides new, high-added-value, shelf-stable products with a quality unachievable by the traditional processing technologies. The process can be used in (1) the thermal processing of high-acid food products, such as tomato-based sauces, (2) pasteurization of whole liquid eggs,[9] (3) fish pastes, and (4) on meat products processed as an alternative to the traditional smokehouse.

14.5.1 Meat Products

The first experiments using OH in meat products were done in Finland in the 1970s, but operational difficulties led to the abortion of the project. Later on, in the 1990s, a project for cooking liver pâté and hams was carried out in France by the Meat Institute Development Association (ADIV) and Électricité de France (EDF).

One OH application is the thawing process, when traditional thawing methods cannot provide high-quality products. Wang et al.[71] applied the technology to frozen meat samples, in a liquid-contact thawing method. The results demonstrated a uniform and quicker thawing process. Also, meat properties such as color and pH were not changed significantly, and the final products achieved a good thawing quality. These results demonstrate the potential uses of OH in contact thawing, especially for meat products. Although the initial batch results were very promising, the attempts to develop a prototype version for a continuous cooking process were unsuccessful.

Canadian scientists[70] have been working on the ohmic cooking of meat products (sausages and ham) with promising results in batch operations. Brine-cured meat products were found to be admirably suited to OH having extremely reduced cooking times (e.g., a ham weighing 1 kg was cooked in less than 2 min). However, these flash cooking times did not reduce the bacterial load to levels that guaranteed product safety. Pasteurization had to be taken into consideration and a time–temperature profile was established. However, under these conditions, no noticeable changes were reported in the products' taste, texture, or shelf life.

14.5.2 Fruit and Vegetable Products

Strawberry fruit jams are extremely important for the Portuguese fruit jams industry because they account for most of its sales (around 90%). The search for alternative processing technologies leading to higher-quality products is one of the main goals, and the economic viability of this technology depends on the possibility of applying it to most of the products processed by this industry.[8] In the study by Castro et al.,[8] several strawberry-based products were tested by OH. The obtained results showed that for most of the products, high heating rates could be achieved, despite the significant differences of σ between the products tested. Also, the increase of the applied electric field could increase the heating rate (Figure 14.8a and b).

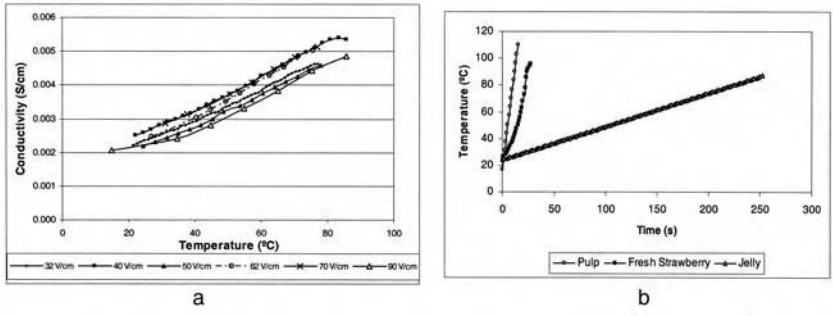

FIGURE 14.8 (a) The influence of electric field on electrical conductivity of strawberry pulp. (b) Differences in heating rates of three strawberry-based products. (Adapted from Castro, I. et al., *Innovative Food Sci. Emerging Technol.*, 26, 17–29, 2003.)

The suitability of OH for strawberry products having different solids concentrations, or Brix values, was also tested.[8] σ was shown to decrease with the increase of solids content in a mixture of particles with a bimodal particle size distribution, but the decrease was more significant for the bigger particles tested (Figure 14.9a). The results also suggest that for higher solids content (>20% w/w) and sugar contents over 40.0°Brix, σ is too low to use in the conventional ohmic heaters, and a new design is required (Figure 14.9b).

Most of the commercially available vegetables are submitted to more than one thermal treatment (e.g., blanching, sterilization). Wang and Sastry[7] studied the effects of an ohmic pretreatment and found no significant changes in the moisture content of the final products. This technology might be an alternative to conventional blanching treatments.

It has already been demonstrated that the texture of fruits and vegetables is greatly influenced by temperature and thermal processing.[72,73] The firmness of processed vegetables (e.g., canned cauliflower, asparagus) can be improved by

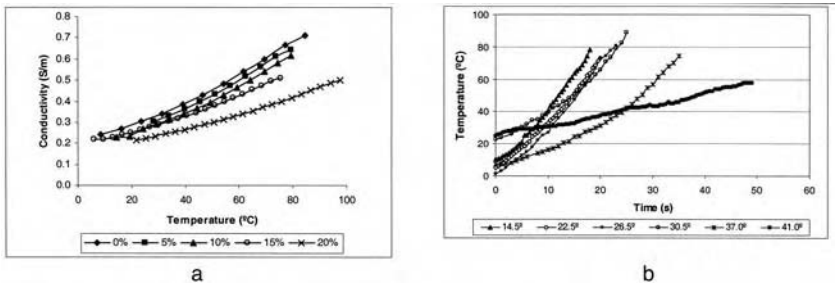

FIGURE 14.9 (a) The influence of solid particles concentration on the electrical conductivity of the strawberry pulp. (b) Differences in heating rates of strawberry pulps with different Brix values. (Adapted from Castro, I. et al., *Innovative Food Sci. Emerging Technol.*, 26, 17–29, 2003.)

low-temperature, long-time pretreatments. Eliot et al.[74] studied the influence of precooking by OH on the firmness of cauliflower. The experimental data showed that OH combined with low-temperature precooking in saline solutions offers a viable solution to HTST sterilization of cauliflower florets. A similar study was also performed with potato cubes,[75,76] and concluded that an ohmic pretreatment prevented loss of firmness when compared to a conventional pretreatment (50% in some cases).

14.5.3 Seafood Products

Most of the scientific literature concerning seafood products deals with surimi. Surimi is stabilized myofibrillar proteins from fish muscle, which is used in several Japanese food products. The textural properties of the products treated by OH were found to be superior to those heated in a 90°C water bath. Also, an increase in shear stress and shear strain of surimi gels was found when ohmic technology was applied,[77] and in addition, a superior gel quality was achieved. Higher heating rates are not beneficial to surimi manufacture.[47] Instead, slow heating rates produce stronger gels. Ohmic processing of surimi is very effective in obtaining a wide range of linear heating rates, which plays an important role in the study of surimi gelation.

It is expected that with the continuous research and development of new electrode materials and of equipment with innovative design, several other food applications using OH will soon be possible.

14.6 ECONOMICS

Although there are some OH facilities in operation around the world, it is not widespread and the data on commercial OH operations are scarce. Several applications of OH are still under study, and various products are being processed in pilot-scale equipment, but not at the industrial scale. As a consequence, processing costs have not yet been fully assessed.

With the objective of determining the economic viability of this technology, a comparison of OH with other food processing methods was made by Allen et al.[78] In their study, several assumptions were made about the products, facilities, and components of costs. Estimated values for labor, energy, quality control, packing, maintenance, and equipment depreciation were provided by well-trained food technologists and researchers. The product and production characteristics of the food products under analysis are summarized in Table 14.10 and Table 14.11.

The main difference between the two types of ohmic heaters used in this study, OH 75 and OH 300, is their power, 75 and 300 kW, respectively.

The conclusions withdrawn from this study show the importance of the type of product and of the power of the ohmic heater on the economics of the process. The OH 300 appears to be a viable alternative to conventional processing technologies when processing low-acid foods. It may also be a useful technology for high-acid foods, but only if high-quality products are required.

TABLE 14.10
Low-Acid Formulated Products: Product and Production Characteristics for Various Processing Technologies

	Processing Technology		
	Retorting	**Freezing**	**Continuous-Flow OH**
Studied products	Fresh or frozen meat and vegetables	Fresh or frozen meat and vegetables	Fresh or frozen meat and vegetables
Carrier	Gravy or sauce	Gravy or sauce	Gravy or sauce
Package	Microwavable tray	Microwavable tray	Microwavable tray
Product storage	Shelf stable	Frozen	Shelf stable
Product shelf life	About 1 year	About 1 year	About 1 year
Annual production	5.44 million kg	5.44 million kg	OH 75: 3.18 million kg[a] OH 300: 12.70 million kg[a]

[a]Per main ohmic heater.

Source: Adapted form Allen, K. et al., *Food Technol.*, 50, 269–273, 1996.

Studies conducted at the Agri-Food Canada's Food Research and Development Centre (FRDC) with meat products, where traditional smokehouse cooking was replaced by an ohmic process, indicated that energy savings of at least 70% could be achieved. In fact, the specific energy consumption required to cook a brine-cured meat product was on the order of 210 and 258 $kJ \cdot kg^{-1}$, compared to

TABLE 14.11
High-Acid Formulated Products: Product and Production Characteristics for Various Processing Technologies

	Processing Technology		
	Freezing	**Conventional Thermal Heating (Tubular Heat Exchanger)**	**Continuous-Flow Ohmic Heating**
Studied products	Fresh fruit	Fresh fruit	Fresh or frozen fruit
Carrier	Sugar syrup	Sugar syrup	Sugar and starch syrup
Package	Plastic tubs	Bag-in-box	Bag-in-box
Product storage	Frozen	Shelf stable	Shelf stable
Product shelf life	About 1 year	1 year	1 year
Annual production	15.88 million kg	15.88 million kg	OH 75: 1.58 million kg[a] OH 300: 6.3 million kg[a]

[a]Per main ohmic heater.

Source: Adapted from Allen, K. et al., *Food Technol.*, 50, 269–273, 1996.

859 kJ·kg^{-1} for conventional cooking.[70] In an industrial production context, energy savings would undoubtedly be even greater, as considerably less energy would be lost because of optimally designed equipment. Also, timesavings would probably be considerable (a few minutes with ohmic cooking, as opposed to a week with the traditional smoking house), indicating that ohmic cooking is an economic method for making excellent meat products.

Studies on the economic viability of OH for continuous aseptic processing of strawberry pulps and strawberry particulate jams (high-acid products) are currently being conducted in Portugal, but no further details are available at this time.

To obtain more accurate results on the profitability of this technology when applied to specific facilities, it is necessary to consider full production schedules, start-up costs, and considerations on product type.[78] Such actions must be taken in order to establish the commercial feasibility in this technology.

14.7 OVERVIEW, PROBLEMS, AND FUTURE CHALLENGES

Recently, several thermal and nonthermal technologies have been proposed for food processing, having as their main objective to contribute to the production of safer and higher-quality food products. OH is one of these technologies, presenting as its main advantage that heat generation occurs inside the material being processed. It is emphasized here that the internal heat generation induced by OH eliminates the problems associated with heat conduction in food materials, preventing the overcooking typical of conventional thermal food processing. Moreover, as the heating process is generally faster than that with heat exchangers, the killing of microbial cultures is obtained with a less pronounced degradation of most food components. Therefore, OH is indicated for the processing of foods containing particulate materials and foods with non-Newtonian rheological properties. The characterization, modeling, and control of all the phenomena associated with the application of OH in food processing will lead to the achievement of the main goal when heating foods — to have an effective control on the temperature profile of food materials.

Several applications have been proposed and developed for OH in relation to microbial control to replace the heating methods for food pasteurization, sterilization, and food processing — blanching, evaporation, dehydration, fermentation, and extraction — and several units are already working at the industrial scale.

Various reactions must be considered to occur in a food matrix that includes in its composition several components with different electrical, heat, mass, and momentum transfer properties. Obviously, each individual component and their interactions will play a decisive role in the efficiency of the OH process. Such a role may be played on the thermal killing of the microbial population or on the modification of the functional, nutritional, and organoleptic properties of foods. This reasoning clearly points out the complexity associated with thermal processing of foods, and in particular with OH thermal processing.

Several additional points associated with the fundamentals of ohmic processing must be addressed. In the particular case of a continuous-flow ohmic heater, the flow properties of the food components must be fully characterized and related to the temperature profiles of those components. These phenomena may be considered from a macroscopic point of view. However, microscopic phenomena also take place. At this level, disruption of cell membranes, structural changes in food components (including enzyme inactivation), and mass transfer phenomena must be considered.

Also, novel applications and a deeper knowledge of current applications must be obtained. Obviously, further research and development work on OH in these areas are essential.

Research is required in the following areas:

- To elucidate on the relative importance of electric current properties and the corresponding temperature values on the killing of microbes and in particular resistant structures (e.g., spores).
- To evaluate the effect of OH on microbial toxins (e.g., mycotoxins).
- To characterize the effect of OH on the nutritive, organoleptic, and functional properties of foods. This work should be initiated by studying the effects on individual food components, including water, and should be extended to whole food products. At this point, it must be emphasized that each food product requires specific treatments.
- To characterize the flow of the food components when being processed in an ohmic heater by developing adequate hydrodynamic models.
- To develop methods that will allow for a more precise mapping of temperatures on foods submitted to OH.
- To develop models that can adequately describe ohmic processing of foods.
- To implement these models so that an adequate control of the rate of heating can be achieved, thus minimizing the thermal degradation effects on desirable product attributes but maintaining a safe product.

In terms of process development, the more relevant points to be addressed are:

- Food preservation (with respect to spores and filamentous fungi).
- Food processing — Application of OH to particulate foods (food purees containing particles, food suspensions, etc.) and foods with a non-Newtonian rheological behavior.
- Food processing — Integration of OH in existing food industries as an alternative to conventional preheating, in those cases where higher-quality products and more efficient processing are to be obtained.
- Food thawing and water removal processes (evaporation and dehydration).
- Application to fermentation processes. This includes how electrical current affects microbial metabolism and membrane and cell wall transport properties.
- Extraction and purification processes — The possibility of applying an electrical field to existing processes to increase the yields and purification of biological macromolecules.

- To develop alternative designs for ohmic heaters, adapted to specific food processes.
- To extend the use of OH to processes other than food processes.

14.8 CONCLUSIONS

OH is a food processing technology that presents several advantages when compared to existing technologies. It can improve food quality and is a clean technology. Also, the economic advantages of its use have been demonstrated.

The application of OH for food processing is not well characterized, and not all its potentialities have been fully exploited due to the complexity of the phenomena occurring during OH processing and the complexity of food materials.

In conclusion, if attention is paid to the phenomena occurring during OH, there is (1) electrical current generation and transport, (2) heat generation and transport, and (3) eventually mass and momentum transport. These phenomena are intimately associated and interact with each other. Also, there are several consequences occurring as a result of the electrical current passage and heat being generated because of the electrical current. These reactions include thermal and electrical microbial killing, nutrients modification, and enzyme inactivation.

This technology will gain an increasing importance in food processing as a deeper understanding of the fundamental science is achieved.

NOMENCLATURE

A_{fP}	Cross-sectional area of parallel fluid (m^2)
A_{fS}	Cross-sectional area of serial fluid (m^2)
A_p	Area of each solid particle (m^2)
A_{pP}	Cross-sectional area of parallel particles (m^2)
C_A	Activity (U)
C_{A0}	Initial activity (U)
C_{pf}	Fluid specific heat ($J \cdot kg^{-1} \cdot K^{-1}$)
C_{pp}	Particle specific heat ($J \cdot kg^{-1} \cdot K^{-1}$)
D	Decimal reduction time (sec)
D_{conv}	Decimal reduction time, under conventional heating conditions (sec)
D_{oh}	Decimal reduction time, under ohmic heating conditions (sec)
E_a	Activation energy ($J \cdot mol^{-1}$)
F	Electric field ($V \cdot m^{-1}$)
I	Current intensity (A)
$\dot{Q}$	Heat generated ($J \cdot sec^{-1}$)
$\dot{Q}_f$	Heat generated in the fluid ($J \cdot sec^{-1}$)
$\dot{Q}_p$	Heat generated in the particle ($J \cdot sec^{-1}$)
R	Electrical resistance (Ω)
R	Radius of the heater tube (m)

R_{fP}	Parallel resistance of fluid (Ω)
R_{fS}	Serial resistance of fluid (Ω)
R_{pP}	Parallel resistance of particles (Ω)
S	Dissolved solids content ($kg \cdot m^{-3}$)
T_{0p}	Initial temperature of the particle (K)
T_{air}	Temperature of the air surrounding the walls of the heater (K)
T_f	Fluid temperature (K)
T_p	Particle temperature (K)
T_{ps}	Temperature at the surface of the solid particle (K)
T_{ref}	Reference temperature (K)
U	Overall heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$)
V	Voltage (V)
V_f	Volume of the fluid (m^3)
V_p	Volume of the particle (m^3)
V_{sys}	Volume of the relevant part of the system (m^3)
V_{sys}	Volume of the system between the electrodes (m^3)
Z	Dependence on temperature of D value (K)
h_{fp}	Fluid–particle heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$)
I	Node number (–)
k	Frequency constant (sec^{-1})
k_0	Preexponential factor (sec^{-1})
k_f	Fluid thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
k_p	Particle thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
k_x	Thermal conductivity in the x direction ($W \cdot m^{-1} \cdot K^{-1}$)
k_y	Thermal conductivity in the y direction ($W \cdot m^{-1} \cdot K^{-1}$)
l_{fP}	Length of parallel fluid (m)
l_{fS}	Length of serial fluid (m)
l_{pP}	Length of parallel particles (m)
m	Temperature coefficient ($S \cdot m^{-1} \cdot K^{-1}$)
m_f	Temperature coefficient of the fluid ($S \cdot m^{-1} \cdot K^{-1}$)
m_p	Temperature coefficient of the particle ($S \cdot m^{-1} \cdot K^{-1}$)
n	Flow behavior index (–)
n	Time step index (–)
$\vec{n}$	Unit vector normal to the surface of the tube's wall (–)
n_p	Number of solid particles in the considered volume (–)
r	Radial coordinates (–)
t	Time (sec)
$\overline{v}_z$	Mean fluid velocity profile in the axial direction ($m \cdot sec^{-1}$)
w	Tube's wall (–)
x, y	Space coordinates (–)
z	Axial coordinates (–)

∇V	Voltage gradient (V)
$\beta(\varepsilon_f)$	Fraction of heat transfer by conduction through the mixture in the fluid phase (–)
ε_f	Fluid volume fraction in the heater (–)
ε_p	Volume fraction (–)
ρ_f	Fluid density ($kg \cdot m^{-3}$)
ρ_p	Particle density ($kg \cdot m^{-3}$)
σ_{0f}	Electrical conductivity of the fluid before the heating takes place ($S \cdot m^{-1}$)
σ_{0p}	Electrical conductivity of the particle before the heating takes place ($S \cdot m^{-1}$)
σ_{eff}	Effective electrical conductivity ($S \cdot m^{-1}$)
σ_{ref}	Electrical conductivity at a reference temperature ($S \cdot m^{-1}$)
σ_T	Electrical conductivity at temperature T ($S \cdot m^{-1}$)
σ_x	Electrical conductivity in the x direction ($S \cdot m^{-1}$)
σ_y	Electrical conductivity in the y direction ($S \cdot m^{-1}$)
σ	Electrical conductivity ($S \cdot m^{-1}$)
ALP	Alkaline phosphatase
β-GAL	β-Galactosidase
LOX	Lipoxygenase
OH	Ohmic heating
PEC	Pectinase
PPO	Polyphenoloxidase

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15 Radio Frequency Dielectric Heating

Yanyun Zhao

CONTENTS

15.1 INTRODUCTION

Radio frequency (RF) dielectric heating is a heating technology that allows for rapid, uniform heating throughout a medium. This technology generates heat energy within the product and throughout its mass simultaneously due to the frictional interactions of polar dielectric molecules rotating in response to an externally applied AC electric field.[1,2] RF dielectric heating offers several advantages over conventional heating methods in food application, including saving energy by increasing heat efficiency; achieving rapid and even heating; reducing checking, the uneven stresses in the product as a result of evening the product moisture profile; avoiding pollution, as there are no by-products of combustion; increasing production without an increase in overall plant length; saving floor

space, as efficient heat transfer results in faster product transfer and reduced oven length; and automatically compensating for variations in product moisture. In addition, this technology can be easily adapted during implementation to be compatible with automated production batch or continuous-flow processing.[1–4]

RF heating of foods dates back to the 1940s. Early efforts attempted to apply RF energy to cook various processed meat products, heat bread, and dehydrate and blanch vegetables.[1,5,6] However, the work resulted in very few commercial installations, primarily because of the high overall operating costs associated with using radio frequency energy in the 1940s. By the 1960s, studies on the application of RF energy in foods focused mainly on thawing frozen products, which resulted in several commercial production lines.[7–9] The next generation of commercial applications of RF energy in the food industry was postbake drying of cookies and snack foods, starting in the late 1980s.[3,4,10,11] The use of RF heating resulted in reduced energy consumption and improved product quality, both considered great advantages over the traditional baking oven. By the 1990s, due to increased food safety requirements, great attention has been given to the use of RF energy for pasteurization and sterilization of foodstuffs for providing high-quality and safe food products. However, commercial RF dielectric heating systems for the purpose of food pasteurization or sterilization are not known to be in use in the U.S. due to reasons such as the inability to ensure sterilization of the entire package, lack of suitable packaging materials, and unfavorable economics when compared with conventional thermal processing technologies.

This chapter will consider the major technology aspects of RF dielectric heating, discuss the potential use of mathematical modeling for the design of the RF heating system, discuss RF applications in food pasteurization and sterilization, and provide insights on the major technical challenges in RF pasteurization and sterilization of foods, especially ready-to-eat, packaged items.

15.2 THE TECHNOLOGY OF RF DIELECTRIC HEATING

RF heating is a subset of several electromagnetic-based methods of heating materials. Table 15.1 lists the most common electromagnetic-based heating methods, the critical parameters that most affect heating rate, and the common frequency range of applications.

The technology of RF heating involves applying a high-voltage AC signal to a set of parallel electrodes set up as a capacitor (Figure 15.1). The medium to be heated is sandwiched between the electrodes, and an AC displacement current flows through the medium. As a result, polar molecules in the medium align and rotate in opposite fashion to match the applied AC electric field. Heating occurs as polar molecules interact with neighboring molecules, resulting in lattice and frictional losses as they rotate. The higher the frequency of the alternating field, the greater the energy imparted to the medium, until the frequency is so high that rotating molecules can no longer keep up with the external field due to lattice limitations.

TABLE 15.1
Electromagnetic-Based Heating Methods

Heating Method	Key Parameter	Frequency Range	Common Frequencies
Ohmic (Lower f) (Electric field)	σ, E	<1 MHz	50 Hz, 60 Hz
Capacitive dielectric (Medium f) (Electric field)	f, ε'', E	100 kHz < f < 100 MHz or wavelength >> sample size	10 MHz, 27 MHz, 39 MHz, and others
Radiative dielectric (Higher f) (Electric field)	f, ε'', E	100 MHz < f < 100 GHz or wavelength ≤ sample size	915 MHz, 2.45 GHz, 5.8 GHz, 24.124 GHz, and others
Inductive–ohmic combination (Lower f) (Magnetic field)	Hysteresis losses f(B-H curves, f) and eddy current losses $f(H, \sigma)$	50 Hz < f < 1 MHz	50 Hz, 60 Hz, 1–50 kHz, 450 kHz, and others
Inductive (Medium f) (Magnetic field)	f, μ'', H	1 MHz < f < 100 MHz or wavelength >> sample size	50 MHz and others
Radiative magnetic (Higher f) (Magnetic field)	f, μ'', H	100 MHz < f < 100 GHz or wavelength ≤ sample size	915 MHz, 2.45 GHz, 5.8 GHz, 24.124 GHz, and others

Note: σ = Electrical conductivity (S/m); E = RMS electric field intensity (V/m); ε'' = electric permittivity (F/m); H = RMS magnetic field intensity (A/m); μ'' = magnetic permeability (H/m); B = magnetic flux density (W/m^2); f = electric field frequency (Hz).

Source: from Zhao, Y. et al., *J. Food Process. Eng.*, 23, 25–55, 2000. With permission.

The frequency at which lattice limitations occur is called the *Debye resonance*. It is the frequency at which maximum energy can be imparted to a medium for a given electric field strength. Other higher-frequency limitations include the reduction of field penetration into a medium as frequency is increased in the presence of high electrical conductivity and high dielectric loss components. A typical existing design for a dielectric heating system is shown in Figure 15.2.

RF dielectric heating differs from higher-frequency electromagnetic radiative dielectric heating (e.g., microwave ovens). With RF heating, the wavelength of the chosen frequency is large compared to the dimensions of the sample being heated. With electromagnetic radiative heating, the wavelength is comparable to

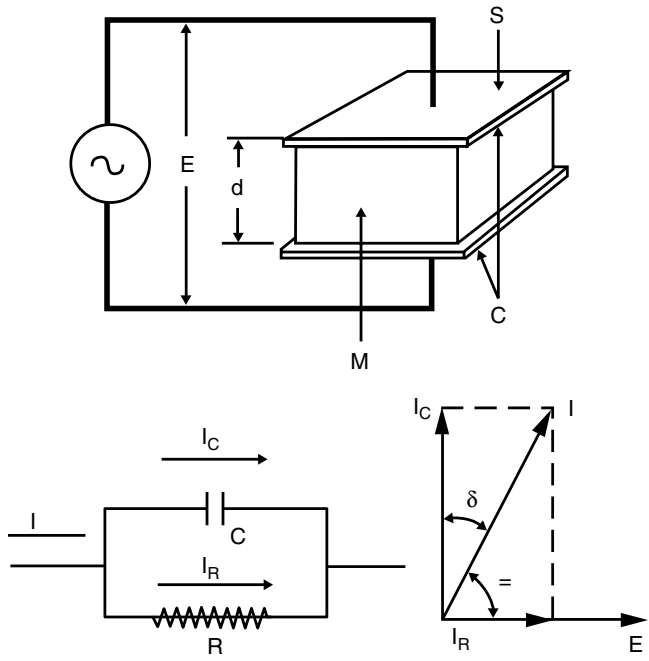


FIGURE 15.1 Diagram of RF dielectric heating (C = capacitor, d = distance between two electrodes, E = electric supply, M = magnetic field, R = resistor) (From Zhao, Y. et al., *J. Food Process. Eng.*, 23, 25–55, 2000. With permission.)

or even smaller than the dimensions of the sample being heated. An example of RF dielectric heating would be two large parallel electrodes placed on opposite sides of a sample with an AC displacement current flowing through it. An example of electromagnetic radiative heating would be a metal chamber with resonant electromagnetic standing wave modes, as in a microwave oven. Thus, the RF dielectric heating method offers the advantages of providing more uniform heating over the sample geometry due to deeper wave penetration into the sample, as well as simple uniform field patterns (as opposed to the complex nonuniform standing wave patterns in a microwave oven). RF dielectric heating operates at frequencies low enough to use standard power grid tubes, which are both lower cost (for a given power level) and allow for generally much higher power generation levels than microwave tubes.

RF heating also differs from lower-frequency ohmic heating. RF heating depends on dielectric losses; ohmic heating relies on direct ohmic conduction losses in a medium and requires the electrodes to contact the medium directly (i.e., the current cannot penetrate a plastic film or air gap). RF dielectric heating methods also offer advantages over low-frequency ohmic heating, including the ability to heat a medium that is enclosed inside an insulating plastic package or

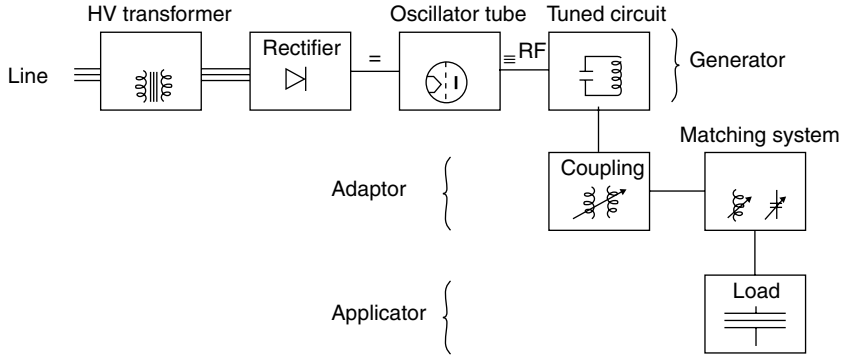


FIGURE 15.2 Block diagram of a typical capacitive (RF) dielectric heating system. (From Zhao, Y. et al., *J. Food Process. Eng.*, 23, 25–55, 2000. With permission.)

surrounded by an air or deionized water barrier (i.e., the electrodes do not have to contact the medium directly). The performance of RF dielectric heating is therefore also less dependent on the product making a smooth contact to the electrodes. RF dielectric heating methods are not dependent on the presence of DC electrical conductivity and can heat insulators as long as they display polar dielectric losses. Examples of electromagnetic heating (microwave ovens), ohmic heating, and RF dielectric heating systems are shown in Figure 15.3.

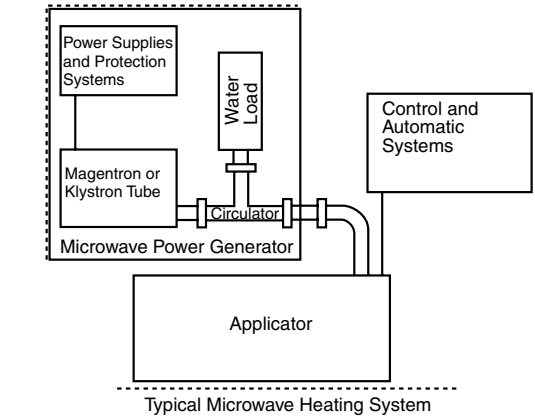
15.3 DIELECTRIC PROPERTIES OF FOOD MATERIALS IN RADIO FREQUENCY RANGE

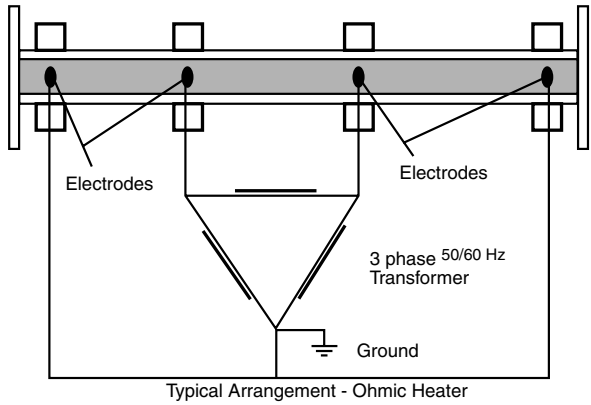
Knowledge of dielectric properties of food materials in the RF range is essential in guiding further development, improvement, and scale-up of RF dielectric heating in the food industry. The two dielectric properties of greatest interest are the *energy storage* and *loss terms* of the electric permittivity (ε' and ε'', respectively). Permittivity describes dielectric properties that influence reflection of electromagnetic waves at interfaces and the attenuation of the wave energy within material. The complex relative permittivity ε of a material can be expressed in the following complex form:

$$\varepsilon = \varepsilon' - j\varepsilon'' \tag{15.1}$$

The real part, ε', is referred to as the dielectric constant and represents stored energy when the material is exposed to an electric field, while the dielectric loss factor, ε'', which is the imaginary part, influences energy absorption and attenuation, and $j = -1$.

The three most popular methods for measuring dielectric properties of foods and commodities are open-ended coaxial probe, transmission line, and resonant





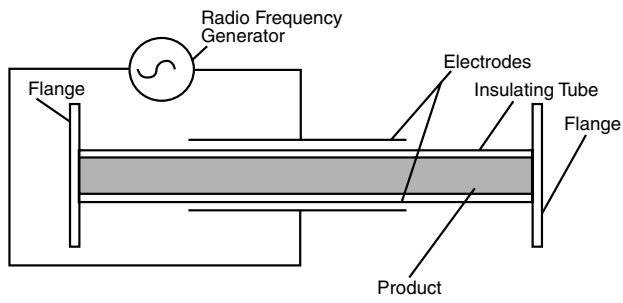


FIGURE 15.3 RF dielectric heating as compared with microwave and ohmic heating. (From Zhao, Y. et al., *J. Food Process. Eng.*, 23, 25–55, 2000. With permission.)

cavity method.[12] The probe method is based on a coaxial line ending abruptly at the tip that is in contact with the material being tested. This method offers broadband measurements while minimizing sample disturbance. The measured reflection coefficient is related to the sample permittivity.[13] The probe method is the easiest to use because it does not require a particular sample shape or special containers. The transmission line method involves placing a sample inside an enclosed transmission line. The cross section of the transmission line must be precisely filled with sample. This method is usually more accurate and sensitive than the probe method, but it is difficult to use and time consuming. The resonant cavity method uses a single-mode cavity. Once a sample of known geometry is placed in the cavity, the changes in reflected power of the cavity and the frequency of resonance are used to compute the dielectric property of the sample. The cavity method can be accurate and is especially suited for samples with a very low dielectric loss factor. However, this method provides dielectric properties at only one fixed frequency.[14]

Frequency, temperature, salt content, moisture content, and the state of moisture (frozen, free, or bound) are the major factors that influence dielectric properties of food materials. Many studies on dielectric properties of food in the microwave frequency range have been reported for different frequency ranges, temperatures, and moisture contents.[15–21] Several comprehensive reviews on dielectric properties provide good sources of useful experimental data from many foods and agricultural products.[22–27] However, the amount of information available on the dielectric properties of foods in the frequency range most common to RF dielectric heating (1 to 200 MHz) is very limited. Some of the reported studies are summarized below.

Ede and Haddow[28] measured the dielectric constant, power factor, and specific conductivity of foods, including beef, pork, eggs, flour, and vegetables, using a Marconi Q-meter over the temperature range of –39 to 100°C and frequency range of 0.1 to 40 MHz. Results indicated that for foods that are poor conductors, the electrical conductivity varied very little with frequency. For foods that are poor dielectrics, the variation in electrical conductivity with frequency was high. They also found that for most foods, the electrical conductivity decreased with reduced temperature and showed a sharp drop at the freezing point.

Bengtsson et al.[29] measured the dielectric constant and loss tangent for lean beef and codfish over the temperature range of –25 to 10°C and frequency range of 10 to 200 MHz using a Boonton RX-meter. They found that the values of dielectric constant and loss tangent decreased with increased frequency and also showed a sharp increase at defrosting temperatures (~1 to 2°C). Variation in dielectric properties caused by variability in raw material and by frozen storage was relatively small for meat and codfish. Dielectric properties were quite similar for lean meat, lean fish, and herring, but of much lower value for fats.

Kent and Jason[30] elucidated the nature of the mechanisms that influenced the dielectric properties of frozen fish muscle (cod and haddock) and measured the dielectric properties over the frequency range of 0.1 Hz to 10 GHz. The results revealed that the time dependence of the dielectric properties was attributable to changes in the distribution of water between the solid and liquid states.

Tran and Stuchly[15] measured dielectric properties of raw beef (meat and liver), chicken, and salmon at three temperatures between 1.2 and 64°C in the frequency range of 100 to 2500 MHz using an open-ended coaxial-line sensor and an automatic network analyzer. This method has proved to be very suitable for measuring high-water-content substances.

Kent[25] published the dielectric properties of cooked and raw fish, including codfish, herring, haddock, and sprat, at selected frequencies from 10 Hz to 10 GHz and selected temperatures from –78.5 to 90°C.

Cole et al.[31] used time-domain spectroscopy (TDS) to study dielectric properties of water–oil and oil–water microemulsions from 10 MHz to 3 GHz. Merabet and Bose[32] used time-domain reflectometry (TDR) to measure the dielectric constant and loss factor of water in the radio and microwave frequencies (10 MHz to 8 GHz). Puranik et al.[33] used TDR to determine the dielectric properties of a honey–water mixture in the frequency range of 10 MHz to 10 GHz at 25°C. Looan and Smulders[34] also used TDR to measure the dielectric permittivity of foodstuffs (including solutions of mono-, di-, and polysacchrides) in the frequency range of 20 kHz to 5 GHz, considering the influences of species, composition, and temperature.

Ikediala et al.[35] studied dielectric properties of four apple cultivars between 30 and 3000 MHz at 5 to 55°C, using the open-ended coaxial-line probe technique. The dielectric constant of apples decreased with frequency and decreased slightly with increasing temperature. The dielectric loss factor increased linearly with temperature in the radio frequency range, but was nearly constant at the microwave frequencies. A minimum dielectric loss factor of apples was observed at about 915 MHz. The dielectric constant and loss factor were not influenced by cultivar, pulp section, or degree of ripeness of apples.

Wang et al.[36] determined the dielectric properties of a whey protein gel, a liquid whey protein mixture, and a macaroni and cheese product and their constituents by using a custom-built temperature-controlled test cell and an Agilent 4291B impedance analyzer over a temperature range from 20 to 121.1°C, at frequencies of 27, 40, 915, and 1800 MHz. As temperature increased, dielectric constants of whey protein products increased at 27 and 40 MHz, but decreased at 915 and 1800 MHz. Dielectric loss factors of whey protein products increased sharply with increasing temperatures at 27 and 40 MHz, but increased mildly at 915 and 1800 MHz. Similar results were observed with macaroni and cheese. The penetration depths of electromagnetic energy at 27 and 40 MHz were about four times as great as those at the microwave frequencies 915 and 1800 MHz in all tested samples.

Wang et al.[37] also measured dielectric properties of six fruit and nut commodities between 1 and 1800 MHz using an open-ended coaxial-line probe technique and at temperatures between 20 and 60°C. The dielectric loss factor of fresh fruits decreased with increasing frequency at constant temperatures. The loss factor of fresh fruits increased almost linearly with increasing temperature at 27 MHz. Both dielectric constant and loss factor of nuts were very low compared to those of fresh fruits. The temperature effect on dielectric properties of nuts was not significant at 27 MHz.

15.4 MATHEMATICAL SIMULATION OF RF DIELECTRIC HEATING

Due to the complexity of the RF system, where the heating pattern depends on a large number of factors, simulation-based design can save significant time and resources in developing microbiologically safe processes. Such simulation-based design can drastically reduce the number of experiments needed to predict the location of cold points and the time–temperature history at these locations for the actual food and equipment combinations. State-of-the-art commercial software simulating the electromagnetic and heat transfer properties has been used for microwave food process design. Such software can provide a comprehensive insight into the heating process by showing interior power absorption in a three-dimensional object. Simulation-based design can allow the process and equipment designers to judiciously choose proper combinations of food and process parameters in an efficient manner, reducing some of the time and expenses in prototype building.

Based on mass and heat transfer in processed foods, mathematical electromagnetic models for dielectrics can be adapted to model the composite food, packaging, and water barrier layered arrangement. These models can be combined with a two- or three-dimensional electric field finite-difference method (FDM) or finite-element method (FEM) model program described by Ishii[38] and Roussy and Pearce[39] to account for material heterogeneity, field penetration variations, and temperature distribution in whole materials. In addition, the time domain in the modeling needs to be considered. Two currently employed techniques of the time-domain approach to RF heating circuit modeling are the transmission-line matrix (TLM) method developed by Johns[40] and the finite-different time-domain (FDTD) method formulated by Yee.[41] Both techniques are extensively used to analyze electromagnetic structures of arbitrary geometry. FDTD is heavily favored by the scattering problem and radiation, while TLM is used mostly by researchers interested in guided propagation problems. Although they have been developed independently, both methods have been extensively applied to solve similar electromagnetic field diffusion and network problems in the time domain.

15.4.1 Governing Equations

The heat transfer is considered due to conduction within the food material, convection at the material surface, and heat generation due to RF heating. The guiding heat transfer equation in an electromagnetic field is

$$\rho C_p \frac{\partial T}{\partial t} = \nabla(k\nabla T) + Q \tag{15.2}$$

where the RF power absorption density, Q, delivered to the food sample for a given electric field intensity, E, can be described as[39,42]

$$Q = 2\pi f \varepsilon_0 \varepsilon_r'' E^2 \tag{15.3}$$

where $\varepsilon_0\varepsilon_r'' = \varepsilon'.\ \varepsilon_0$ is the permittivity of free space, 8.854×10^{-12} F/m; the subscript r designates the relative energy loss term of permittivity. The electric field intensity, E, is governed by the electromagnetic field and affected by the dielectric properties of samples. Zhao et al.[43] described the modeling of the electromagnetic field, and their determination is discussed in the modeling approach of this chapter. Equation 15.2 can be written as Equation 15.4 in a three-dimensional rectangular coordinate:

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left(k\frac{\partial T}{\partial y}\right) + \frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right) + Q \tag{15.4}$$

Heat generation is a function of temperature and moisture at a particular location (x, y, z). Time–temperature profiles of the food materials in an RF heating system can be predicted using the above models with known thermal and dielectric properties of food samples, as described in Equation 15.2.

In general, mathematical modeling can play a crucial role in the design and optimization of the product and processing parameters during RF heating. The model has to take into account conductive heat transfer, internal heat generation, and convective and evaporative heat losses at the boundaries. The composite model can be developed by combining heat transfer models with dielectric property models in a two- or three-dimensional node. If the material is heterogeneous, assumption about that heterogeneity has to be made to be able to create a two- or three-dimensional finite element model, based on known mesh or grid of electromagnetic field values. In addition, a food sample is usually packaged in plastic or other materials, as well as surrounded by an air layer. Those factors add to the complexity of the model, which becomes a composite model of multiple dielectrics.

The heating time t_h for a given temperature rise (ΔT) is then given by Equation 15.5:[44]

$$t_h = \frac{C_P \rho \Delta \mathrm{T}}{E^2 \omega \varepsilon''} = \frac{C_P \rho \Delta \mathrm{T}}{P_V} \tag{15.5}$$

where C_p = specific heat of the medium (J/kg °C), P_v is the maximum power per unit volume (W/m^3), ω is the angular frequency, $2\pi f$ (rad/sec), and ρ is the density of medium (kg/m^3).

The penetration depth (skin depth) δ at which the field has dropped to 37% of its surface level is approximated by Equation 15.6 for the case of high conduction or dielectric losses:

$$\delta = \frac{\sqrt{2}}{\sqrt{\omega\mu\ (\sigma + \omega\varepsilon'')}} \tag{15.6}$$

15.4.2 Modeling Approach

Mathematical electromagnetic models for layered composite dielectrics can be adapted to model the composite food, packaging, and air–water barrier layered arrangement. These models can then be combined with a two- or three-dimensional electric field FEM model or FDM model program, such as described by Roussy and Pearce[39] and Ishii,[38] to account for any material heterogeneities and field penetration variations. Examples of electromagnetic field FEM programs for complex composite geometrical structures include the High Frequency Structure Simulator (HFSS) and the Maxwell Extractor electromagnetic field solver programs developed by Ansoft, Inc., of Pittsburgh, PA. These programs can solve for electromagnetic field quantities in a FEM mesh or grid (two-dimensional), or in tetrahedral or other shape finite-element blocks (three-dimensional) based on imported arrays of electrical permittivity (both storage and loss terms), electrical conductivity, and magnetic permeability tensors for all the constituent components. They can also be based on mechanical drawings (e.g., AutoCAD.DXF format) of the complex geometrical structures, such as packaged foods.

A separate simulation run will need to be conducted for every value of frequency as well as for every value of temperature, since the dielectric terms are functions of both. The electric field solutions are exported to a program that calculates the power delivered and heat generated for a given time increment in each finite-element block. These arrays of heat generation values can then be used as heat source terms in a FEM or FDM heat transfer conservation of energy program. The energy program also accounts for thermal fluxes between adjacent finite-element blocks based on modeled values for thermal conductivity between blocks, for the thermal heat capacity of the blocks, and for various boundary conditions between the blocks. Then the true temperature rise vs. time can be solved for each FEM block with a two-dimensional model.

The overall computer simulation will iterate cyclically back and forth between the electromagnetic field program and the heat transfer program. Each cycle will correspond to some time increment, and the solution for temperature rise in each FEM block will be used to influence the imported dielectric and conductivity properties for each FEM block in the next run of the electromagnetic field. This overall simulation can then be used to predict the temperature rise vs. time of all the various constituents of the composite packaged samples. By containing the temperature dependence of the dielectric properties of the food and packaging constituents, this model will aid in predicting thermal runaway or hot spots when different heterogeneities are assumed and small thermal mass pockets of lossy dielectric materials exist (e.g., water or food trapped in package seams). The level of complexity of the model will depend on assumptions relating to material homogeneity, composite constituent geometry, and field penetration depth non-uniformity.

Yang et al.[45] investigated the application of a three-dimensional finite-element computer program package, TLM-Food-Heating (FAUSTUS Scientific Corp.,

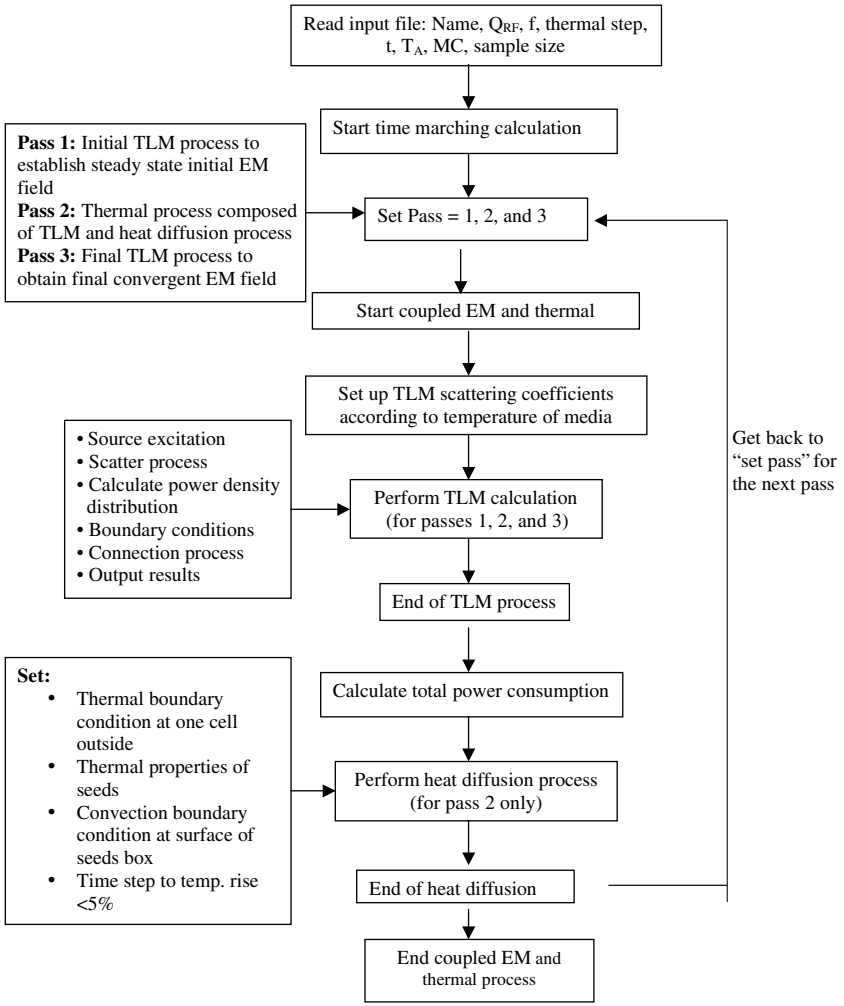


FIGURE 15.4 Flow diagram of the TLM-Food-Heating program. (From Yang, J. et al., *J. Food Process. Eng.*, 26, 239–263, 2003. With permission.)

Victoria, Canada), on the simulation of RF dielectric heating of radish and alfalfa seeds. The flow diagram of the TLM-Food-Heating program is illustrated in Figure 15.4. Seeds placed inside polystyrene boxes were described as a rectangle, where nonuniform boundary conditions presented complications in the simulation. Temperature- and moisture-dependent thermal properties and temperature- and frequency-dependent dielectric properties of seeds were considered in the modeling. The time–temperature profiles of seeds at different locations within the rectangle seed boxes were simulated. The model was then validated using

experimental data. Simulated temperature distribution in seeds was consistent with the measured results. The absolute temperature differences between simulated and measured values in radish seeds packed in a $100 \times 25 \times 50$ mm rectangle seed box were 1.8, 1.1, 8.9, and 13.6°C in the center, top, edge, and bottom locations, respectively, when seeds reached about 80°C, and were 0.9, 2.4, 7.75, and 14.3°C, respectively, in an alfalfa seed box in the same conditions.

15.5 PASTEURIZATION AND STERILIZATION OF FOODSTUFFS USING RF DIELECTRIC HEATING

RF dielectric heating has been used in the food industry with proven processes available for a wide range of applications (Table 15.2), including heating packaged bread,[46,54] blanching vegetables,[5] thawing frozen foods,[7,8,46,47,55] baking and postdrying snack foods,[3,4,10,11] and pasteurizing and sterilizing processed meat products.[48–51]

The interests in using RF dielectric heating to pasteurize and sterilize foodstuffs have increased as a result of its capability for achieving rapid and uniform heating. It is anticipated that RF dielectric heating will probably serve as an improved means of producing higher-quality, shelf-stable foods for civilian and military use.[52]

The study of RF pasteurization of meats dates back to the 1950s. Pircon et al.[53] described a process for diathermal (energy generated by combination of the ionic and molecular mechanisms) sterilization of boned ham at 9 MHz. Based on fundamental studies of capacitance and conductivity of cured luncheon meats, they designed test cells (into which hams were placed in Pyrex tubes between steel electrodes) using an expansion follower plate for the hot electrode to take up pressure caused by expansion of the meat. Due to the high conductivity of the meat, the tubes had to be made long and narrow. Experiments were also conducted with plastic-walled cans with concentrically corrugated metal caps as the electrodes. An industrial-model 15-kW oscillator with 9 kV across the plates and operating at 9 MHz was used. They achieved energy conversion efficiency of 56.6%, and reported that ~2.7-kg pieces of ham could be heated to sterilization temperature (~80°C) in about 10 min. However, the process had not been used commercially, probably because of high costs and problems with designing processing cells or cans suitable for large-scale operation in the 1950s. Also, after processing, the ham had to be transferred under aseptic conditions to separate containers for supplementary surface heat treatment.

In the late 1960s, Bengtsson and Green[48] developed continuous RF pasteurization of cured hams packaged in Cryovac casings at 60 MHz. They used a generator of 1-kW output and a conveyor for feeding the material between the electrodes of the load condenser. The frequency could be shifted between 35 and 60 MHz by a simple modification of the circuit. They obtained power efficiency of about 25% at 60 MHz, and with knowledge of the dielectric properties of the material, the power efficiency could have been improved by proper design of the generator. Results showed that for lean 0.91-kg hams, treatment time to reach the desired central temperature of 80°C could be reduced to 1/3 by heating in a condenser tunnel

TABLE 15.2
Summary of Applications of Capacitive (RF) Dielectric Heating in Food Materials

Applications	Frequency (MHz)	Processing Temperature(°C)	Processing Time	Advantages	Food Items	References
Heating	14–17	~52–66	20–59 sec	Killing mold, refreshing stale bread	Bread	46
Blanching of vegetables	150	100	3 min	Limiting loss of nutritive value	Fruits, vegetables	5
Thawing of frozen foods	14–17 36–40 35	>1.67	2–15 min 34 min	Maintaining color and flavor of thawed foods, faster thawing, less drip loss	Egg, fruits, vegetables, fish, beef blocks, sausage, pies, bacon	7, 8, 46, 47
Baking and postbaking	27.12	~100	—	Rapid drying, improved color and flavor	Crackers, cookies, bread	3, 4, 10, 11
Pasteurizing and sterilizing of foodstuffs	9 27 60	~80	~10 min	Improved sensory quality, reduction of juice losses	Cured ham, sausage emulsion, meat loaf, military ration, polymeric tray food	48–53

Source: Modified from Zhao, Y. et al., *J. Food Process. Eng.*, 23, 25–55, 2000.

operating at 60 MHz. Results also showed substantial reduction of juice losses and a tendency to improve sensory quality compared with hot-water processing.

Houben et al.[50,51] described RF pasteurization of moving sausage emulsions. They performed stationary heating tests at 27 MHz, with sausage emulsions of varying formulations stuffed in tubes (inner diameter of 50 mm) made of different materials. The integrated 27-MHz heating station consisted of two Colpitt generators with power levels of 25 and 10 kW, both equipped with a heating unit. They found that polytetrafluoroethylene (PTFE), polycarbonate, and borosilicate glass performed well as tube materials, but polyvinyl chloride (PVC) and polyvinyliden chloride (PVDC) both heated selectively, and therefore could not be used in RF heating. They also found that energy absorption in the working load could be drastically increased by surrounding the tube with demineralized water instead of air. The time required to heat a sausage emulsion from 15 to 80°C at a mass flow of 120 kg/h was about 2 min. By using RF energy, a heating rate of up to 40°C/min was achieved, compared to about 1°C/min in the center of a sausage during a conventional process (product diameter of 50 mm). The overall energy efficiency (power effectively absorbed in the mass to be heated divided by the power supplied from the mains to the generator) was around 30%, a value the authors thought could probably be improved, especially in designing the generator–heating unit combination. Sausage products heated using RF energy had a good appearance, smooth surface, and did not show moisture or fat release.

Proctor Strayfield at Horsham, PA, developed a Magnatube pasteurization system[2] that demonstrated success in the cooking/sterilization of scrambled eggs, as well as in the creation of a skinless meat loaf from a pumped slurry using a vertical 100-mm-diameter tube system. The slurry entered from a meat pump at the base of the tube, passed up through the electrode system, and emerged as a skinless meat loaf at the top of the heating tube. An extremely uniform temperature distribution across the heated product was achieved, with very good yield.

Recently, a study was conducted with a pilot-scale 6-kW, 27-MHz RF system (COMBI 6-S; Strayfield Fastran, U.K.) to investigate the effectiveness in shortening process time and improving quality for foods sealed in 6-lb military-ration polymeric trays.[52] The applicators and tuning system were modified to improve the electromagnetic field uniformity between the two plate applicators. A pressurized vessel was developed to provide an overpressure of up to 0.276 MPa gauge that allows foods in large polymeric trays to be heated up to 135°C without bursting (Figure 15.5). The system consisted of two exchangers: one used steam for heating, and the other used tap water for cooling. A surge tank was used to help maintain an overpressure with compressed air. The circulating water temperature could be varied from 20 to 130°C, an overpressure from 0.136 to 0.204 MPa gauge (20 to 30 psig). To reduce a fringe effect at the interface between the side of the food package and the air in the RF applicators, low-conductivity water was used to immerse the food tray to approximately match the dielectric properties of the food. Together, the water and package present a very flat surface to the imposed field and push the boundary with air away from the food package. This is expected to reduce the effect of variations in package thickness that could lead to nonuniform heating in the food. Temperature-controlled water from a

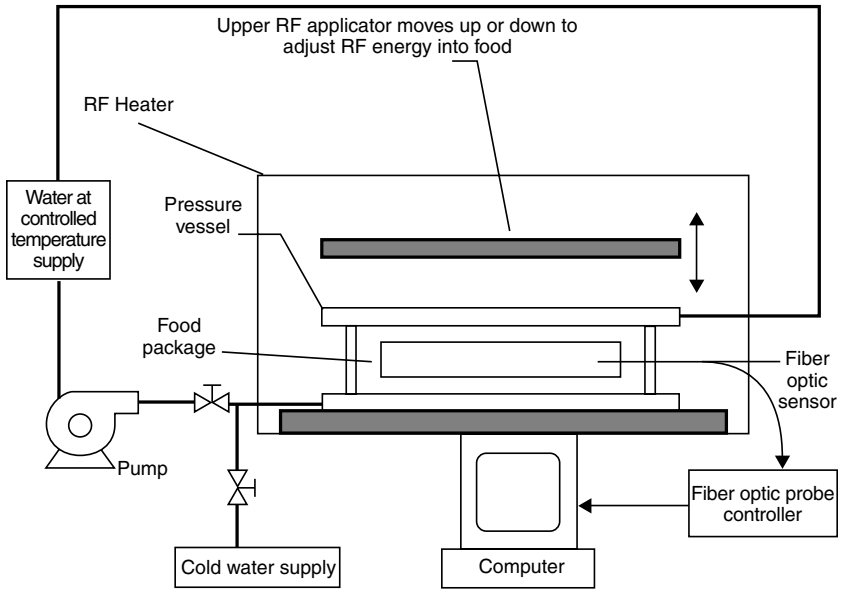


FIGURE 15.5 Simplified schematic diagram of the RF sterilization system developed at Washington State University (Pullman, WA). (From Wang, Y. et al., *J. Food Sci.*, 68, 539–544, 2003. With permission.)

water-conditioning system is used to match the temperature of the heated food to prevent cooling of the package surface. The chemical marker *M-1* was used to evaluate heating uniformity in 20% whey protein gels as a model food, and macaroni and cheese was processed to assess the influence of the RF process on product quality. With the RF system, a lethality (F_0 = 10 min) on *Clostridium botulinum* spores was achieved in both model food and macaroni and cheese within 30 min with relative uniform heating, compared to a 90-min conventional retort process that delivered a similar lethality.

The potential for controlling human pathogens on alfalfa seeds, used in production of sprouts by RF heating at 39 MHz, was studied by experimental exposure of alfalfa seeds, which were artificially contaminated with *Salmonella*, *E. coli* O157:H7, and *Listeria monocytogenes*.[56] Significant reductions in the populations of all three pathogens were achieved without reductions in seed germination. However, the desired levels of reduction in bacterial populations (5 log CFU/g) were not achieved without severe reductions in germination of the alfalfa seed. Bacterial reductions appeared better when the seed moisture content at the time of treatment was in the 5 to 7% (wet-base) range than at higher moisture levels. The study also confirmed that seeds can tolerate higher temperature without damage to viability when moisture contents at the time of dielectric

heating are lower. The study concluded that RF dielectric heating treatments can increase the germination of alfalfa seed lots with substantial hard-seed content, thus increasing sprouting yield, without abrasion of the seed coat, and the process might be considered for this purpose as well as for reduction of the human pathogen population in sprouting seeds.

Despite the research, commercial RF dielectric heating systems for the purpose of food pasteurization or sterilization are not known to be in use. The reasons for the lack of success in commercial operation are complexity, expense, nonuniformity of heating, inability to ensure sterilization of the entire package, lack of suitable packaging materials, and unfavorable economics when compared to prepared frozen foods in the U.S.[57]

15.6 TECHNICAL CHALLENGES AND ENERGY EFFICACY OF RF APPLICATIONS IN FOODSTUFFS

A number of potential problems need to be addressed before the RF technology can be successfully commercialized to food pasteurization and sterilization, especially packaged foods. The major technical challenges include avoiding dielectric breakdown (arcing) and thermal runaway heating, which can lead to both packaging failure and product destruction. In addition, economic constraints exist that inhibit the use of the technology in its present form.

The effectiveness of RF dielectric heating is highly dependent on the products' dielectric properties, which are in turn strong functions of both frequency and temperature. The energy efficiency or heating rate will be maximized at or near the location in frequency of a Debye resonance — the frequency at which the dielectric loss factor is at the maximum for a particular material. Multiple Debye resonances might occur in a product made up of many different materials, causing the packaging materials to overheat or even burn, resulting in packaging failure.

15.6.1 Radio Frequency Dielectric Breakdown (Arcing) and Thermal Runaway Heating

One potential problem of RF dielectric heating is the potential for thermal runaway or hot spots in a heterogeneous medium. Sanders[47] mentioned that in most applications of dielectric heating to food, runaway heating is unavoidable if contacts with both electrodes are maintained. Dielectric loss factors are often strong functions of temperature. Thus, small pockets of lossy dielectric food materials (e.g., a small thermal mass trapped in the seams of a package) might heat very rapidly, burning and then melting the package. Another problem is the potential for dielectric breakdown (arcing) if the electric field strength across the sample is too high. This can be complicated by surface irregularities and edge effects of the surface in contact with the electrodes.[47]

Cathcart et al.[46] found that while heating packaged bread using RF power, arcing occurred between the upper electrode and the edges of the cylindrical loaf, resulting in some burning at those points. This difficulty was overcome by rounding the edges of the loaf so that there were no corners adjacent to the electrodes. Moyer and Stotz[5] indicated that when blanching vegetables at 7, 10, and 30 MHz, arcing and burning occurred between the upper electrode and the vegetables, and between the individual particles, due to the high voltages at the electrodes. By decreasing voltage (lowering the electric field across a given sample thickness) while increasing frequency to 150 MHz to maintain the same output power density in the medium, the arcing problem was solved. Sanders[47] further demonstrated the significance of using an air gap between the top electrode and the upper material surface to lower the voltage, and therefore the electric field across the sample thickness. By introducing an air gap, some of the voltage between the electrodes appears in this gap, the exact amount depending on the relative heights of the gap and of the material, and on the dielectric properties of the material. The effective voltage is reduced by a factor f_p:[47]

$$f_p = [(\varepsilon_r \tan\delta\, h_a/h_s)^2 + (\varepsilon_r\, h_a/h_s + 1)^2]^{-1/2} \tag{15.7}$$

where ε_r is the relative permittivity (or dielectric constant, $\varepsilon_r = \varepsilon'/\varepsilon_o$), and h_a and h_s are the heights of the air gap and material (m), respectively. Sanders[47] also noted that arcing could be controlled by immersing the product in deionized water or surrounding it with ice, thus minimizing field distortions due to any irregularities, and again lowering the voltage or effective electric field across the sample thickness. Dielectric breakdown (arcing) and thermal runaway heating were also observed during preliminary tests to heat-packaged surimi seafood in a commercial RF oven.[58]

15.6.2 Packaging Failure

When using RF power to heat packaged food products, it was found that certain packaging materials failed in an RF field. When heating packaged bread, Cathcart et al.[46] found that some wrappings, including wax and glassing paper, were unsatisfactory. Wax paper softened when bread showed an internal temperature above 38°C, and glassing papers became tacky between 52 and 60°C. However, they found that cellophane is a satisfactory wrapping material because it did not break or become unsealed in any of the heat treatments employed. As stated before, Houben et al.[50,51] found that PTFE, polycarbonate, and borosilicate glass performed well as tube materials when using RF power to pasteurize sausage emulsion; however, PVC and PVDC both heated selectively (due to their polar molecular structures), and therefore could not be used in RF heating. Burning of packaging material was also observed under some conditions during preliminary tests with RF heating of vacuum-packaged surimi seafood.[58]

Thus, a major challenge in the use of RF power to pasteurize and sterilize packaged food products is avoiding packaging failure or modification by selecting

satisfactory packaging materials. This requires a full understanding of the dielectric properties of packaging material over a range of frequencies and temperatures. Moreover, it is important to avoid any factors that may cause high local power densities, such as the concentration of a small amount of food/water within the seam of the packaging material. This could result in a small thermal mass combined with a large dielectric loss factor being exposed to a potentially large localized voltage gradient or electric field.

Two patent technologies may help to solve some of the problems that RF heating faces in food pasteurization and sterilization.[59,60] Frequency could be controlled to match Debye resonances of the dominant constituents of the medium, adjusting appropriately with temperature and continually controlling electric field strengths.[59] Product geometry and packaging materials could be optimized to prevent dielectric breakdown (arcing), although packaging methodologies would have to ensure that food could be kept out of the seams. The electrode system could also be developed to lower the field strengths on the packaging seams. To prevent or reduce the risk of thermal runaway, a gridded electrode system could be developed with an infrared scanner to monitor the overall medium. This would add the capability of heating subcomponents of the medium independently with different field strengths, or even switching off some of the electrode sections in different duty cycles to prevent hot spots.[59,60]

15.6.3 Energy Efficiency and Economic Analysis

Many concerns have been raised about the potential high overall operational cost of using RF dielectric heating in food processing, which has delayed the commercialization of this technology. Although no complete investigation on economic analysis has been conducted, several studies show estimated data of energy efficiency and cost.[1,7,47,48,50,53]

Kinn[1] illustrated the cost in dollars per hour for operating various-size standard RF generators and the cost of RF power in dollars per kilowatt for the various generators. Pircon et al.[53] reported that an average energy conversion efficiency (comparing the thermal energy output to the electrical energy input) of 56.6% can be achieved for a 15-kW and 29-MHz generator. An approximate cost analysis indicated an electricity cost of $0.00722/kg of meat compared to a steam cost of $0.0026/kg of meat, based on a 910-kg batch. Pircon et al.[53] believed that because of the sliding cost scale for electricity, a large volume of meat would bring the costs closer together. In addition, a continuous dielectric process would not involve any losses between batches, as would a steam process. Jason and Sanders[7] did some economic analysis of thawing using RF energy and concluded that the cost of dielectric thawing is about one eighth that of freezing, and only a very small fraction of total cost. Sanders[47] reported that a value of 0.2 kW/kg has been shown to be a suitable (though not necessarily the maximum) power density for thawing blocks of meat. Bengtsson and Green[48] reported that using RF power to pasteurize ham, the highest power efficiency that could be obtained (with salted ham in the generator–electrode combination used) was 25%, but 50 to 60% would

be required in an industrial application. They believed that with knowledge of the dielectric properties of the materials to be heated, this higher level of power efficiency could be achieved through proper design of the generator. In the RF pasteurization of sausage emulsions, Houben et al.[51] found that optimum overall energy efficiency, defined as power effectively absorbed in the mass to be heated divided by the power supplied from the mains to the generator, was somewhat higher than 30%, and could probably be improved by careful design of the generator–heating unit combination.

New technology and quantity production in manufacturing facilities have reduced the cost of equipment and operations. Many of these RF applications may now be considerably economically sound. In addition, RF dielectric heating has the potential to improve the quality of food products, and this improvement must in some way be evaluated in the economic study. Newer technologies available for RF dielectric heater application systems, such as synthesizers, broadband RF amplifiers, and tunable matching networks, offer the promise of greater energy efficiency due to the ability of the system to tune to the optimum Debye resonance frequencies of a heated medium. In addition, greater control of the applied voltage and resulting electric field will lead to the reduction of arcing and thermal runaway problems inherent in older RF heating systems. Most of the published economic studies conducted on RF heating focused on older technologies under greatly different economic circumstances. For that reason, there is a need for an updated economic analysis on RF heating that takes into account the latest technological improvements, as well as the economic conditions in place in today's marketplace.

15.7 CONCLUSIONS

RF dielectric heating technology has vast potential applications in the food industry. The rapid and uniform heating patterns of RF energy are very attractive for providing safe, high-quality food products. To maximize the performance of an RF dielectric heating system and to move the technology to commercial pasteurization and sterilization of foodstuffs, the following areas of research are necessary:

- To understand more about the effects of food formulation on heating patterns
- To study the effects of equipment design factors, such as frequency to achieve better uniformity of heating
- To develop variable-frequency RF systems for improved uniformity of heating
- To understand the factors affecting heating patterns, including qualitative changes occurring with frequency changes
- To monitor and real-time adjust for process deviations in RF processing

NOMENCLATURE

α	Thermal diffusivity (m^2/sec)
C_p	Specific heat (kJ/kg °C)
δ	The penetration depth (skin depth) δ at which the field has dropped to 37% of its surface level in Equation 15.6
E	The strength of electric field of the wave at the location permittivity or dielectric
ε_0	The permittivity of free space in Equation 15.3, 8.854×10^{-12} F/m
ε'	Energy storage term of permittivity
ε''	Energy loss term of permittivity: $\varepsilon_0 \varepsilon_r'' = \varepsilon''$; the subscript r designates the relative permittivity
ε_r	Relative permittivity (or dielectric constant, $\varepsilon_r = \varepsilon'/\varepsilon_0$) in Equation 15.7
f	The frequency of the radio frequency waves (Hz)
h	The heat transfer coefficient (W/m^2 K)
h_a, h_s	Heights of the air gap and the material (m) in Equation 15.7
j	Constant and $j = \sqrt{-1}$
k	Thermal conductivity (W/m °C)
Pv	Maximum power per unit volume (W/m^3) in Equation 15.5
Q	RF power absorption density (W) in Equation 15.2
ρ	Density (kg/m^3)
T	Temperature in the food samples (°C)
∇T	Temperature gradient
$\partial T/\partial n$	Temperature gradient in n direction (K/m)
t	Time (sec)
ω	Angular frequency = $2\pi f$ (rad/sec) in Equation 15.5
(x, y, z)	Three dimensions in x, y, and z directions (m)

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16 Infrared Heating

Noboru Sakai and Weijie Mao

CONTENTS

16.1 INTRODUCTION

In thermal processing in the food industry, conduction and convective heat transfer have mainly been used, and as a radiant heat transfer, *infrared radiation* (IR) of short wavelength, such as solar light and an infrared lamp, has been used. Recently, interest in heating by *far-infrared radiation* (FIR) has increased owing to the development of commercial FIR heaters, which have high emissivity in the infrared region of long wavelength.

It is considered that meat and fish cooked by charcoal or bread baked in a stone oven are more delicious than those cooked or baked in a usual gas oven. However, these heating methods are not suitable in industrial production with

respect to the cost. Heating using FIR heaters is a heating method that is similar to the charcoal or stone oven, and thus it may produce delicious foods. In addition, recent developments in FIR equipment offer rapid and economical methods for manufacturing food products with high organoleptic and nutritional value.

In FIR heating, heat is supplied to food by electromagnetic radiation from the FIR heaters. The rate of energy transfer between the heater and the food depends on the temperature difference between the heater and the food. The FIR energy emitted from the heater passes through air and is absorbed by the food; the energy is then converted into heat by interaction with molecules in the food. Heat passes throughout the food from the surface layer by conduction. The related process of near-infrared radiation (NIR) heating is based on the same principle, using the appropriate wavelength. On the other hand, in conventional heating, heat is mainly supplied to the surface of the food by convection from circulating hot air and products of combustion.

The difference of heating mechanism between IR and conventional heating makes the difference in cost and quality of the products. The features of IR heating for food processing are as follows:

- The efficient heat transfer to the food reduces the processing time and energy costs.
- The air in the equipment is not heated, and consequently the ambient temperature could be kept at normal levels.
- It is possible to design compact and automatic constructions with high controllability and safety.
- Exact heating control is required, because there is danger of overheating owing to the rapid heating rates.

16.2 BASIC PRINCIPLES OF INFRARED HEATING

Infrared energy is a form of electromagnetic energy. It is transmitted as a wave, which penetrates the food, and is then converted to heat. Infrared radiation is classified as the region of wavelength between visible light (0.38 to 0.78 μm) and microwaves (1 to 1000 mm). Furthermore, infrared radiation is divided into three classes[1] according to the wavelength, as shown in Figure 16.1. However, the classification presented in Figure 16.1 is not established universally. The wavelengths of the electromagnetic energy emitted from industrial FIR heaters are mainly in the range of 2.5 to 30 μm.[2] Hence, FIR heating usually means irradiative heating at wavelengths of 2.5 to 30 μm. The peak wavelength, at which the maximum energy is irradiated from the heater, is determined by the temperature of the heater. This relationship is described by the following basic laws.

16.2.1 Plank's Law

When a black body is heated to a temperature *T*, electromagnetic energy is emitted from the surface. This energy has a definite distribution, which is represented by

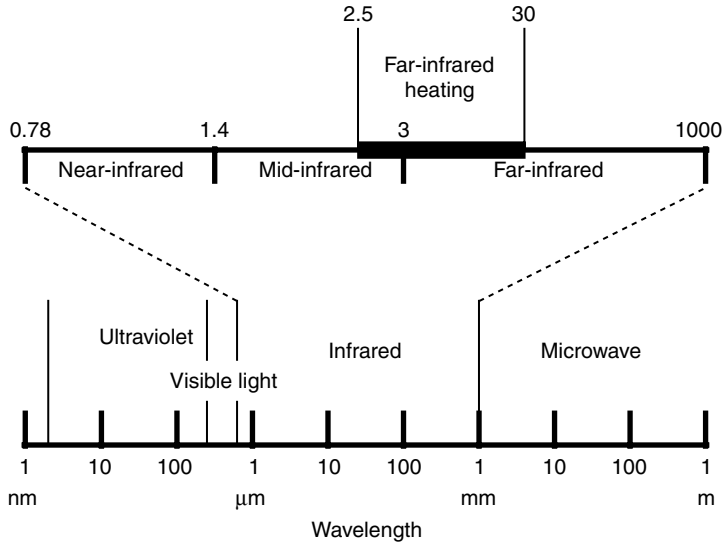


FIGURE 16.1 Classification of infrared radiation.

Plank's law. Plank's law gives the energy flux E_λ irradiated from the black body in the wavelength range λ to $\lambda + d\lambda$:

$$E_\lambda = \frac{2\pi c^2 h}{\lambda^5} \frac{d\lambda}{\exp(ch/\kappa\lambda T) - 1} \tag{16.1}$$

where h is *Plank's constant*, c is the velocity of light, κ is Boltzmann's constant, and T is the absolute temperature in degrees Kelvin (K). A plot of Equation 16.1 is given in Figure 16.2 and shows that the radiation energy increases as the temperature of a black body rises.

16.2.2 Wien's Displacement Law

It is proven from Figure 16.2 that the peak wavelength, λ_{max}, in which the radiation energy becomes a maximum, shortens with the rise in the temperature. The relationship between λ_{max} and T can be determined by differentiating Equation 16.1 with respect to λ at constant T and setting the result equal to zero:

$$\lambda_{max} = \frac{2898}{T} \tag{16.2}$$

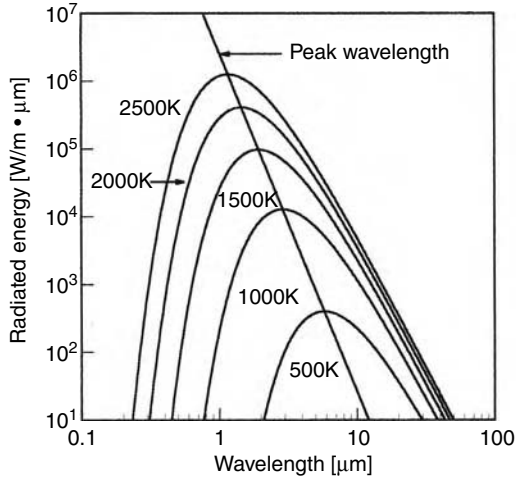


FIGURE 16.2 Spectral characteristics of black body radiation at different temperatures.

16.2.3 Stefan–Boltzmann Law

The total emissive energy radiated from a black body with temperature T is given by the integral of Equation 16.1 over all wavelengths:

$$E_b = \int_0^\infty E_\lambda d\lambda = \frac{2\pi\kappa^4 T^4}{c^2 h^3}\left(\frac{\pi^4}{15}\right) \equiv \sigma T^4 \tag{16.3}$$

This is known as the Stefan–Boltzmann law, and σ ($= 5.670 \times 10^{-8}$ W/m$^2 \cdot$K^4) is the Stefan–Boltzmann constant. This law shows that the radiation energy of a black body is proportional to the fourth power of its temperature.

The energy emitted from an actual material such as an infrared heater or food is smaller than that emitted from a black body at the same temperature. This efficiency is represented as the emissivity of the material, ε, which is defined as the total radiated energy of the material divided by the total radiated energy of the black body:

$$\varepsilon = \frac{E}{E_b} = \frac{E}{\sigma T^4} \tag{16.4}$$

The equation can be rewritten

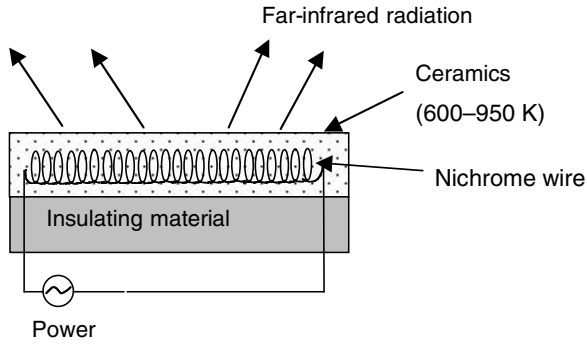
$$E = \varepsilon\sigma T^4 \tag{16.5}$$

ε is a number between 0 and 1, and materials or bodies obeying this equation are called *gray bodies*.

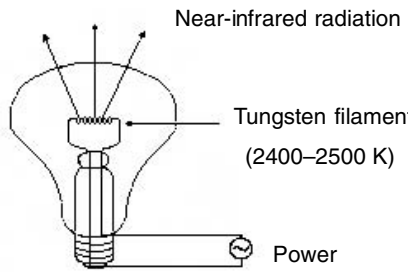
A black body also absorbs the energy, according to the same law, Equation 16.1, and gray bodies absorb a fraction of the quantity that a black body would absorb, corresponding to their absorptivity, β. Under thermodynamic equilibrium, the monochromatic emissivity and absorpitivity of a body are equal from Kirchhoff's law. The fraction of the incident energy that is not absorbed is reflected, corresponding to their reflectivity, γ. The relationship between these fractions is shown by the following equation:

$$\varepsilon = \beta = 1 - \gamma \tag{16.6}$$

As the temperature of the heater is raised, the amount of radiant energy delivered to the food increases and the peak wavelength decreases. Since the maximum running temperature of FIR heaters, which are usually made from fine ceramics (Figure 16.3a), is 600 to 950 K, the peak wavelength is 3 to 5 μm.[3] In NIR heating, the maximum temperature for a short-wave radiator such as a *tungsten filament lamp* (Figure 16.3b) is 2400 to 2500 K, which corresponds to a peak wavelength of 1.1 to 1.3 μm.[4]



(a) Ceramic FIR heater



(b) IR ramp

FIGURE 16.3 Schematic diagrams of FIR heater and IR ramp.

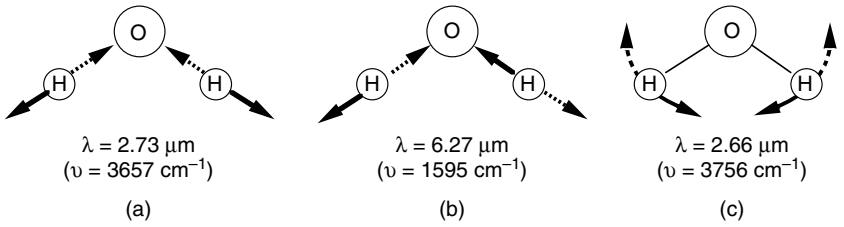


FIGURE 16.4 Normal vibration of water.

When radiant electromagnetic energy impinges upon a food surface, it may induce changes in the electronic, vibrational, and rotational states of atoms and molecules. The kinds of mechanisms for energy absorption are determined by the wavelength range of the incident radiative energy:[2] changes in the electronic state correspond to wavelengths in the range of 0.2 to 0.7 μm (ultraviolet and visible light), changes in the vibrational state correspond to wavelengths in the range of 2.5 to 100 μm (FIR), and changes in the rotational state correspond to wavelengths above 100 μm (microwaves).

Generally, food has been composed of water and organic compounds such as carbohydrates, proteins, and fat, and the infrared absorption characteristic of those materials is important. The normal vibration of water is represented as follows:[2] (1) the symmetrical stretching vibration, (2) the antisymmetric stretching vibration, and (3) the symmetrical deformation vibration, as shown in Figure 16.4. These vibrational frequencies, namely, the wave number, are shown in the figure. The IR energy in proportion to these frequencies is efficiently absorbed in a body. Therefore, food absorbs the IR energy at wavelengths greater than 2.5 μm most efficiently through the mechanism of changes in molecular vibration state, which can lead to heating.

16.3 ATTENUATION FACTOR AND PERMEABILITY

The penetration of infrared energy into the food is an important factor to discuss with regard to infrared heating.

The incident energy would be partly reflected and transmitted at the air–food boundary. The energy transmitted into the food is attenuated exponentially with penetration distance. The attenuation factor determines the energy absorption within the food as a function of depth from the surface of the food, as described by Lambert's law:

$$I_\lambda = I_{\lambda 0} \exp(-\alpha_\lambda x) \tag{16.7}$$

where I_λ is the energy flux at the wavelength of λ and α_λ is the spectral attenuation factor. The attenuation factor of water, which is shown in Figure 16.5, changes remarkably with wavelength. For example, α_λ =0.355, 10800, and 2138 cm^{-1} when λ =1, 3, and 6 μm,[5] respectively.

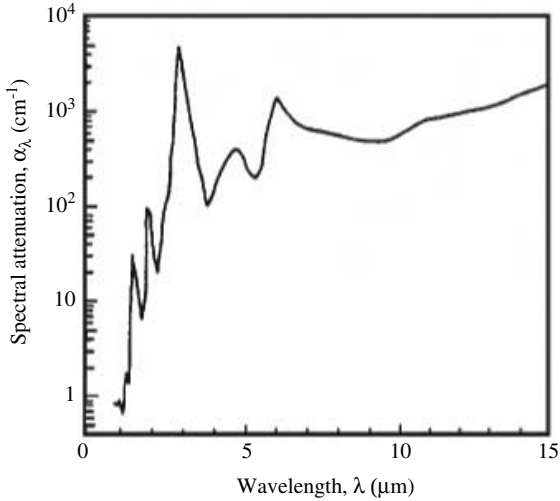


FIGURE 16.5 Absorption coefficient of water. (Courtesy of A. Hashimoto, Mie University, Mie, Japan.)

The *spectral transmittance* is defined as a ratio of the incident energy, and its transmission is as follows:

$$\gamma_\lambda(x) = I_\lambda / I_{\lambda 0} = \exp(-\alpha_\lambda x) \tag{16.8}$$

From the above equation, the penetration distances in which the spectral transmittance becomes 0.01 are 12.97 cm, 4.26×10^{-4} cm, and 2.15×10^{-3} cm, for = 1, 3, and 6 μm, respectively. This indicates that the permeability of IR energy is greatly dependent on the wavelength.

Since the energy irradiated from an IR heater has distribution, the average permeability has to be calculated by integrating the equation over the full wavelength:

$$\gamma_{av}(x) = \frac{\int_0^\infty I_\lambda d\lambda}{\int_0^\infty I_{\lambda 0} d\lambda} = \frac{\int_0^\infty \exp(-\alpha_\lambda x) d\lambda}{\sigma T^4} \tag{16.9}$$

The average permeability changes corresponding to the heater temperature, since emitted energy I_0 changes with temperature. Figure 16.6 shows the calculated average permeability in assuming the attenuation factor to be the value of water. It is proven in Figure 16.6 that the permeability of IR decreases as the radiator temperature is reduced.

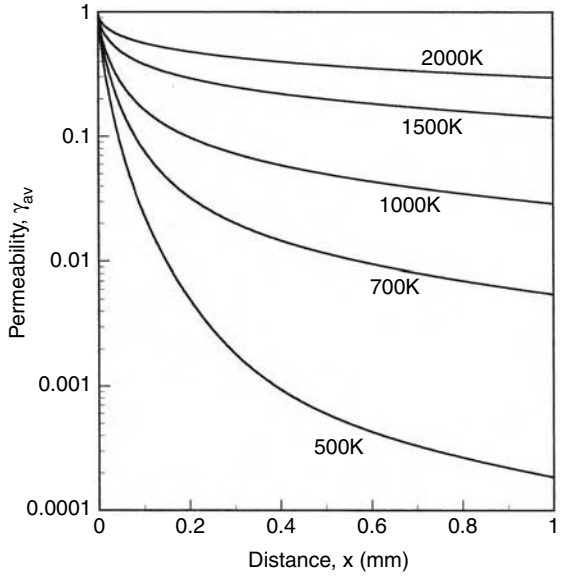


FIGURE 16.6 Average permeability of energy emitted from different temperature radiators.

Regarding the features of FIR, there are reports of two different standpoints: (1) the energy is almost absorbed in the surface vicinity, and the penetration could be neglected, and (2) the energy permeates to the food inside and can uniformly heat the food. Using two different models, the effect of the permeability of the IR on the temperature distribution in the food could be shown.[6]

16.3.1 Energy Penetration Model (Model 1)

The IR energy was considered to be irradiated from the top surface of a cylindrical sample and to penetrate in the axial direction, while it is converted to heat energy, as shown in Figure 16.7. A heat transfer equation with a term of internal heat generation is represented by the following:

$$\frac{\partial T}{\partial t} = \alpha\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \frac{\partial^2 T}{\partial z^2}\right] + Q \tag{16.10}$$

where Q is the internal heat generation term, which can be described by the following based on Lambert's law:

$$Q = -\frac{dI}{dx} = \int_0^\infty a_\lambda I_{\lambda 0} \exp(-a_\lambda x) d\lambda \tag{16.11}$$

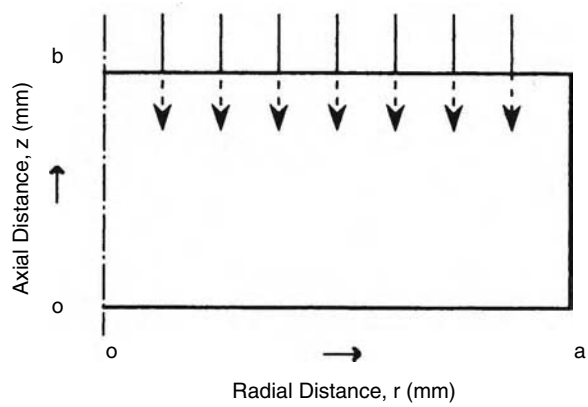


FIGURE 16.7 Penetration model of radiation energy.

The surface energy flux with wavelength λ, $I_{\lambda 0}$, is represented by the following based on Plank's law:

$$I_{\lambda 0} = \phi \left[\frac{2\pi c^2 h}{\lambda^5} \frac{d\lambda}{\exp(ch/\kappa\lambda T_h) - 1} - \frac{2\pi c^2 h}{\lambda^5} \frac{d\lambda}{\exp(ch/\kappa\lambda T_f) - 1} \right] \tag{16.12}$$

where ϕ is the overall absorption coefficient, which can be estimated from a radiation shape factor, F_{21}, the emissivity of the IR heater, ε_1, and the emissivity of food, ε_2, as follows:[6]

$$\phi = \varepsilon_1 \varepsilon_2 F_{21} \tag{16.13}$$

16.3.2 Surface Absorption Model (Model 2)

Assuming that irradiated energy is all converted to thermal energy at the surface without permeating to the inside of food (Figure 16.8), the fundamental equation is represented by the simple heat conduction equation:

$$\frac{\partial T}{\partial t} = \alpha \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \right] \tag{16.14}$$

Heat generation term by infrared radiation is included in the boundary condition, by using the Stefan–Boltzmann law:

$$\text{At } z = Z, \qquad k \frac{\partial T}{\partial z} = -h(T - T_a) + \sigma\phi(T_h^4 - T^4) \tag{16.15}$$

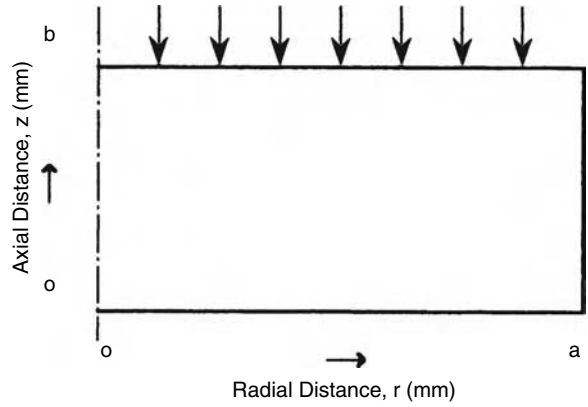


FIGURE 16.8 Surface absorption model.

In order to compare the two models, numerical calculation was performed by using a finite-element method to solve the fundamental equation. Figure 16.9 shows the temperature history of the cylindrical sample at the points of axial direction. Calculation conditions were as follows: the IR heater temperature, 500 K; the ambient temperature, 293 K; the initial temperature of the sample, 278 K; and the overall absorption coefficient, 0.4. The lines and points in the figure represent

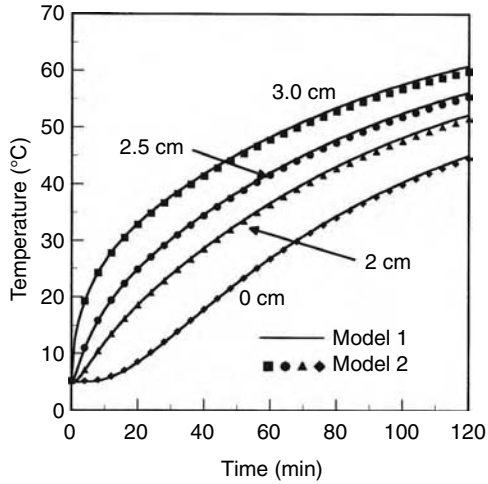


FIGURE 16.9 Comparison of calculated temperature histories between the two models at 500 K.

the calculated temperature based on the energy penetration model (Model 1) and that based on the surface absorption model (Model 2). In the energy penetration model the attenuation factor was adopted from the value of water. The calculation results according to the two models almost agree, though there are some differences in the surface temperatures. This indicates that at the temperature range of which FIR is mainly irradiated, the heat source term can be included in the boundary condition. This boundary condition could be used in the modeling of heat transfer in the food heated by FIR.[7]

In assuming the IR heater temperature to be 1500 K, the temperature histories of the cylindrical sample are shown in Figure 16.10. The overall absorption coefficient was assumed to be 0.02, so that the temperature rise may become similar to that of 500 K. In the case of a high-temperature radiator, such as an *IR ramp*, the overall absorption coefficient is small, because the shape of the heat source is mainly a thin wire (filament), and then the radiating area is small. In the penetration model (Model 1), the surface temperature is lower than that of Model 2 and the difference between the central and surface temperature decreases, since the energy permeates into the food.

This difference of the permeability of IR greatly affects the quality of food during a heating process. In a cooking or baking process, it is important to properly control the physical change, such as crust formation, protein metamorphism, and fat melting, as well as burning colors of the surface and moisture profile in the food. The rapid surface heating of foods by FIR can be used to seal in moisture (or water), fat, and aroma compounds without burning the surface, and results in products with highly acceptable sensory characteristics.

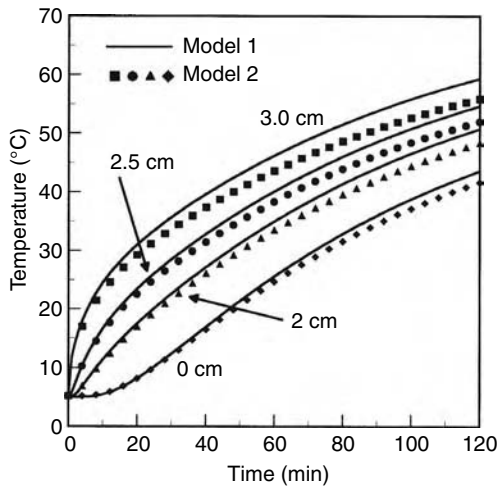


FIGURE 16.10 Comparison of calculated temperature histories between the two models at 1500 K.

16.4 APPLICATIONS

The IR heating technique is widely used in nonfood industries, such as the automobile industry and electronics industry, for heating and drying purposes. In these fields, the NIR heater, which is a high-temperature radiator, is used, because high energy is required. On the other hand, in food processing, the FIR heater is used more than the NIR heater because high-load energy damages the food, and the energy is efficiently absorbed in the wavelength range of FIR. In this section, the application of FIR to the food industry is mainly described.

Industrial food applications of FIR heating may be classified into four major unit operations: baking (roasting, cooking), drying, thawing, and pasteurization. Although FIR has been used in other operations, for example, in the aging of liquors[8] and the frying of snack foods,[9] in this chapter we concentrate on FIR applications in the four major unit operations.

16.4.1 Baking (Roasting) and Cooking

Many examples of baking, roasting, and cooking of foods by IR have been reported in the literature, and some have been successful in practical applications: baking of bread[10,11] and cookies,[12,13] roasting of coffee[14] and green tea,[15] cooking of beef patties,[16,17] roasting of edible seaweed,[18] heating of legume seeds,[19] etc.

As a feature of IR heating, the efficient heat transfer to the food reduces the baking time, and infrared ovens may consume less energy than conventional electric or gas ovens. Wade[20] tested biscuit baking using NIR and reported that biscuits could be baked in approximately half the time required in a conventional oven. In a cooking process of meat products, Sheridan and Shilton[21] reported that the gas consumption when using the longer-wavelength infrared source was reduced by 55% over that for the shorter-wavelength, higher-energy source.

Table 16.1[22] compares the performance of FIR and conventional ovens and reveals that FIR ovens are superior in terms of energy cost and compactness of size. Table 16.1b shows the heating equipment for oysters. Oysters are usually frozen for preservation. When frozen oysters are thawed, drip and loss of water-soluble nutrients occur. To solve this problem, the oysters were heated by FIR before freezing, resulting in higher-quality products.[23]

16.4.1.1 Baking of Bread

In a baking process of bread, an IR oven has been developed as a substitute for conventional ovens using gas or electricity as a heat source. In order to compare between IR baking and conventional baking, it is necessary to know the baking process of bread. The physical and chemical changes taking place during baking of bread would progress as follows.[10,11]

As shown in Figure 16.11, at the first phase of baking bread, the rate of expansion of the dough increases markedly, due to the expansion of the carbon dioxide produced by fermentation of yeast and other volatile substances. In the second phase, when the temperature increases to 60°C, the yeast becomes extinct

TABLE 16.1
Comparative Performance Characteristics of FIR Oven (A) and Conventional Oven (B)

	FIR (A)	LPG (B)	(A/B) × 100
(a) Oven for Baking Rice Cracker			
Calorie consumption	2.23×10^5 (kJ/h)	8.36×10^5 (kJ/h)	26.7%
Production rate	10,000 (pieces/h)	10,000 (pieces/h)	100%
Baking time	10 (min)	15 (min)	66.7%
Energy cost	1336 (¥/h)	2505 (¥/h)	54.5%
(b) Heating Equipment for Oyster			
Length of equipment	7.4 (m)	16.4 (m)	45%
Fuel consumption	40 (kW)	4.2 (m^3/h)	
Production rate	100 (kg/h)	100 (kg/h)	100%
Heating time	6 (min)	15 (min)	40%
Energy cost	1178 (¥/h)	1470 (¥/h)	80%

Source: from Sasaki, T., in *Bioelectromagnetics and Its Applications*, Omori, T., Ed., Fuji Techno-System, Tokyo, 1992, pp. 376–384.

and its action disappears, while evaporation of alcohol and expansion of gas are performed succeedingly. Then gluten will solidify at approximately 75°C. Next, solidification will progress completely until 110°C, and rapid evaporation from the surface will create a dry and elastic shell, which forms the crust (third phase). Finally, above 160°C, the browning reaction takes place very quickly, which contributes to not only the characteristic color, but also the flavor of the bread crust (fourth phase).

In this process, the crust formation and the surface browning are important sensory characteristics of baked foods. Skjölderbrand and Andersson[11] have compared the bread baked in an IR oven with that in a conventional oven and have obtained the following results. A shorter time is required to obtain the desired color of the crust on bread baked in an IR oven, compared with a conventional baking oven, and the IR-baked bread has a thinner crust, but a softer crumb than the conventionally baked bread, with reference to a desired crust color.

Sato and Shibukawa[24] and Sato et al.[25] discussed the effects of the radiant characteristics of heaters on the crust formation and color development processes at the surfaces of a white bread and a wheat flour batter using five different kinds of heaters. Radiant heating with an NIR heater led to a greater heat sink in the food samples, resulting in the formation of relatively wet crust layers, compared with the dry layers formed by heating with FIR heaters. The rate of color development with FIR heaters was greater than that with NIR heaters because of the more rapid increase in surface temperature.

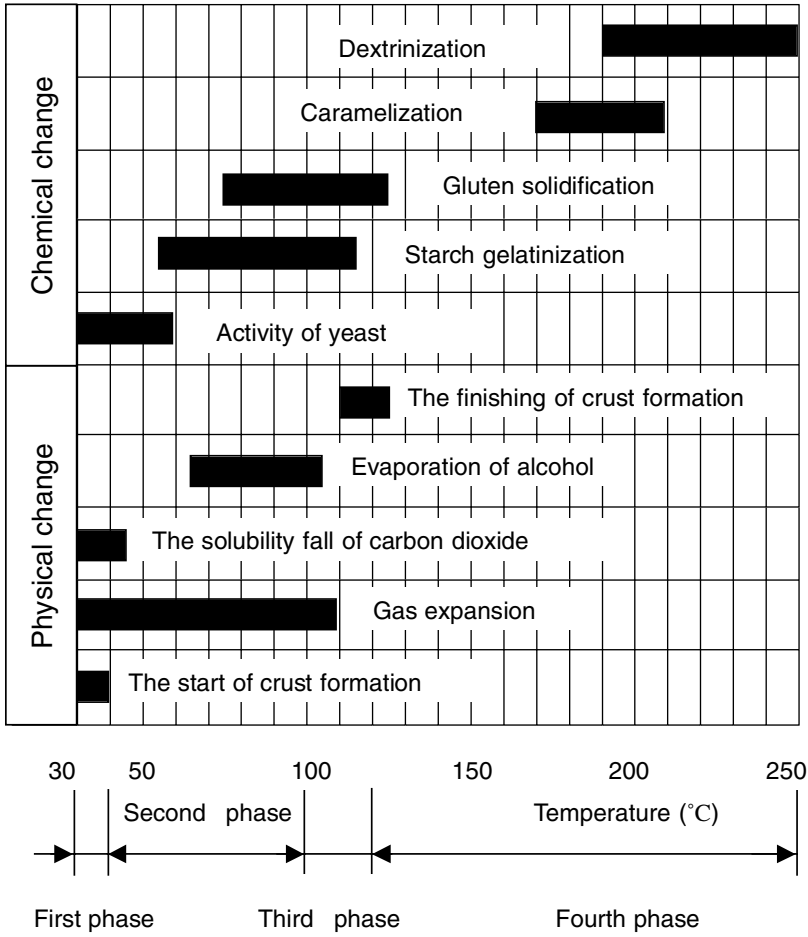


FIGURE 16.11 Physical and chemical changes during baking of bread. (From Nakamura, A., *Food Ind.*, 42, 46–51, 1999. With permission.)

16.4.1.2 Roasting of Coffee

Unprocessed coffee beans have no taste, but roasting changes the chemical composition of the beans, producing a mellow aroma and bringing out an acidic, bitter, and strong flavor. The flavor of coffee changes depending on how the beans are roasted and how strongly they are roasted, so the roasting process is important in determining the taste of the coffee.

Most conventional roasters for coffee beans use hot air for roasting. In this hot-air method, air heated to between 350 and 450°C in a combustion unit is sent to a roasting unit where the beans are roasted (Figure 16.12a).[26] The temperature

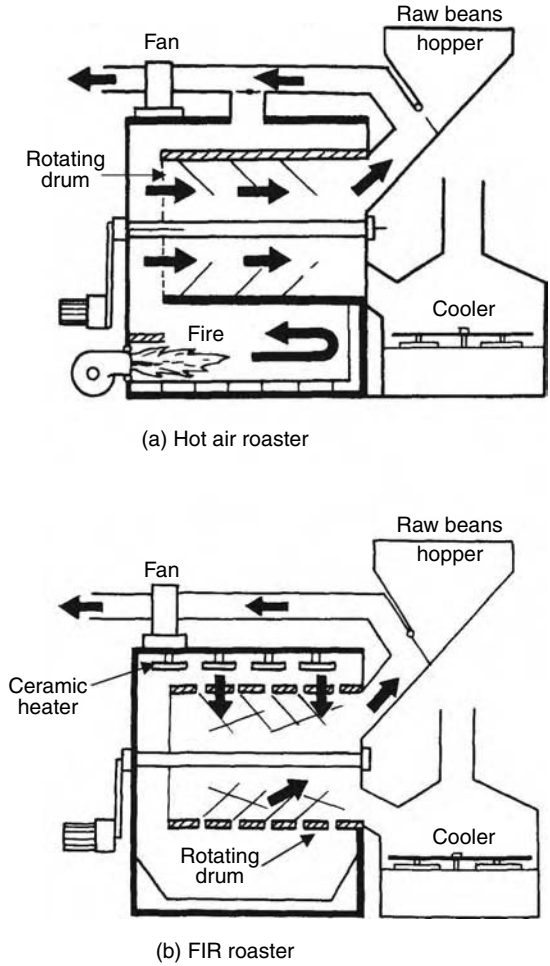


FIGURE 16.12 Schematic diagram of coffee roaster. (From Takagi, T. and Takahashi, H., *Jpn. Food Sci.*, 27, 36–41, 1988. With permission.)

of the coffee beans when the roasting is finished varies between 180 and 230°C, depending on the strength of the roasting and the type of bean, and roasting takes up to 20 min. FIR roasting was developed as a substitute for the hot-air method. The FIR roaster has numerous ceramic heaters installed on the inner walls of the oven, and the FIR rays that are given off pass through small holes in the walls of a rotating drum containing the coffee beans, which are then irradiated with the rays (Figure 16.12b).[26]

Internal temperature changes have been reported for coffee beans heated using hot air and infrared rays, respectively.[14] Temperature changes were measured by a thermocouple inserted in unprocessed coffee beans. These beans were put into an

oven in which the temperature was controlled to 200°C using either a far-infrared heater or hot air. When the same energy was introduced to both test units, the internal temperature of the unprocessed coffee beans rose more quickly with the FIR heating than with the hot-air heating.

The difference in the temperature rise speed affects chemical reactions during the roasting. Kino[14] conducted component analysis on both coffee roasted with hot air and coffee roasted with FIR. He analyzed the chemical components of the extract from the coffee beans that were roasted with different roasting times, using high-performance liquid chromatography. When the unprocessed coffee beans are roasted, hydrolysis of the cane sugar creates organic acids, and when the beans are heated further, the organic acids are also broken down. Consequently, light roasting produces a strong sour taste, while medium and deep roasting produce a successively weaker sour and more bitter taste. As an example of the organic acid, the change of malic acid and citric acid, and chlorogenic acid in the coffee extract are shown in Figure 16.13 and Figure 16.14, respectively. For the abscissa, the brightness of the beans color, *L*, was used as the index that shows the degree of roast progress. In the FIR roast, there are smaller quantities of the organic acid than those by hot-blast roast, because the temperature rise of coffee beans began from early roasting time. In the meantime, the formation of the chlorogenic acid, which would be important in respect to the taste, was almost the same for both roasting methods. Therefore, in FIR roasting the quantity of the chlorogenic acid relatively increased and seemed to have a delightful and mild taste.[14]

It is thought that, in addition to caffeine, the products of thermal decomposition of the proteins also contribute to the bitterness of the coffee, and these

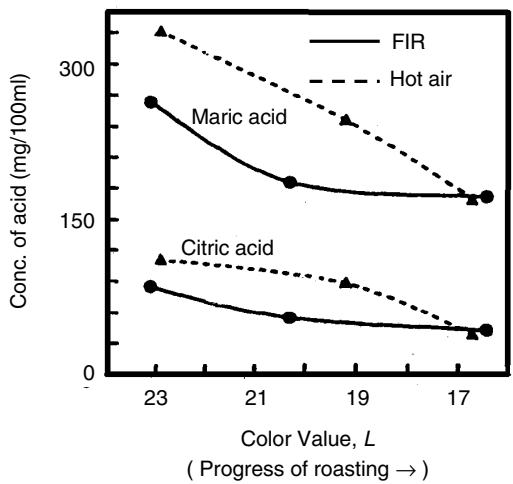


FIGURE 16.13 Acid concentration changes in the coffee extract with the roast progress. (From Kino, T., *Food Ind.*, 42, 29–38, 1999. With permission.)

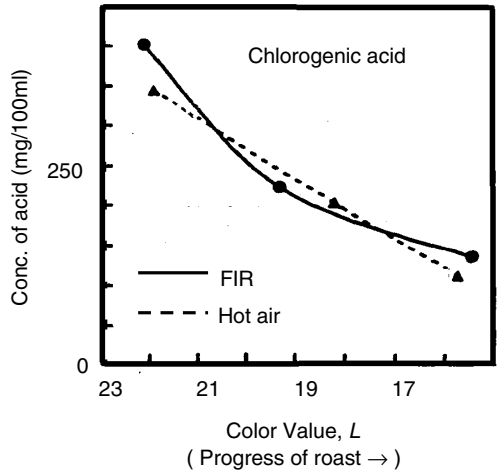


FIGURE 16.14 Concentration changes of chlorogenic acid in the coffee extract with the roast progress. (From Kino, T., *Food Ind.*, 42, 29–38, 1999. With permission.)

increase as the roasting progresses. Furthermore, the coffee aroma component changes in complex ways as the roasting progresses. Kino[14] measured the flavor component as well as the organic acid by gas chromatograph. The sum total of peak area for the aroma component in the measurement of the gas chromatograph is shown in Figure 16.15. It is proven in the figure that the component contained

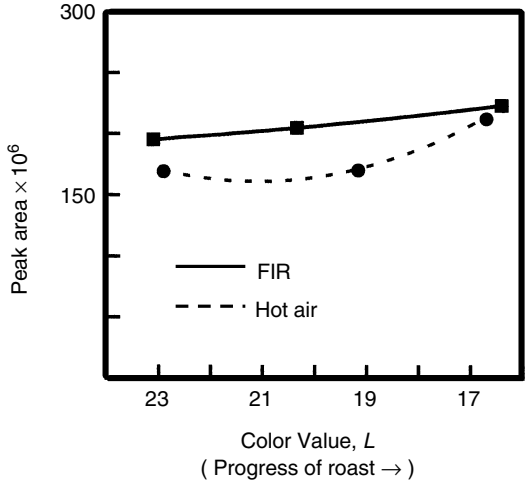


FIGURE 16.15 Peak area for the aroma component in the measurement of a gas chromatograph. (From Kino, T., *Food Ind.*, 42, 29–38, 1999. With permission.)

in the beans increased as the roast progressed, and that its formation in the FIR roaster is more abounding than that of the hot-blast roast. In order to draw out the aroma component to the maximum, the coffee beans need to be heated uniformly and at the appropriate heating speed.

16.4.1.3 Roasting of Green Tea

Ninety percent of the tea produced in Japan is green tea, which is produced by drying the tea leaves and roasting them through a firing process. In this firing process, the tea leaves are dried to a moisture content between 3% and 5% (wet basis), and at the same time the fragrant aroma that is characteristic of green tea is drawn out. The aroma that is special to the fired tea is thought to be created when the leaves are dried and heated to between 100 and 120°C. Because this aroma is not produced when the temperature of the leaves is less than 100°C, the tea has an unpleasant smell before being fired.[15]

Lower-grade tea leaves that contain a lot of stems have a green smell and are strongly bitter and astringent. This problem of bitterness and astringency is eliminated in hoji-cha, which is roasted tea. Toasting the green tea to a temperature of around 200°C, and thus changing the flavor component, is called the *torrefaction process of tea*. This torrefaction breaks down the tea polyphenol, which is the component that causes the bitterness and astringency of the tea, causing the transpiration of the green smell component and forming the torrefaction flavor component (types of pyrrole and pyrazine).[15]

Conventionally, in the firing and torrefaction processes, gas has been used as the heat source for direct heating or hot-air heating. As a substitute for hot-air heating, equipment using FIR or microwaves and FIR in combination[15,27] has been developed. Takeo[15] conducted composition analysis and sensory tests on the tea and indicated that the FIR heating methods could heat the tea leaves more uniformly, preventing the scorching that could occur from partial overheating and making it possible to produce tea with a better flavor.

16.4.1.4 Roasting of Sweet Potato

It is well known that the taste of sweet potato and chestnut roasted by heated pebbles, which emit FIR, is better than those roasted by other methods.[28] As a reason for this, when sweet potato or chestnut is roasted by FIR, it seems to become more sweet and delicious, since the FIR energy permeates to the food inside, and it uniformly heats the sweet potato inside. However, as mentioned in Section 16.3, the permeability of the FIR is small in the food, which mainly contains water. Hashimoto et al.[29] estimated the absorption coefficient of the sweet potato from that of water and the drying sweet potato, which was measured individually. As a result, they estimated that the depth in which the irradiated energy to the sweet potato attenuated to 1% was 0.1 to 0.22 mm. Therefore, in the case of sweet potato, the permeability of FIR is not large.

When the sweet potato is heated, the maltose that is the origin of the sweetness is formed by the following processes:[30]

1. The gelatinization of the raw starch begins when the temperature of the sweet potato reaches 65°C.
2. The gelatinized starch is saccharified by the action of hydrolase (β-amylase) and maltose is formed.
3. The thermal deactivation of the β-amylase is accompanied with the temperature rise, and the generation of the maltose gradually drops.

In this process, the FIR effect was explained[30] by the difference in the maltose content. The yield of maltose did not depend on the mechanism of heat transfer (radiation or conduction), but on the time required to raise the center temperature of the sweet potato from 338 to 353 K. When this time was 8 min, the maximum yield of maltose was obtained under FIR heating.

16.4.1.5 Setting of Surimi-Based Products

The most typical surimi-based product in Japan is *kamaboko*, which is cooked by either steaming or baking to carry out the completion of the gelation of fish protein. The finally steamed and baked products are called *mushi* (steaming) kamaboko and *yaki-ita* (baked on a board) kamaboko, respectively. Before the cooking process, the surimi paste is subjected to the setting process. During this process, the gel-forming ability of solubilized myofibrillar proteins is highly enhanced, which yields a strong gel.[31] Usually, two methods of setting are employed with temperature: low temperature setting, done at below 20°C for a long time, and high temperature setting, done at 30 ~ 50°C for a short time. The FIR has been applied to the high-temperature setting. Yamamoto[32] tested the setting of plastic-cased kamaboko using three methods: FIR setting, setting in a constant temperature box at 45°C for 30 min, and setting at 5 ~ 7°C for 18 h. The breaking strength of kamaboko, which was set by the different methods, is shown in Figure 16.16. The breaking strength of kamaboko set by FIR in short time was larger than that set by conventional methods. FIR has also been used for the setting of other surimi-based products, such as *chikuwa* and age kamaboko (fried kamaboko).[32,33] Chikuwa is broiled in a furnace, and its shape is typically like a pipe or tube. The elasticity of chikuwa heated by FIR was stronger than that of chikuwa heated in the baking furnace of electricity or gas.

16.4.2 Drying

IR drying operations have been increasingly successful for use with vegetable products and marine products. In vegetable drying, it is important to pay attention to discoloration and nutrient retention, as well as the drying efficiency. Chemical changes to chlorophyll or carotenoids are caused by heat and oxidation during drying. Itoh and Han[34] measured the degradation rate of β-carotene and chlorophyll

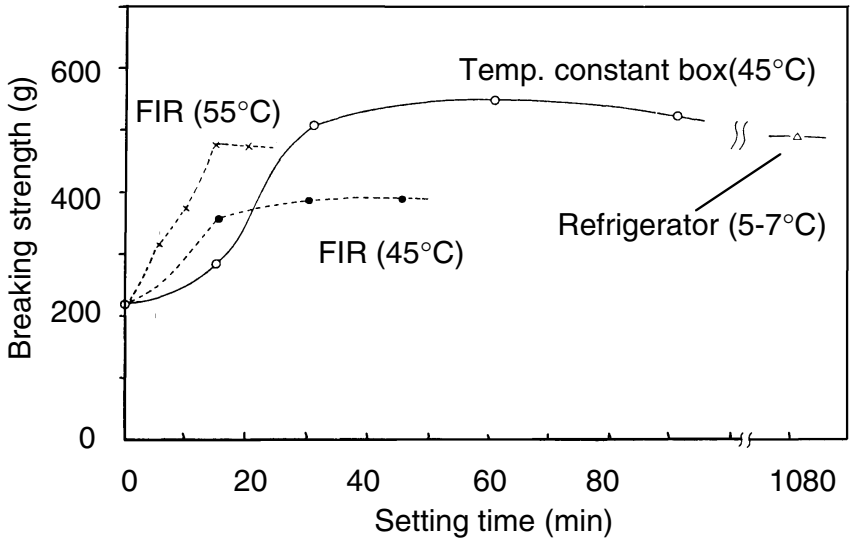


FIGURE 16.16 Breaking strength of kamaboko set by different methods. (From Yamamoto, T., *Jpn. Food Sci.*, 8, 43–52, 1988. With permission.)

a, which are the typical pigments contained in vegetables, during irradiating of FIR. In the samples, β-carotene and chlorophyll a were dissolved in benzene and ethanol, respectively. These samples were heated in FIR (a plate-type heater) and NIR (an infrared ray lamp), while their surface temperature was adjusted to be 60°C. For comparison, the following heat sources were also tested: the solar light and hot air of 60°C. Their results for β-carotene and chlorophyll a are shown in Figure 16.17 and Figure 16.18, respectively. In the case of the solar light, the pigments were decomposed remarkably, whereas the sample temperature was almost maintained at room temperature. A reason for this seems to be that the decomposition rate of the pigment by ultraviolet ray and visible light in solar light was high. The pigmentary degradation rate with an infrared ray lamp, which would irradiate partially visible light, was higher than that of the solar light. From the result that both degradation rates of β-carotene and chlorophyll a by the FIR heater were low, it was shown that there is an advantage of FIR as a heat source for vegetable drying.

Itoh[35] has also compared the qualities of a vegetable (Welsh onion) from the viewpoint of the chlorophyll decomposition, using three different drying methods: FIR with forced-air drying, FIR with vacuum drying, and forced-air drying. Itoh's experimental results showed that FIR with forced-air drying resulted in the least loss of chlorophyll, because the drying time was reduced. Mongpraneet et al.[36] investigated drying of a Welsh onion by FIR under vacuum conditions and reported that the intensity of FIR had significant effects on chlorophyll content. Similarly, the FIR drying of carrot and pumpkin was reported to result in

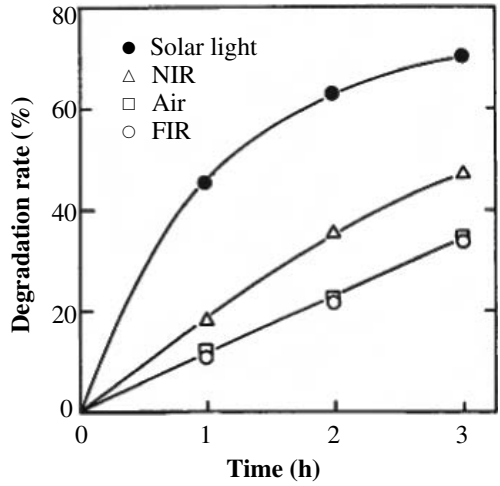


FIGURE 16.17 Degradation rate of β-carotene. (From Itoh, K. and Han, C.S., *J. Soc. Agric. Struct. Jpn.*, 25, 39–45, 1994. With permission.)

decreased loss of β-carotene.[37] Another report[38] has shown that FIR drying reduced the losses of vitamin C and volatile components or flavors in the drying of parsley and Yamato yam. Thus, the FIR drying process may be suitable for foods that have a high economic value due to their characteristic nutrition or color.

The rate of rehydration may be used as another indicator of food quality; foods that are dried under optimum conditions suffer less damage and rehydrate more

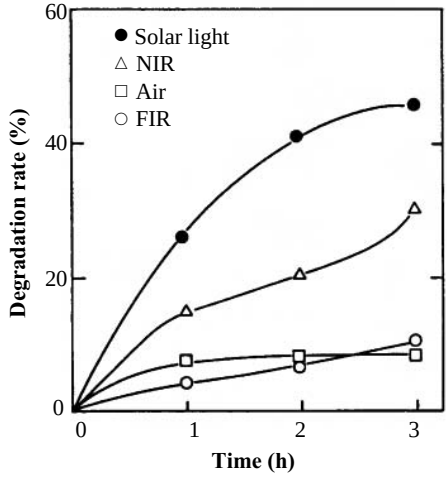


FIGURE 16.18 Degradation rate of chlorophyll a. (From Itoh, K. and Han, C.S., *J. Soc. Agric. Struct. Jpn.*, 25, 39–45, 1994. With permission.)

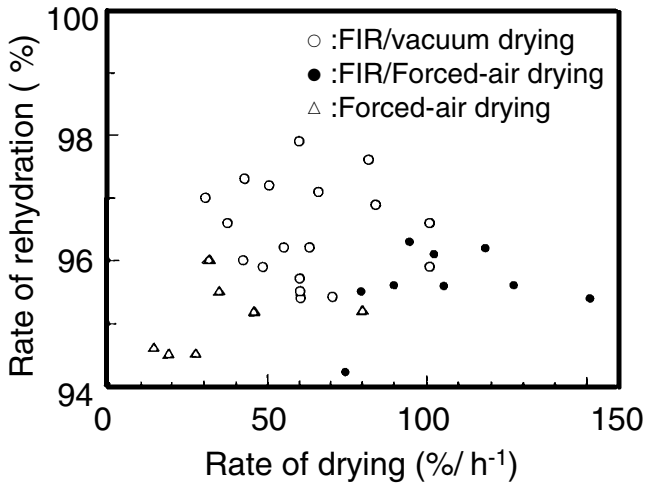


FIGURE 16.19 Relationship between the rate of drying and the rehydration rate. (From Itoh, K., *Shokuhin Kikai Souchi*, 23, 45–53, 1986. With permission.)

rapidly than poorly dried foods. Furthermore, if dried vegetables are used as ingredients in instant foods, quick rehydration is required. Freeze drying is a competitive alternative process for this application, but is comparatively expensive. The IR drying process is expected to represent a process for dried foods that have a high rehydration rate. Itoh[35] has also examined the rehydration rate of the Welsh onion and reported that FIR with vacuum drying gave the best rehydration rate, whereas FIR with forced-air drying gave the best color retention (Figure 16.19).

FIR drying has also been used in drying of marine products to improve the final quality. Tokunaga[39] reported on the quality differences of horse mackerel samples dried using three different drying methods: solar drying (21°C, 65 min), hot-air drying (30°, 45 min), and FIR drying (27 to 40°C, 25 min). In the tests of the sensory characteristics of the products, FIR drying gave the best score, followed by hot-air drying. The good taste of horse mackerel dried by FIR was related to the high concentration of inosinic acid,[40] which is recognized as an ingredient of the taste of fish.

16.4.3 Pasteurization

It is well known that ultraviolet radiation has a pasteurization effect, and it is used for pasteurization of water, air, food containers, etc. Ultraviolet radiation has a sufficient quantum energy for exciting and ionizing organic molecules; DNA of the microorganism may be directly damaged by the germicidal action, which does not originate from heat. On the other hand, it is generally recognized that incident FIR energy does not have enough power to impair or destroy microorganisms directly. The FIR energy is believed to inactivate microorganisms

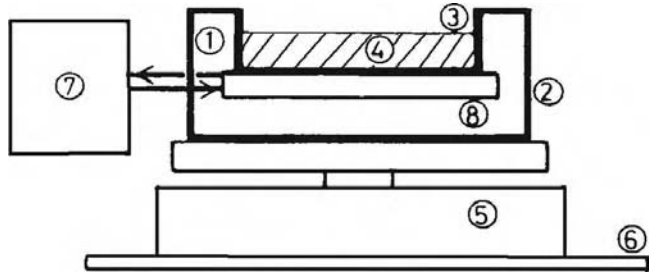


FIGURE 16.20 Sample for pasteurization by FIR. (From Hashimoto, A. et al., *J. Chem. Eng. Jpn*., 25, 275–281, 1992.)

by conventional thermal mechanisms (e.g., thermal denaturation of proteins and nucleic acids), whereas a nonthermal effect of FIR on enzyme activity has been reported.[41,42] This thermal effect of FIR is supported by experiments[43] comparing the characteristics of damaged cells exposed to either FIR or conductive heating. However, Hashimoto et al.[44] observed that the bacteria were impaired and killed by FIR even when the bulk of the suspension was kept below the lethal temperature. They have investigated the effects of FIR radiation on *Escherichia coli* and *Staphylococcus aureus* in phosphate-buffered saline under the condition that the bulk of the suspension was kept below 40°C by cooling it (Figure 16.20). Figure 16.21 shows the effect of irradiation power, q_{ir}, on the ratio of the colony-forming unit of the test bacteria irradiated by FIR for 20 min to that of the control (N_1/N_{10}). The explanation given for the FIR effect was that the bacteria were impaired and killed in the very thin region near the surface, since the FIR energy was almost entirely absorbed at the surface, raising the surface temperature. It should be noted that FIR heating is more effective for pasteurization than NIR.[45] The superiority of FIR pasteurization over NIR was explained by the very high absorption coefficient of the bacterial suspension in the FIR region. In addition, it was found experimentally that FIR was more effective than hot-air heating for the pasteurization of bacteria on a solid model food (agar).[46]

Bacteria such as the *Bacillus* or *Clostridium* group form spores under some conditions. When the sterilization of the food is considered, this spore is important, since it is heat resistant. Sawai et al.[47] have investigated the effect of FIR on spores. They used spores of *Bacillus subtilis*, which were suspended in phosphate-buffered saline, and irradiated FIR to the spore suspension, which was dispensed

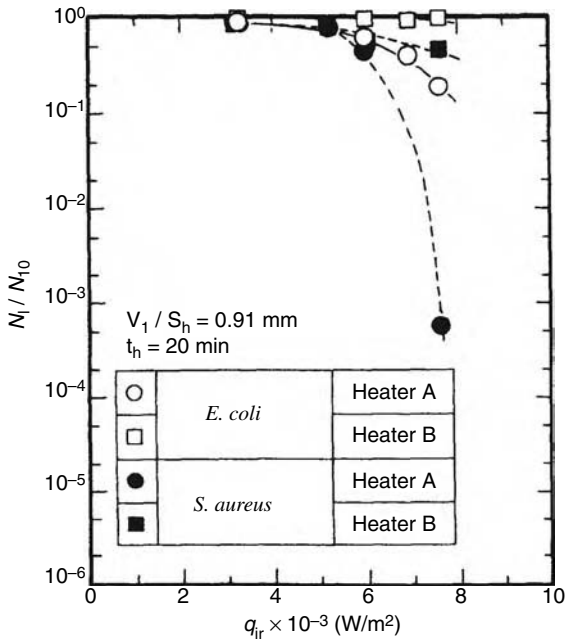


FIGURE 16.21 Comparison of effect of q_{ir} on N_1/N_{10}, using FIR heater (a) and NIR heater (b). (From Hashimoto, A. et al., *J. Chem. Eng. Jpn.*, 25, 275–281, 1992.)

in a Petri dish made of stainless steel. Figure 16.22 illustrates the bulk temperature histories of spore suspension irradiated by FIR with different powers (Figure 16.22a) and survival curves of spores of *B. subtilis* (Figure 16.22b). The ordinate of Figure 16.22b (N_1/N_{10}) represents the ratio of the number of colonies on the agar medium for the spores irradiated by FIR to that for intact spores. During the first few minutes, the number of colonies of the spore increased, and then gradually decreased after that. This decrease in N/N_0 means that FIR irradiation causes the death of the spore. The highest temperature of suspension was 354 K. At this temperature, thermal conductive heating did not cause changes in the number of colonies of the spores. It was explained that the pasteurization effect of FIR was due to the absorption of radiative energy by spore suspension in a very thin layer near the surface, as well as the pasteurization of bacteria.

In the beginning of the survival curve, the number of colonies of bacterial spores temporarily rises. In the bacterial spores, it is known that there are cell groups of activated states with colony-forming ability and cells groups of dormant state without colony-forming ability. Even if the spore of the dormant state exists in the sample, the colony cannot be measured as a viable count, since it does not have the forming ability of the colony. However, it will have the colony-forming ability when it changes to the activated cell by heating. The survivor curve in the figure shows that activated spore number is more abounding than dying out spore

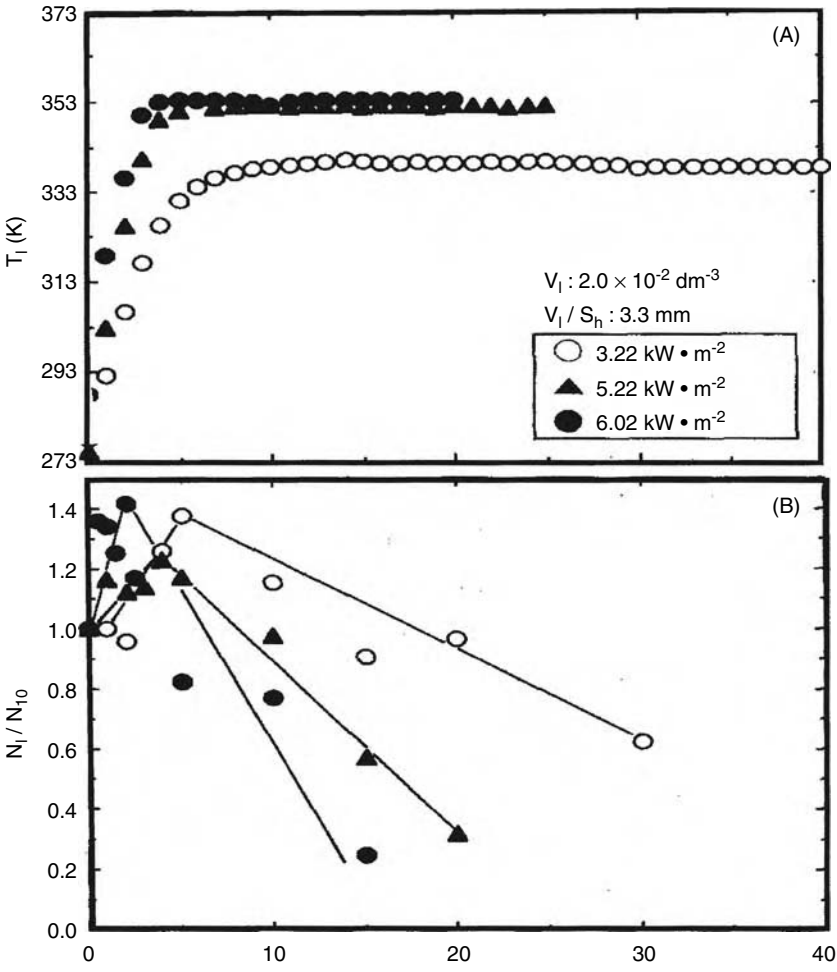


FIGURE 16.22 (a) Transient behavior of bulk temperature of spore suspension irradiated by FIR. (b) Effect of FIR irradiation of spores of *B. subtilis*. (From Sawai, J. et al., *J. Chem. Eng. Jpn*., 30, 170–172, 1997.)

number. Activated spores easily germinate under their suitable conditions, and their high heat resistance decreases extremely after the germination. These results suggest that the activation of the spore is possible by the FIR in a short time, and that FIR heating will be able to apply the pasteurization of bacterial spores.

The pasteurizing action of FIR heating has been confirmed in some applications: the heating of oysters,[23] the heating of Japanese noodles,[48] and the secondary pasteurization of boiled fish paste.[32] FIR pasteurization is more effective than conventional heating under specific conditions, and is particularly effective at the surface of foods. Since some baked or cooked foods may be contaminated by

microorganisms in a later operation, it would be desirable to pasteurize such products after packaging. However, pasteurization using conventional heating methods requires such a long time and so high a temperature that the package would deform or the products would denature. FIR heating has been successfully used for the efficient pasteurization of packaged products such as sausages and boiled fish paste.[49]

16.4.4 Thawing

Recently, the quality of frozen foods has improved remarkably with the advancement of freezing technology. However, its quality may deteriorate in the thawing stage corresponding to the thawing conditions, such as thawing method, temperature, and speed. Frozen foods generally thaw more slowly than they freeze, because water has a lower thermal conductivity than ice. In conventional thawing methods, heat is supplied at the surface of the frozen food and is conducted slowly toward the interior. Conventional thawing methods involve several disadvantages: a long thawing time, undesirable changes in food quality, and product loss (drip loss). Microwave thawing is one possible method to reduce the thawing time. However, in microwave thawing, at temperatures slightly below 0°C, the outer layer of the food may absorb most of the microwave energy and cause "runaway heating" or overheating near the product surface.[50] This well-known phenomenon occurs due to the significant difference in the dielectric properties of frozen and unfrozen food, which decide the absorbability of microwave energy.[51,52] On the other hand, in the region of the IR wavelength, the values of the absorption coefficients for ice and water are approximately equal.[5] Thus, the runaway heating effect does not occur during FIR thawing; FIR has the potential for broad use in food thawing processes.

In comparison with meat, which may be cooked after thawing, the quality of thawed fish that is eaten in the raw state, such as *sashimi* or *sushi*, is greatly affected by the thawing conditions. In particular, drip loss or discoloration of the red muscles of frozen tuna occurs readily during thawing. To minimize the extent of deterioration, the surface temperature of the tuna should be kept below 10°C during thawing.

Since frozen food can be heated directly in FIR heating, regardless of the temperature of the circumference, it is possible to thaw a frozen food while its surface is cooled. Kimura[53] demonstrated experimentally that a frozen tuna could be thawed within 30 min without drip loss and discoloration by using FIR heating in association with cooling of the surface by cold air. It was also demonstrated that the surface temperature could be controlled by intermittent FIR irradiation to frozen foods under a low-temperature atmosphere.[54]

In order to reduce the thawing time, if the heater temperature is kept at a higher temperature, the surface temperature of tuna may increase to an unacceptable level. Thus, it is important to know how temperature distribution is formed in the food corresponding to the thawing condition. The authors have investigated the effect of the thawing conditions on the temperature distribution of frozen tuna.[55] Simulation results of the temperature histories in changing the FIR heater temperature are shown in Figure 16.23. The simulation conditions are as follows: the food is assumed to be tuna of 15-mm thickness, initial temperature is −28°C, and

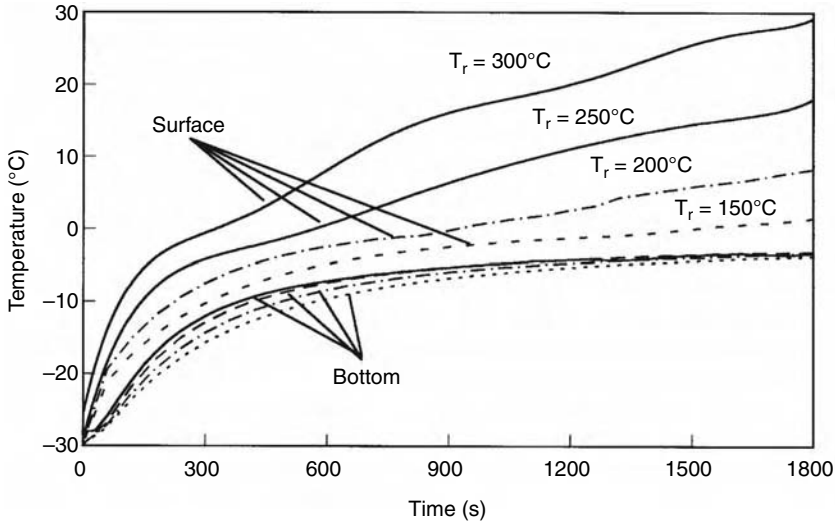


FIGURE 16.23 Simulated temperature histories of frozen food with different heater temperatures. (From Liu, C.M. and Sakai, N., *Nippon Shokuhin Kagaku Kougaku Kaishi*, 46, 652–656, 1999. With permission.)

ambient temperature is 7°C. When the heater temperature is reduced, the surface temperature of tuna is kept at a low level. However, the bottom temperature simultaneously decreases, and it takes longer time for the bottom temperature to reach –4°C. Since frozen tuna of –4°C could be cut off by a kitchen knife, it is possible to finish the thawing process when the lowest temperature within the food reaches this temperature. In order to reduce the thawing time, when the heater temperature is raised to 300°C, the surface temperature of tuna may increase to an unacceptable level. When frozen tuna was thawed experimentally under this condition, its surface was actually discolored and remarkable degradation was observed.

A case was then simulated in which the heater temperature was changed during thawing: when the surface temperature of the sample reached the ambient temperature of 7°C, the FIR heater temperature was reduced from 300 to 250, 200, or l50°C, respectively. These simulation results are shown in Figure 16.24. When the temperature of the FIR heater was reduced to 150°C, the surface temperature was suppressed and maintained below 7°C. However, the bottom temperature was almost the same as the other case before thawing. The thawing of frozen tuna could be stopped when the lowest temperature reaches about –4°C. From this viewpoint, the frozen tuna could be thawed within 30 min, while the surface temperature remained below l0°C, when the FIR heater temperature was reduced from 300 to 150°C during thawing.

In the case of thawing of thick frozen food, it would take a longer thawing time because the permeability of FIR is low, and it is difficult to heat uniformly inside the food. Figure 16.25 shows the simulated correlation between sample thickness

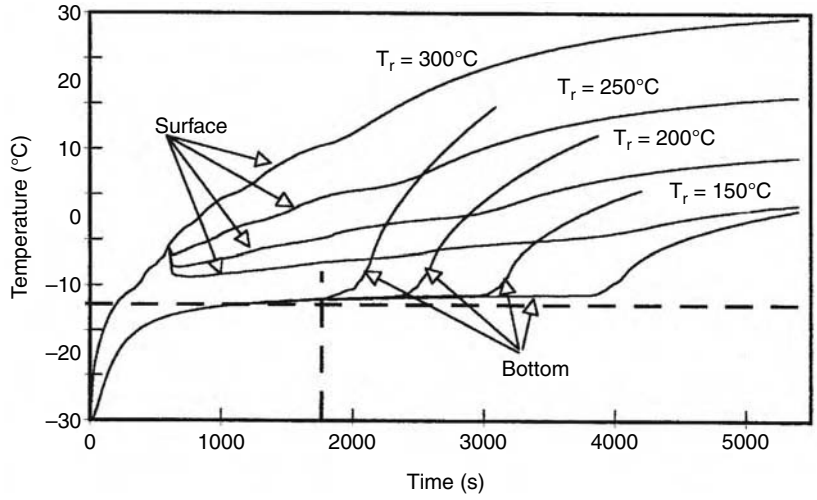


FIGURE 16.24 Simulated temperature histories of frozen food when the heater temperature lowered from 300 to 250, 200, and 150°C. (From Liu, C.M. and Sakai, N., *Nippon Shokuhin Kagaku Kougaku Kaishi*, 46, 652–656, 1999. With permission.)

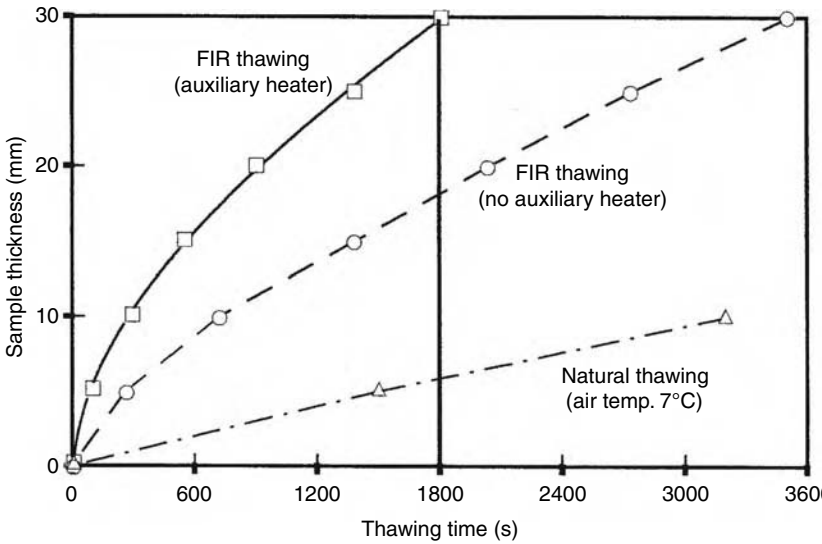


FIGURE 16.25 Relation between sample thickness and thawing time. (From Liu, C.M. and Sakai, N., *Nippon Shokuhin Kagaku Kougaku Kaishi*, 46, 652–656, 1999. With permission.)

and thawing time when the lowest temperature of the sample reached –4°C. The ambient temperature was maintained at 7°C during thawing. In Figure 16.25 the results are also shown for natural thawing, in which heat was supplied by natural convection. As can be seen in Figure 16.25, a 17.5-mm-thick sample was thawed within 30 min using FIR thawing, four times faster than natural thawing. Therefore, it is effective to use an auxiliary heater to heat from the bottom of the food, when the thicker food is thawed. The simulated correlation between food thickness and thawing time using an auxiliary bottom heater is shown in Figure 16.25 as a solid line. In this case, the heat flux of the auxiliary heater was assumed to be almost equal to that of the FIR heater. As can be seen, the use of the auxiliary heater increases the thawing speed and enables 30-mm-thick tuna to be thawed within 30 min.

Thawing equipment has been developed for frozen foods[56,57] and for frozen small packs of prepared meals.[58] The equipment can maintain the temperature at 60 or 100°C after thawing and is expected to be used in office kitchens and fast-food restaurants. Ohashi[59] reported on a refrigerator with a partial defrosting system, which consists of heating by an FIR heater and blowing with cold air. This system also keeps raw foods such as tuna at a partial freezing temperature (approximately –3°C) after thawing. The thawing time of beef (400 g) or tuna (200 g) in the device is less than 30 min, three times faster than thawing at room temperature.

16.5 CONCLUSIONS

Infrared heating applications are expected to grow as a result of the increasing demand for safe food products of high nutritional value and organoleptic quality. There are many examples that IR heating is superior to conventional heating. However, there are few theoretical explanations of the IR effects; therefore, there is a need for the basic research on mechanisms of energy transfer and its effect on changes in taste and nutritional components in the food. Furthermore, in order to provide an improved basis for infrared heating process design, the practical development of quantitative models is needed to predict temperature and product quality as a function of temperature. Finally, innovations of infrared heating equipment combined with microwave or ohmic heating will lead to greater energy efficiency and higher-quality products in the food industry.

NOMENCLATURE

c	Velocity of light (m/sec)
E	Emissive power (W/m^2)
F_{21}	Radiation shape factor
h	Plank's constant (m·K)
I_λ	Energy flux (W/m^2)
k	Boltzmann's constant (J/K)
Q	Interheat generation (J/sec)
T	Absolute temperature (K)

α_λ	Spectral attenuation factor (μm^{-1})
β	Absorptivity
γ	Reflectivity
ε	Emmissivity
ε_1	Emmissivity of food
ε_2	Emmissivity of the IR heater
λ	Wavelength (μm)
λ_{max}	Peak wavelength (m)
σ	Stefan–Boltzmann constant, $\sigma = 5.670 \times 10^{-8}$ ($W/m^2 K^4$)
Φ	Overall absorption coefficient

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17 Pressure-Assisted Thermal Processing

Takashi Okazaki and Kanichi Suzuki

CONTENTS

17.1 INTRODUCTION

Many foodstuffs have been treated through various types of thermal processings, such as boiling, steaming, baking, and frying. By such treatments the foodstuffs are remade into foods and dishes with favorable tastes, and with nutritive function to ease digestion, as well as extending the shelf life and safety. Changes in such functions depend on the relationship between temperature and time. When pressure is added as another factor to the relationship, it is largely unknown whether the functions will change favorably or unfavorably, or will not change at all. To clarify these matters, the authors investigated kinetically such changes and the effects of sterilization through thermal treatment combined with pressure.[1–6] Furthermore, the combination of high hydrostatic pressure (HHP) and mild heating has also been tested as an innovative and practical technique for food processing.[7]

Nearly a century ago, Hite,[8] for the first time, started investigating HHP for pasteurizing milk. Since then, a lot of studies related to HHP, such as the sterilization of microorganisms by HHP,[9–13] enzyme reaction under pressure,[14] and the softening of muscle by HHP,[15,16] have been reported. Furthermore, the number of studies of HHP have greatly increased in Japan since the end of the 1980s,[17] and also in the U.S. and Europe. Although HHP treatment had been first investigated as a sterilization procedure without heating, it has also been noticed as a new food processing technique. Some innovative techniques using pressure were recently practiced in the food industry, for instance, shucking of oyster by pressure,[18–20] production of guacamole by pressure in the U.S., production of rice cakes by pressure,[21] and an autolytic technique of unsalted fish protein under pressure.[7]

Although there are many studies on the effects of HHP on sterilization,[22] few studies on thermal treatment combined with pressure have been reported.[23] This is because it is difficult to use HHP at high temperatures, in particular higher than 100°C, and also to keep the pressure during the thermal treatment. The aim of this chapter is to use our data to illustrate the process of pressure-assisted thermal

processing. Therefore, in this chapter, thermal processing assisted by pressure is described, based on our experiments using a compact and simple *pressure vessel*[1] capable of easily controlling the sample temperature and recording the temperature. Using the pressure vessel, the thermal treatment combined with pressure was studied in order to seek the potentiality of pressure as a new technique of thermal processing. The effects of pressure on the softening of vegetables, the browning of glucose–glycine solution, the inactivation behavior of microorganisms due to HHP, the effect on bacterial spores by thermal treatment combined with pressure, and some practical studies of pressure combined with mild heating are also discussed in this chapter.

17.2 PRESSURIZING TREATMENT

17.2.1 Compact Pressure Vessel

The thermal treatments combined with pressure are carried out using the pressure vessel shown in Figure 17.1. Hydrostatic pressure is applied to the pressure vessel from the right side, and a sheath thermocouple (1.5 mm in diameter) is inserted from the left side. A pressure gauge is placed between the pressure vessel and the pressurizing pump.

In the case of liquid samples, two milliliters of sample solution is poured into a sample container (4 × 100 mm silicone rubber tube sealed at one end) without air bubbles, and the open end of the container is sealed up with a silicon rubber plug. The container filled with sample solution is inserted into the pressure vessel. In the case of solid samples, it is directly inserted into the vessel. After each sample has been put in, the pressure is applied to the sample, and then the pressure vessel is maintained in a water bath at 25°C for 5 min to ensure the

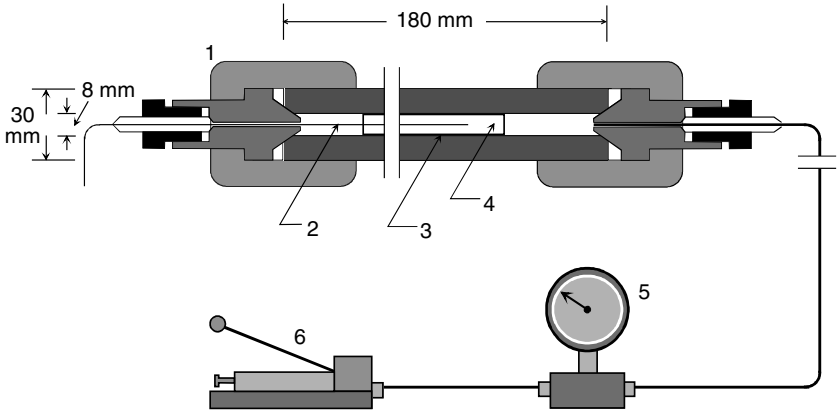

FIGURE 17.1 Schematic diagram of experimental apparatus. 1, pressure vessel; 2, thermocouple; 3, silicon tube; 4, sample; 5, pressure gauge; 6, pressure pump.

initial temperature. Then, thermal treatments combined with pressure are started; the pressure vessel is heated in a water bath (25 to 90°C) or an oil bath (90 to 110°C) for a given time. After the treatment is finished, the vessel is cooled down in a water bath, then the pressure is released, and the sample is taken out of the vessel. For example, in the initial period of pressurization at 400 MPa, the sample temperature rises to about 8°C from the initial temperature because of adiabatic compression. In addition, in an initial period of heating, the pressure increases from 20 MPa ~ 30 MPa due to the thermal expansion of the water in the vessel. To avoid the additional increase in pressure, the pressure is adjusted by controlling the valve. It takes about 15 to 30 sec to reach 100 to 400 MPa and about 15 sec to return to atmospheric pressure. The temperature and pressure history curves of the liquid sample during the pressurizing treatments are shown in Figure 17.2. It takes about 5 min to reach the given temperature. Thus, the treatment time contains the time needed to reach the given temperature, and does not contain the time needed for the temperature to cool down. Furthermore, the time needed to reach and release the given pressure is not contained in the treatment time.

17.2.2 Pressure Treatment Machine

For treating a large volume of samples, a pressure treatment machine, capable of simultaneously pressurizing up to 400 MPa and heating up to 120°C is used (Figure 17.3). The pressure chamber is 100 mm in diameter by 300 mm in height, and the pressurized medium (water) in the chamber is heated by an inner heater (200 W) and an outer heater (400 W). This apparatus is used for the testing of white sauce in Section 17.4, and oysters shucked by pressure and autolysis under pressure combined with mild heating in Section 17.7.

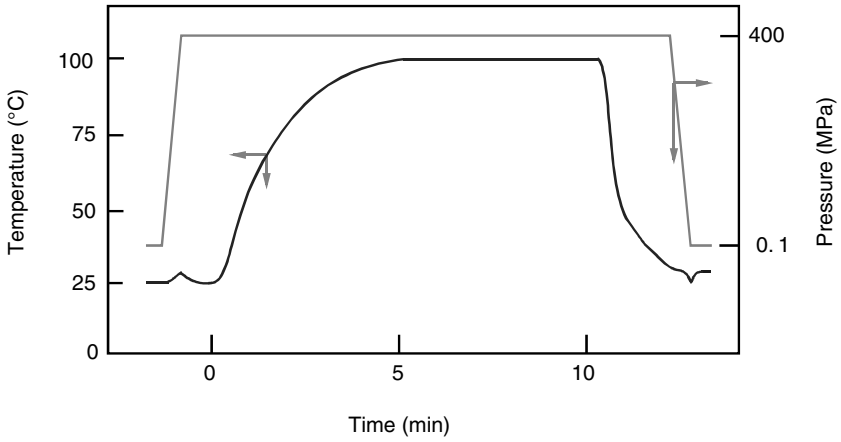

FIGURE 17.2 An example of temperature and pressure history curves of a sample solution during heating at 100°C for 10 min under 400 MPa.

FIGURE 17.3 Photograph of pressure treatment machine for testing the larger volume of samples.

17.3 SOFTENING OF RADISH BY THERMAL TREATMENT COMBINED WITH PRESSURE

Softening of vegetables is one of the many phenomena that occur as a result of thermal processing. The effect of pressure on this phenomenon is introduced in this section. The Japanese radish is used in many tests as a model vegetable for softening. The softening by thermal treatment has also commonly been investigated.[24,25] From those studies, the softening phenomenon of the Japanese radish is known to be closely related to the decomposition (called *trans-elimination*) of pectin substances in it.[24,25] Therefore, the influence of pressure not only on the softening of radish but also on the decomposition of pectin is investigated.[4]

17.3.1 Softening of Radish by Thermal Treatment Combined with Pressure

Since each natural radish has its own hardness attributes, it is difficult to compare their hardness with each other. The degree of softening (DS) was defined as the ratio of the hardness of treated radish to that of the untreated one. The proper value of DS for eating is 0.2 according to the organoleptic test.[4] Thus, a DS value lower than 0.2 indicates that the radish is in an overcooked state. The effect of HHP on the softening of a radish by heating it at 100 and 110°C for 15 min is shown in Figure 17.4. Under atmospheric pressure, the DS values reached 0.2 or lower. However, under pressurized conditions, the DS values were increased with the increase in pressure even under the same temperature.

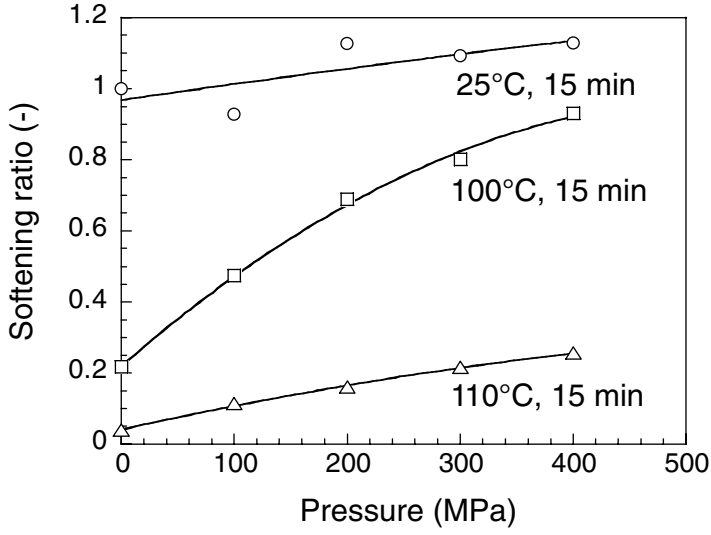

FIGURE 17.4 Effect of pressure on softening of Japanese radish at 100°C and 110°C for 15 min.

The time courses of the softening of a radish heated at 100°C under atmospheric pressures 200 MPa and 400 MPa are shown in Figure 17.5. At atmospheric pressure, the DS value reached 0.2 during heating for only 15 min. However, it took about 36 min to reach the same DS value at 200 MPa, and the radish did not reach the value of 0.2 when heated for more than 50 min at 400 MPa. These results show that HHP significantly delays the softening of the radish, and the degree of the delay becomes larger at higher pressure.

The softening rate constants and the regression coefficients at each pressure level evaluated by linear regression are shown in Table 17.1 (the data at 100 and 300 MPa, and those at 110°C are not shown in Figure 17.5). The obtained values showed relatively high regression coefficients, so that it was judged that the softening of radish by thermal treatment combined with pressure can be analyzed by a first-order kinetics model.[4]

17.3.2 β-Elimination of Pectin by Thermal Treatment Combined with Pressure

The relationship between the softening of vegetables and *trans*-elimination (β-elimination) of pectin in vegetables during cooking is indicated to be similar.[24,25] If the softening of vegetables is closely related to the β-elimination of pectin, pressurization will influence the β-elimination of pectin during thermal processing. Thus, the connection of the softening of radish and β-elimination of pectin by thermal treatment combined with pressure is investigated as follows.

The effect of pressure on the β-elimination of pectin is shown in Figure 17.6, where the experimental conditions are the same as those shown in Figure 17.4.

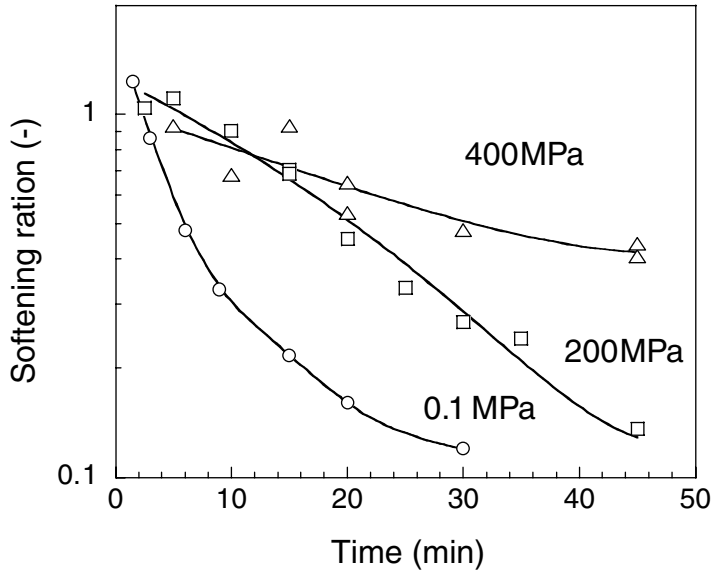

FIGURE 17.5 Progress of softening ratio of Japanese radish by thermal treatments at 100°C combined with pressure.

The β-elimination of pectin was significantly inhibited by pressure. The higher pressure delayed the β-elimination more effectively at both 100 and 110°C. Furthermore, the effect of pressure on the β-elimination indicated nearly the same tendency as that on the softening of radish (Figure 17.4).

TABLE 17.1
Kinetic Parameters for Softening of Japanese Radish by Thermal Treatment Combined with Pressure

Temp. (K)	Pressure (MPa)	Rate Constant ($\times 10^{-3} s^{-1}$)	r*	Apparent Activation Volume ($mm^3 \cdot min^{-1}$)	r*
	0.1	0.557	0.946		
	100	0.365	0.949		
373.2	200	0.339	0.916	4250 ± 590	0.946
	300	0.186	0.715		
	400	0.167	0.813		
	0.1	1.817	0.953		
383.2	200	1.005	0.917	3130 ± 560	0.969
	400	0.735	0.960		

*r = correlation coefficient

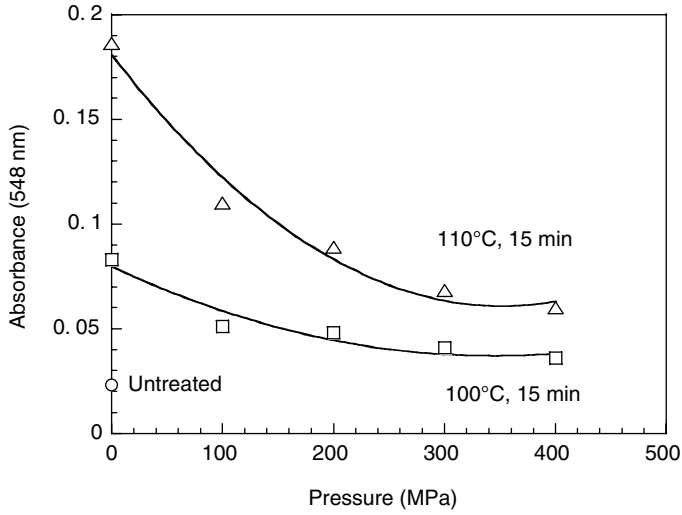

FIGURE 17.6 Effect of pressure on β-elimination of pectin at 100°C and 110°C for 15 min.

The progress of β-elimination of pectin at 100°C under pressure is shown in Figure 17.7. The β-elimination was considerably delayed by HHP. At 400 MPa, the β-elimination decreased by one third of the value at atmospheric pressure, even after the pectin solution was heated for 180 min. The relationship between the progress of β-elimination and pressure at 110°C almost had the same shape as that at 100°C shown in Figure 17.7. Thus, the inhibition of β-elimination by pressure (Figure 17.6 and Figure 17.7) has the same tendency as that of radish softening (Figure 17.4 and Figure 17.5). These results show that the softening of radish is closely related to the progress of β-elimination of pectin even under pressure, as previously clarified at atmospheric pressure.[24,25]

The kinetics study of the β-elimination of pectin during thermal processing at atmospheric pressure is discussed in a previous study,[25] in which the decomposition ratio of pectin (X_p) is defined by the following equation:

$$X_p = (A - A_0)/(A_e - A_0) \tag{17.1}$$

where A is the absorbance (at 548 nm) of the treated pectin solution, A_0 is the initial absorbance of the pectin solution (0.02), and A_e is the equilibrium value of β-elimination of pectin solution heated at 110°C for 8 h (0.243). If the β-elimination process obeys a first-order kinetics model, the following equations are available:

$$dX_p/dt = k(1 - X_p) \tag{17.2}$$

$$\text{In}(1 - X_p) = -k \cdot t \tag{17.3}$$

where k is the rate constant (sec^{-1}) of decomposition, and t is the time (sec). From the relationship between $(1 - X_p)$ and the treatment time, the decomposition rate constant at each pressure is determined by linear regression. The decomposition

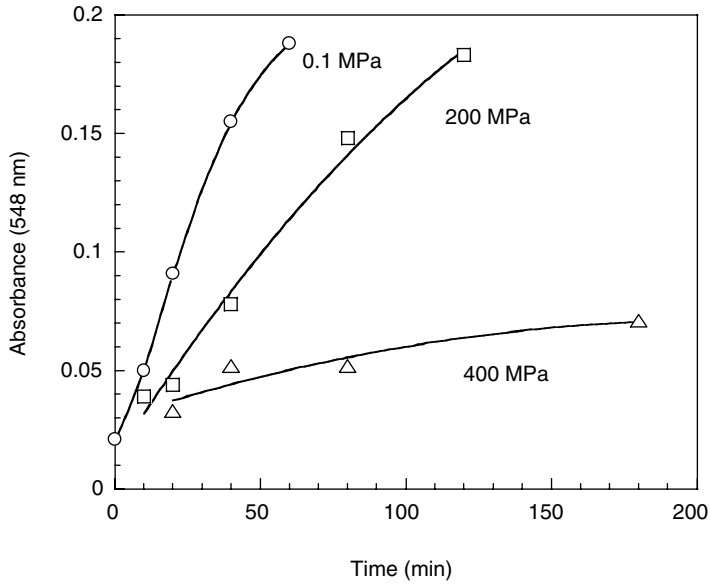

FIGURE 17.7 Progress of β-elimination of pectin by thermal treatments at 100°C combined with pressure.

rate constants and the regression coefficients are presented in Table 17.2. The regression coefficients of the rate constants were in the range of 0.93 to 0.99, except for the case at 100°C under 400 MPa. This result indicated that the thermal decomposition of pectin by β-elimination can be represented by a first-order kinetics model even under pressure.

17.3.3 Activation Volume for Softening Radish and β-Elimination of Pectin

By plotting the logarithmic values of the softening rate constants or the β-elimination rate constants as a function of pressure at a constant temperature, activation volumes (dV, $mm^3 \cdot mol^{-1}$) can be calculated from the slopes of the linear regression curves:

$$\ln k = \ln k_0 - (dV/RT)P \tag{17.4}$$

where $dV/(RT)$ is the slope, where R is a gas constant (8314 mm^3 MPa $(K \cdot mol)^{-1}$), T is the absolute temperature (K), k is the rate (sec^{-1}), and P is the pressure (MPa).

The activation volumes for the softening of radish were 4300 $mm^3 \cdot mol^{-1}$ at 100°C and 3100 $mm^3 \cdot mol^{-1}$ at 110°C (Table 17.1), and those for the β-elimination of pectin were 10,400 $mm^3 \cdot mol^{-1}$ at 100°C and 8100 $mm^3 \cdot mol^{-1}$ at 110°C (Table 17.2). Both values were positive, but the latter values were approximately twice as large as the former ones. However, the ratio of the activation volume at 110°C to that at 100°C

TABLE 17.2
Kinetic Parameters for Decomposition of Pectin by Thermal Treatment Combined with Pressure

Temp. (K)	Pressure (MPa)	Rate Constant ($\times 10^{-4}$ sec^{-1})	r*	Apparent Activation Volume (mm^3·min^{-1})	r*
	0.1	1.467	0.995		
	100	0.922	0.998		
373.2	200	0.690	0.990	10,350 ± 1,700	0.925
	300	0.131	0.930		
	400	0.084	0.855		
	0.1	3.290	0.991		
	100	1.795	0.983		
383.2	200	1.182	0.991	8,140 ± 650	0.986
	300	0.533	0.955		
	400	0.531	0.969		

*r = correlation coefficient

was nearly the same in both phenomena: 1.4 in the softening of radish and 1.3 in the β-elimination of pectin. This suggests that the softening inhibition of radish by pressure is closely related to the inhibition of the pectin β-elimination in the radish.

In general, when bond cleavage, neutralization, diffusion, and charge dispersal are suppressed by pressure, the activation volume has a positive value (+5000 ~ 20,000 mm^3·mol^{-1}).[26] Especially in the case of bond cleavage of chemical reaction, it is known to be +10,000 mm^3·mol^{-1}. The activation volumes of pectin β-elimination are +10,400 mm^3·mol^{-1} and +8100 mm^3·mol^{-1}, which are very close to that of the bond cleavage of the chemical reaction. On the contrary, the activation volumes of the hydrolysis of starch and locust bean gum, which are different from β-elimination, were estimated previously to be +1700 and +900 mm^3·mol^{-1}, respectively.[27] As an activation volume, these values are very small, and therefore, the hydrolysis of polysaccharides must be only slightly inhibited by pressurization.

17.3.4 Application of Pressure to Processed Foods during Thermal Treatment

The hardness or tenderness of foods is one of the key elements in their deliciousness. Plant tissues exposed to thermal treatments at high temperatures for a long time often become too soft. For instance, root vegetables such as Japanese radish, carrot, and other types of vegetables are easily oversoftened by heating, and therefore, it is relatively difficult to control the texture of these foodstuffs in processed foods, especially if they are treated at temperatures higher than 100°C. However, if the thermal processing is combined with HHP, the oversoftening of such foodstuffs will be avoided, since the softening of vegetables during heating

depends on the decomposition of pectic substances by ß-elimination,[24,25] and the ß-elimination is repressed by HHP.

17.4 EFFECT OF PRESSURE ON BROWNING

Browning due to the *Maillard reaction* between sugars and amino acids induces favorable color and flavor for processed foods and dishes, whereas it also deteriorates food quality in some cases. It is known that processing conditions like temperature, pH, and constituents of the ingredients affect the Maillard reaction. The reaction progresses in two stages: the condensation between carbonyl and amino compounds followed by the browning reaction. Tamaoka et al.[28] showed that the Maillard reaction is inhibited by high pressure, which controls the browning reaction considerably more than the condensation reaction. The HHP is therefore considered to be one of the important factors controlling the Maillard reaction. However, the effect of HHP treatment on the Maillard reaction has not yet been determined in the temperature range of around 100°C or higher used in practical circumstances, such as in the food industry. The effect of pressure on browning at high temperatures (100 to 115°C) is introduced in this section, using a glucose–glycine solution as a model of browning, and the applicability of the result is confirmed using a white sauce as one of the model foods.

17.4.1 Browning by Thermal Treatment Combined with Pressure

Browning of a glucose–glycine solution is measured in the temperature range of 100 to 115°C and in a pressure range of 0.1 to 400 MPa, and the result is shown in Figure 17.8. The browning value increased considerably with an increase in temperature at the same pressure. For example, at the atmospheric pressure (0.1 MPa), the value of 0.28 at 100°C for 30 min increased to 6.8 at 115°C for 30 min. When pressure was added to the thermal treatment, the browning was inhibited at each temperature depending on the pressure. This inhibition of browning by pressure coincides with a previous study,[28] though the heating temperature in the study was much lower than those used here. For 30 min at 100°C, the degree of browning at 400 MPa was about one tenth of that at 0.1 MPa, whereas in the same treatment time at 115°C, the degree of browning at 400 MPa was one third of that at 0.1 MPa, because the progress curves of browning at over 105°C did not obey a first-order reaction equation, as shown below.

The relationship between the treatment time and logarithm of the browning values is also shown in Figure 17.9. Only the curves at 100°C are straight ($r = 0.997 \sim 0.982$), as shown in Figure 17.9a, indicating that the browning at each pressure obeys a first-order reaction equation at 100°C. The slope of the curves decreased with an increase in pressure. However, in experiments conducted at temperatures other than at 100°C, none of the browning curves were straight but became concave upward; thus, the browning did not obey first-order kinetics. The browning rates can therefore be calculated from the experimental results at 100°C by linear

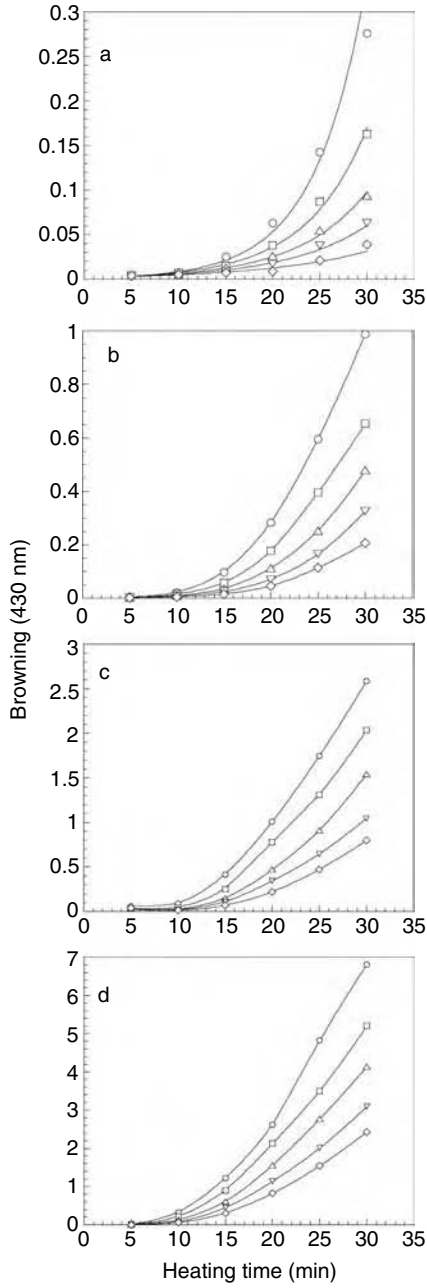

FIGURE 17.8 Effect of pressure on browning of glucose–glycine solution in a temperature range of 100 to 115°C. ○, 0.1 MPa; □, 100 MPa; △, 200 MPa; ▽, 300 MPa; ◇, 400 MPa. (a) 100°C, (b) 105°C, (c) 110°C, (d) 115°C.

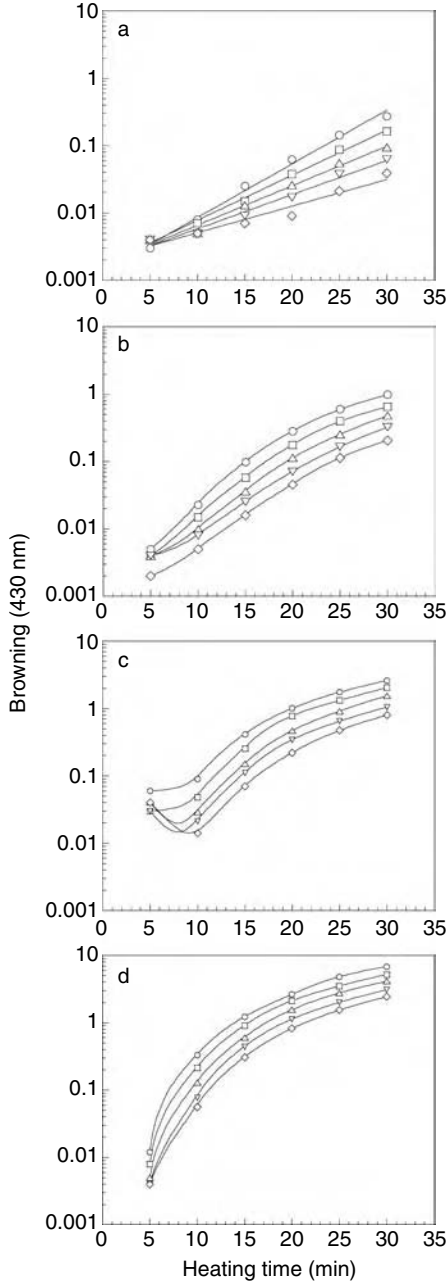

FIGURE 17.9 Relationship between heating time and logarithm of the browning value. ○, 0.1 MPa; □, 100 MPa; △, 200 MPa; ▽, 300 MPa; ◇, 400 MPa. (a) 100°C, (b) 105°C, (c) 110°C, (d) 115°C.

TABLE 17.3
Browning Rates of Glucose-Glycine Solution at 100°C in a Pressure Range of 0.1–400 MPa

Pressure (MPa)	Browning Rate* (min^{-1})	r**	Activation Volume ($mm^3 \cdot mol^{-1}$)
0.1	0.184	0.987	
100	0.154	0.991	
200	0.135	0.997	5220
300	0.117	0.989	(**r = 0.995)
400	0.091	0.982	

*The browning rates were calculated from the linear curves in Fig. 17.9a.

**r = correlation coefficient

regression and are shown in Table 17.3. The logarithmic values of these browning rates were plotted linearly against pressure (r = 0.995, not shown), and the *activation volume* estimated from the slope of the linear curve was 5220 $mm^3 \cdot mol^{-1}$.

At temperatures higher than 105°C, the browning did not obey the first-order equation, as shown in Figure 17.9, and therefore, linear regression cannot be applied to estimate the browning rate. So, presuming that the early step of the browning curves at temperatures higher than 105°C also follows a first-order reaction equation, like those at 100°C, apparent browning rates can be calculated in the following way.

The time required to reach the browning value of 0.1 at each temperature and each pressure was estimated in Figure 17.9 and abbreviated as $t_{0.1}$. The reverse value $t_{1.0}^{-1}$ of $t_{0.1}$ was used instead of the real browning rate to compare the effect of pressure on the Maillard reaction, as shown in the following section.

17.4.2 Effect of Pressure on Kinetics Parameters of Browning Reaction

17.4.2.1 Activation Volume of Browning

The relationships between the pressure and apparent browning rate $t_{1.0}^{-1}$ are shown in Figure 17.10. The curves almost became linear in the temperatures ranging from 100 to 115°C and were almost parallel. The apparent activation volume calculated from each curve was within 3800 $mm^3 \cdot mol^{-1} \sim 4500$ $mm^3 \cdot mol^{-1}$, as shown in Table 17.4. The value of 100°C (4500 $mm^3 \cdot mol^{-1}$) was slightly less than the value 5200 $mm^3 \cdot mol^{-1}$, which was calculated from the real browning rates in Table 17.3. It is known that the bond cleavage of chemical reactions is inhibited by pressure, and bond formation is accelerated by pressure; the activation volume of each is +10,000 and −10,000 $mm^3 \cdot mol^{-1}$, respectively.[26] When the values of activation volumes (3800 to 4500 $mm^3 \cdot mol^{-1}$) become positive, it shows that browning is inhibited by pressure, and the browning reaction might

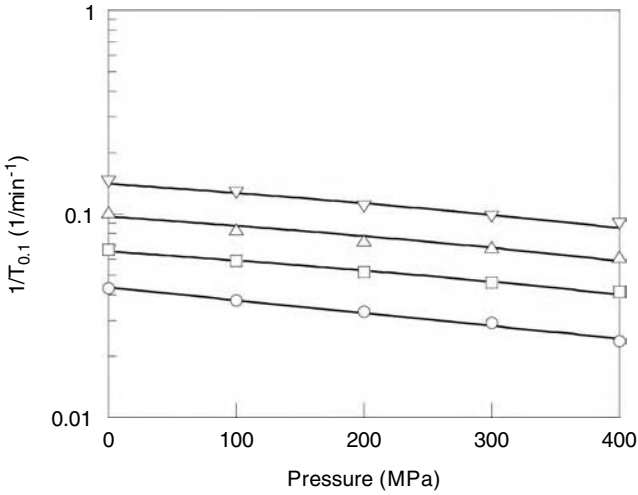

FIGURE 17.10 Relationship between pressures and apparent browning rates in a temperature range of 100 to 115°C. ○, 100°C; □, 105°C; △, 110°C; ▽, 115°C.

be controlled at a certain stage of bond cleavage in a series of complicated browning reactions. Furthermore, the browning value evaluated from absorbance at 430 nm is expected to be the result of the total reaction products through the two steps of the Maillard reaction, the condensation reaction and the browning reaction. Therefore, it is not clarified that the pressure affects either of the two reactions or both of them. Tamaoka et al.[28] estimated the two activation volumes separately from the condensation reaction and the browning reaction; the former is 1300 to 8900 $mm^3 \cdot mol^{-1}$ and the latter is 12,800 to 27,000 $mm^3 \cdot mol^{-1}$. The activation volumes (3800 to 4500 $mm^3 \cdot mol^{-1}$) obtained are within the former values (1300 to 8900 $mm^3 \cdot mol^{-1}$).

TABLE 17.4
Apparent Activation Volumes of Browning on the Glucose-Glycine Solution in a Pressure Range of 0.1–400 MPa

Temperature (°C)	Activation Volume* ($mm^3 \cdot mol^{-1}$)	*r***
100	4470	0.995
105	3770	0.999
110	3860	0.983
115	3940	0.996

*The values were estimated from the linear curves in Fig. 17.10.

***r* = correlation coefficient

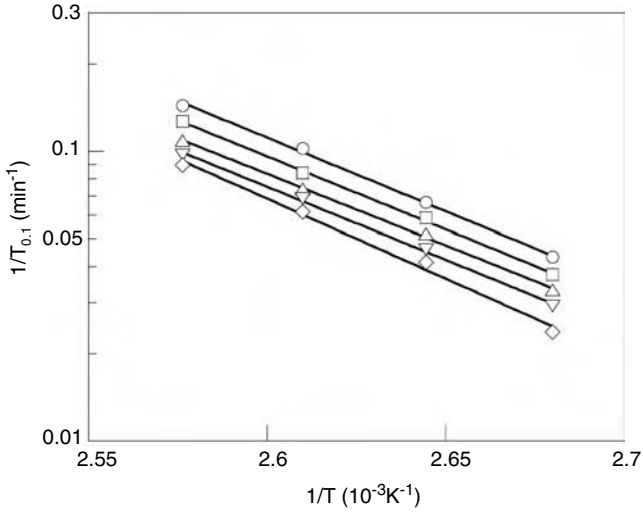

FIGURE 17.11 Arrhenius plots of apparent browning rates in a pressure range of 0.1 to 400 MPa. ○, 0.1 MPa; □, 100 MPa; △, 200 MPa; ▽, 300 MPa; ◇, 400 MPa.

17.4.2.2 Activation Energy of Browning

Figure 17.11 shows the Arrhenius plots of the apparent browning rates in a pressure range of 0.1 to 400 MPa. Each curve became linear and almost parallel in the temperature range of 100 to 115°C. Thus, the browning reaction of a glucose–glycine solution obeyed an Arrhenius equation for thermal treatment combined with pressure. Table 17.5 shows the apparent activation energies of the browning reaction calculated from each curve shown in Figure 17.11. The activation energies

TABLE 17.5
Apparent Activation Energies of Maillard Reaction on the Glucose-Glycine Solution in a Temperature Range of 100–115°C

Pressure (MPa)	Activation Energy* (kJ·mol^{-1})	A** ($\times 10^{12}$·min^{-1})	r***
0.1	97.4*	1.865*	0.999
100	96.3	1.149	0.999
200	94.3	0.528	0.999
300	96.1	0.869	0.999
400	105.3	13.811	0.997

*Each value was calculated from each linear curve in Fig. 17.11.
**A = frequency factor;
***r = correlation coefficient

(94.3~105.3 kJ·mol^{-1}) were almost equal in the pressure range of 0.1 to 400 MPa. Therefore, the activation energy of the browning reaction might be unchanged even though the pressure increases up to 400 MPa. The activation energies of the Maillard reaction previously reported are 105 ~ 209 kJ·mol^{-1}.[29] The values in Table 17.5 were within the reported values, but among the lowest values of those.

17.4.2.3 Browning Inhibition of White Sauce by Pressure

In order to make sure the inhibition of browning by thermal treatment combined with pressure can be applied to practical food processes, an experiment using white sauce as a model food was conducted.[6] The color difference of the white sauce is shown in Table 17.6. The white sauce heated with pressure browned somewhat more than the preheated one, whereas the white sauce heated without pressure browned considerably more than the one heated with pressure. Thus, the appearance of the white sauce clearly showed a difference in color, depending on heating with or without pressure. When the white sauce was heated without pressure, the *L* value (lightness) decreased considerably. However, the *L* value only decreased slightly for the white sauce treated with pressure. The *a* value for the heating with pressure condition remained at its original value, but the value for the heating without pressure condition increased considerably to a positive value from an originally negative one. The increase in the *a* value toward the positive side indicates an increase in redness. Furthermore, *E* of the white sauce heated with pressure was considerably less than that of white sauce heated without pressure. In addition to the color difference, white sauce heated without pressure had a heated odor compared with that heated with pressure in a sensory test.

From these experimental results, it is clear that thermal treatment combined with pressure inhibits not only a browning reaction between glucose and glycine, but also the browning of white sauce. Consequently, the pressurization during thermal treatments has a possibility of controlling the browning of foods produced through various thermal treatments.

TABLE 17.6
Browning of White Sauce by Heating with and without Pressurization

Sample	*L*	*a*	*b*	Δ*E**
Pre-heated	77.8	–2.8	6.0	—
Heating with HHP	75.0	–2.7	10.4	5.2
Heating without HHP	69.0	0.4	16.0	13.7

White sauce containing 1% glucose and 1% glycine was treated at 0.1 MPa or 300 MPa, 115°C, 30 min. *Δ *E* is color difference between pre-heating and heating with or without HHP.

17.5 PRESSURE RESISTANCE OF MICROORGANISMS

Some of the reports indicate that the treatment temperature during pressurizing significantly affects the inactivation of microorganisms even at room temperatures.[3,5,30] In addition, it is known that change in temperatures takes place as a result of adiabatic compression and expansion,[3] and may affect the inactivation of microorganisms by applying high hydrostatic pressure (HHP). There have rarely been such reports in which the temperature histories during the treatment are indicated. Therefore, the compact pressure vessel shown in Figure 17.1, capable of easily controlling temperature and of recording the change in the temperature, was used to investigate pressure resistance of some microorganisms.

17.5.1 Influence of Temperature Increase during Pressurization

The temperature history curve of the sample measured directly during pressurization has rarely been indicated in the literature, even though the treatment temperature was mentioned. Figure 17.12 shows changes in temperatures when the sample solution is pressurized, taking 30 sec to increase the pressure to 400 MPa, and maintained for a further 120 sec; then after that the pressure is released. The temperature rose about 8°C during pressuring up, and it took more than 60 sec to return to the initial temperature. When the pressure was released, the temperature decreased by about 14°C. In this case, water was used as the pressurizing medium in the pressure vessel. Thus, every pressure treatment follows this temperature history. For

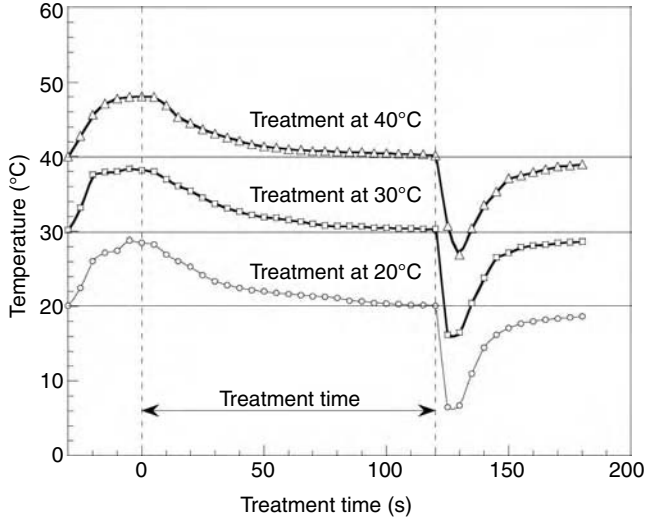

FIGURE 17.12 Temperature history curves of sample suspension during pressure treatment at 400 MPa for 120 sec.

TABLE 17.7
Effect of Increase in Temperature during Pressure Treatment on *E. coli* at 400 MPa

Temperature (°C)		Survivors
Initial	Holding	(CFU/ml)
10.2	18.1	1.7×10^5
20.2	28.4	1.9×10^6
30.2	38.5	3.5×10^3
40.1	49.0	5.0×10
50.1	59.1	no detection

The time for increasing, holding, and releasing pressure was 30 s, 10 s, and 10 s, respectively. Initial population of *E. coli* was 2.6×10^6 CFU/ml.

this pressure procedure, when the microbial suspension of *Escherichia coli* was pressurized, the populations are shown in Table 17.7. The survival populations at 10, 30, and 40°C decreased to one-twentieth, 3 log cycles, and 6 log cycles, respectively, although that at 20°C hardly decreased. A survival population was not detected at 50°C. When the initial temperature of the sample is higher or lower than 20°C, the pressure resistance of *E. coli* becomes lower than that at 20°C. Therefore, the effects of adiabatic compression or expansion should be considered. Some of the reports indicate that the temperature during pressurizing significantly affects the inactivation of microorganisms even at room temperature.[5,32] Furthermore, some pressurizing media, except for water, for example, oil and alcohol, are known to show the change in temperature due to adiabatic compression and expansion more than water. Accordingly, the changes in temperature due to adiabatic compression and expansion should be noticed as one of the experimental conditions, especially in the cases of large sample volume and short treatment time during pressurization.

17.5.2 Effects of Temperature and Time during Pressurizing on Pressure Resistance

The effect of temperature on pressure resistance of *E. coli* is shown in Table 17.8. In this case, the changes in temperature of the initial period and the final period are thought to follow Figure 17.12. The *E. coli* was alive, even though it was pressurized at 20°C for 40 min. However, it was dead at 30°C for 40 min and at 40°C for 30 min. This result shows that the temperatures influence the pressure resistance of *E. coli* in a room temperature range of 20 to 40°C. Some studies have previously reported similar results. When a suspension of *Rhodotorula*, a kind of yeast, was treated at 400 MPa for 15 min, a reduction of about 2 log cycles occurred at 30°C, and a 7 log cycle was inactivated at 45°C.[31] Furthermore, 100%

TABLE 17.8
Effect of Temperature during Pressurizing at 400 MPa on Pressure Tolerance of *E. coli*

Temperature (°C)	Treatment Time (min)				
	10	15	20	30	40
20	5[a)]	5	5	5	5
30	5	5	5	2	0
40	5	5	5	0	0

[a)]Number of positive growth tube per five test tubes. Initial population of *E. coli* was 9.1×10^6 CFU/ml.

of the *Candida parapsilosis* treated at 400 MPa for 10 min survived at 24°C, whereas only 1% did at 34°C.[30]

17.5.3 Pressure Resistance of Microorganisms

Table 17.9 provides the pressure resistance of 14 kinds of microorganisms in a pressure range of 300 to 500 MPa at 20°C for 20 min. *Vibrio parahaemolyticus*, *Pseudomonas fluorescens*, *Acinetobacter* sp., and *Saccharomyces cereviseae* were killed at 300 MPa, so that the pressurizing condition will kill about 7 log cycles of these microorganisms at least. This experiment shows that *V. parahaemolyticus* is rapidly killed at 1700 atm (172 MPa) at 23°C.[32]

Salmonella typhimurium, *Morganella morganii*, *Leuconostoc mesenteroides*, and *Candida parapsilosis* were inactivated at 400 MPa, and a reduction of at least 7 log cycles is expected (Table 17.9). It is indicated that *S. typhimurium* decreases to less than a 3 log cycle at 3400 atm (344 MPa) for 20 min,[33] and to a 6 log cycle at 400 MPa at 20°C for 10 min.[34]

E. coli and *Lactobacillus plantarum* survived at 400 MPa but did not at 500 MPa, and therefore, a reduction of at least 7 log cycles is expected (Table 17.9). *E. coli* decreases to a 6 log cycle at 400 MPa at 20°C for 10 min.[34]

Staphylococcus aureus, *Enterococcus faecalis*, and *Corynebacterium* sp. survived even at 500 MPa (Table 17.9). Previously, it has been shown that *S. aureus*, *E. faecalis*, and *Corynebacterium* sp. survive even at 600 MPa.[35,36] Therefore, it will be difficult to kill them at pressure less than 500 MPa and temperature 20°C for 20 min.

17.6 STERILIZATION OF BACTERIAL SPORES

Inactivation of many kinds of microorganisms by high hydrostatic pressure (HHP) has been investigated since Hite's initial research.[8] The HHP is especially known to be effective in inactivating vegetative cells of various bacteria rather than spores at room temperature.[11] In order to completely kill the bacterial spores at room

TABLE 17.9
Pressure Tolerance of 14 Genera of Bacteria and Fungi

Genera	Initial Population (CFU/ml)	Pressure (MPa)[a] 300	400	500
Gram negative bacteria				
Escherichia coli	1.3×10^7	5[b]	5	0
Salmonella typhimurium	3.3×10^7	5	0	0
Morganella morganii	2.2×10^7	5	0	0
Pseudomonas fluorescens	3.2×10^7	0	0	0
Vibrio parahaemolyticus	3.5×10^7	0	0	0
Acinetobacter sp.	4.8×10^7	0	0	0
Gram positive bacteria				
Staphylococcus aureus	8.2×10^7	5	5	5
Enterococcus faecalis	5.9×10^7	5	5	5
Lactobacillus plantarum	2.4×10^7	5	5	0
Leuconostoc mesenteroides	9.4×10^7	4	0	0
Corynebacterium sp.	1.1×10^7	5	5	5
Fungi				
Saccharomyces cereviseae	—	0	0	0
Candida parapsilosis	1.0×10^7	5	0	0
Neosartorya hiratsukae[c]	2.4×10^7	5	5	5

[a] Pressurization at 20°C for 20 min.

[b] Number of positive growth tubes per five.

[c] Ascospores.

temperature by pressure, a HHP of over 12,000 atm is required.[9] In addition, bacterial spores are not inactivated by pressurization at 981 MPa.[37] On the contrary, it has also been established that HHP is able to inactivate bacterial spores more effectively when combined with temperature.[5,12,22,23,38–42] Even though the temperature is relatively low (below 60°C), the death rate changes considerably, and the inactivation behavior of spores by pressurization is different from that of spores by heating alone.[5,26,39–42] Thus, it is important to clarify kinetically the inactivation behavior of various kinds of bacterial spores due to the function of temperature and pressure. However, though there have been some investigations carried out at temperatures lower than 100°C,[38–42] studies above 100°C are rare.[23]

The inactivation behavior of bacterial spores by thermal treatment combined with HHP has been studied, in which the temperature range is from 25 to 120°C.[1,2,4] The heat-resistant microorganisms used were *Bacillus subtilis*, *Bacillus coagulans*, *Bacillus stearothermophilus*, and *Clostridium sporogenes* (PA3679), which occasionally cause rancidity of pasteurized and sterilized foods. These results are introduced in this section.

TABLE 17.10
Parametric Values Obtained from Survival Curves of the Spores Used in Present Study

Bacterium	*D* Values* (min)/Temperature (°C)				*Z* Values** (°C)
B. subtilis	26.1/102	13.9/105	6.0/108	2.3/111	8.3
B. coagulans	105.0/104	38.2/107	13.9/110	4.6/113	6.7
B. stearothermophilus	28.6/113	6.6/117	2.3/121	0.6/125	7.4
C. sporogenes	10.8/110	4.1/115	0.6/120		7.9

* *D* value is the time required to reduce the number of spores by 1/10 at the temperature shown.
** *Z* value is the temperature to reduce D value by 1/10.

17.6.1 Bacterial Spores

The bacteria used were *B. subtilis*, *B. coagulans*, *B. stearothermophilus*, and *C. sporogenes*. Each spore was prepared according to the procedure outlined above.[5] The *D* values and *Z* values obtained from each survival curve of the four bacteria are shown in Table 17.10. These results were obtained under atmospheric pressure. Each survival curve became almost linear (r = 0.999 to 0.978). The *D* values were large enough compared to those of previous reports,[29,43,44] so that it is difficult to inactivate the spores at temperatures lower than 100°C, and the *Z* values were almost the same as those of the previous reports.[29,43,44] Each kind of spore was suspended in a 1/15 M phosphate buffer solution (pH 7.0) and used for the following experiments. The way of pressurizing the spore suspension was mentioned beforehand in Section 17.2.1.

17.6.2 Death Behaviors of *B. subtilis* Spores

The survival curves of *B. subtilis* at 400 MPa from 25 to 65°C are indicated in Figure 17.13a. The results show that the spores were inactivated even from a relatively low temperature such as 35°C. The death rates became higher in accordance with the increase in temperature. Thus, the temperature would affect the sterilization of spores even from around room temperature. On the contrary, the population of spores significantly declined in the first 5 min of treatment, during which the temperature rose. In the case of 65°C, the degree of the decrease reaches a 3 log cycle of the initial spores in the first 5 min.

After the first 5 min, the temperatures of the spore suspensions are thought to reach the given ones and then become constant, shown in Figure 17.2. The shape of each survival curve proved to be a downward convex. It is reported that survival curves of spores under HHP do not obey a first-order rate equation, as was often previously reported.[5,23,39,40]

The survival curves replotted in the relationship between log (survivors) and log (time) show a clear linear correlation (Figure 17.13b), and therefore obey an exponential equation. The same behavior is also observed in the previous studies, though

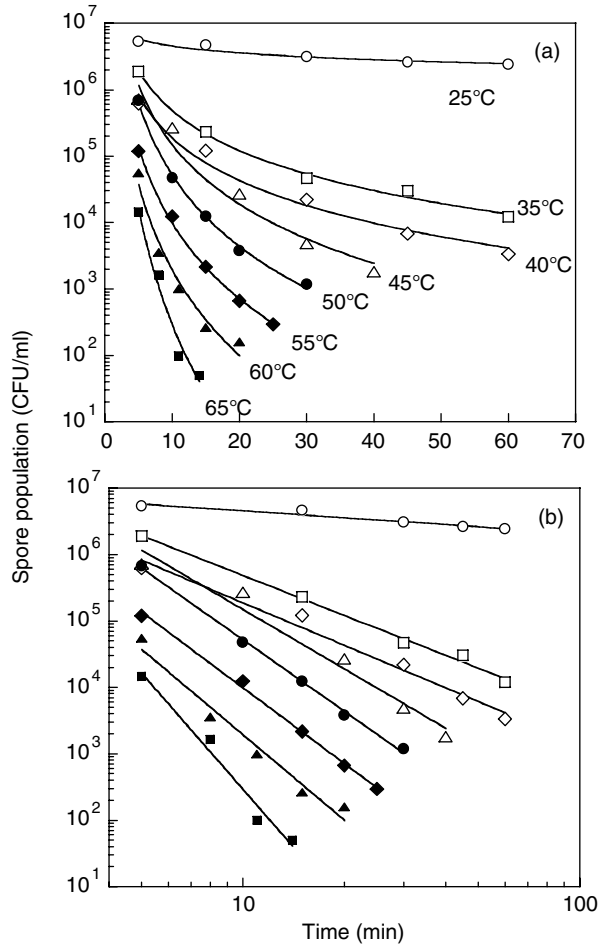

FIGURE 17.13 Survival curves of *B. subtilis* spores in a temperature range of 25 to 65°C under 400 MPa. (a) Shown by semilogarithm, (b) shown by both logarithms.

the microbes are different from *B. subtilis*.[23,39,40] This indicates that some of the spores can potentially survive even though they are treated for a long time under HHP in a moderate temperature range.

In the meantime, it is known that the germination of spores is induced by pressure in the temperature range of 30 to 60°C.[11–13,22] The degree of the germination reached 3 log cycles of spores.[53] Therefore, the death of spores in a moderate temperature range will probably be related to germination under HHP. It is generally agreed that at such pressures, spores germinate, follow by the death of the germinated spores.[22,23] The survival curves of *B. subtilis* spores in the temperature range of 90 to 110°C at atmospheric pressure, at 100 MPa, and at 200 MPa are shown in Figure 17.14a to c, respectively. Each survival curve

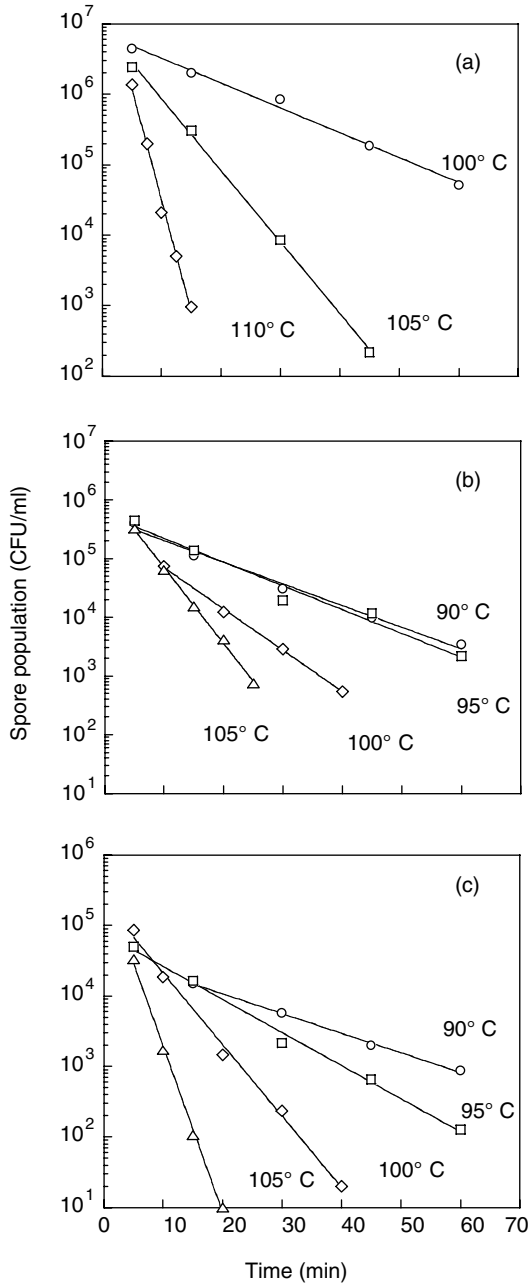

FIGURE 17.14 Survival curves of *B. subtilis* spores in a temperature range of 90°C to 110°C: (a) at atmospheric pressure, (b) at 100 MPa, and (c) at 200 MPa.

TABLE 17.11
Parametric Values Obtained from Survival Curves of *B. subtilis* Spores Used in Present Study

Pressure (MPa)	*D* Value* (°C)					*Z* Values** (°C)
	90	95	100	105	110	
0.1			28.3	10.0	3.2	10.6
100	27.2	24.7	14.3	7.8		20.0
200	35.9	21.4	9.9	5.5		17.1

**D* value is the time required to reduce the number of spores by 1/10 at the temperature shown.

***Z* value is the temperature to reduce D value by 1/10.

at 0.1, 100, and 200 MPa was linear (r = 0.999 to 0.985). The *D* values and *Z* values calculated by linear regression are shown in Table 17.11. The higher pressure reduced the *D* values at 100 and 105°C. The *Z* values at 100 and 200 MPa were approximately twice as large as that at atmospheric pressure and those reported before (*Z* = 7 to 12°C).[29] This might show that pressure reduces the temperature effect on thermal death rate.

17.6.3 Death Behaviors of *B. coagulans* Spores

The survival curves of *B. coagulans* spores by thermal treatments combined with 400 MPa become straight in a temperature range of 50 to 110°C (r = 0.999 to 0.987), which is shown in Figure 17.15. The death rates of the spores increased gradually from 50 to 90°C, and thereafter exponentially rose from 90°C. The *D* values calculated from each curve are shown in Figure 17.16, in which the *D* values at 0.1 MPa in Table 17.10 are also plotted. The *D* values gently decreased when the temperature rose from 50 to 90°C, but exponentially decreased from 90°C. The *Z* values at 400 MPa calculated from the *D* values were 39.1°C in the temperature range of 50 to 90°C, and 12.1°C in the temperature range of 90 to 110°C, and the *Z* value at 0.1 MPa was 6.7°C in the temperature range of 104 to 117°C. Thus, at lower than 90°C the *Z* value is quite large, and therefore the temperature effect on death rate might not be expected in this temperature range. However, the *Z* value at 400 MPa at higher than 90°C becomes approximately one third of that at lower than 90°C. So the temperature effect will be expected at 400 MPa at temperatures higher than 90°C. For example, it takes 13 min to get $D_{105°C}$ multiplied by 5 at 400 MPa, whereas it is almost impossible to kill the spores at 105°C at 0.1 MPa because $D_{105°C}$ at 0.1 MPa is quite large (80 min). However, the *Z* value at 400 MPa (12.1°C) is approximately twice as large as that at 0.1 MPa (6.7°C). This might lead to the pressure reducing the temperature effect on the thermal death rate. And finally, the *D* value at 400 MPa is larger

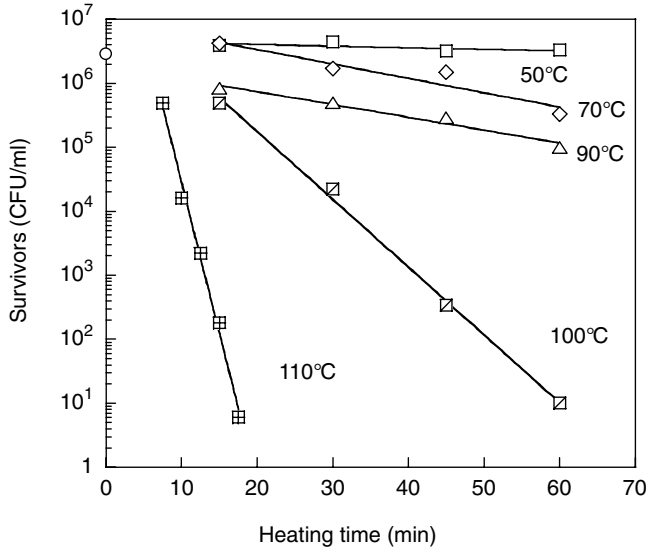

FIGURE 17.15 Survival curves of *B. coagulans* spores by thermal treatments (50 to 110°C) combined with pressure (400 MPa).

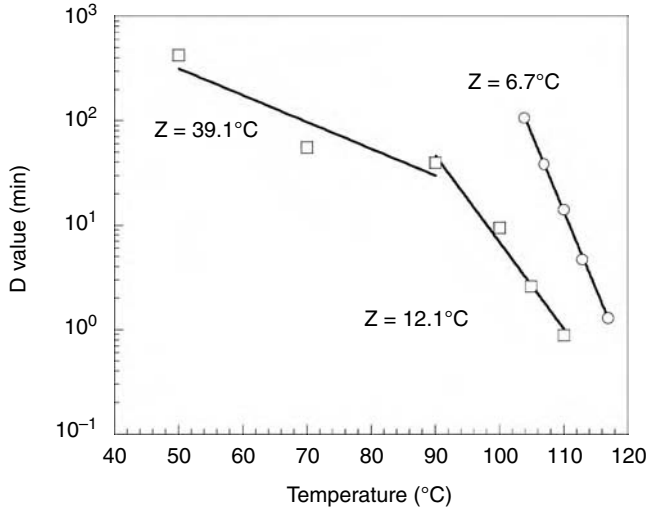

FIGURE 17.16 Comparison of *D* values of *B. coagulans* spores at 400 MPa with those at atmospheric pressure in a temperature range of 50 to 115°C. □, 400 MPa;○,atmospheric pressure.

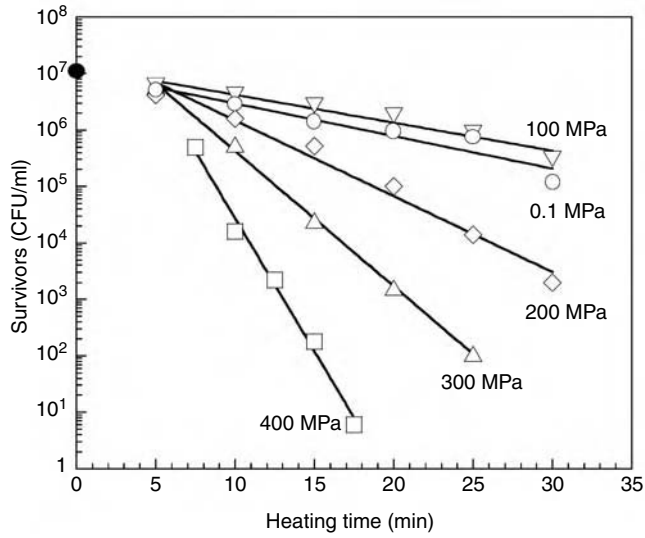

FIGURE 17.17 Death behaviors of *B. coagulans* spores by thermal treatments (100°C) combined with pressure (0.1 to 400 MPa).●, initial spore number.

than that at 0.1 MPa when the treatment temperature is higher than around 120°C. The same phenomenon is observed in *B. subtilis* spores, as shown in Table 17.11.

Figure 17.17 shows the death behaviors of *B. coagulans* spores by thermal treatments combined with HHP in the pressure range of 0.1 to 400 MPa. The *D* value at 100 MPa was almost the same as that at 0.1 MPa. At pressures higher than 200 MPa, the *D* values became considerably small. Each *D* value calculated from the survival curves is listed in Table 17.12. The *D* values at 200 and 400 MPa were

TABLE 17.12
D Values of *B. coagulans* and *C. sporogenes* Spores under Pressure at 110°C

Pressure (MPa)	$D_{110°C}$ Values (min)*	
	B. coagulans	*C. sporogenes*
0.1	17.8	17.7
100	19.1	20.0
200	7.4	3.7
300	4.2	2.3
400	2.1	1.3

*D value is the time required to reduce the number of spores by 1/10 at the temperature shown.

respectively 1/3 and 1/8 times smaller than that at 0.1 MPa. Accordingly, thermal treatments combined with HHP at pressure higher than 200 MPa will be able to assist the inactivation of spores; however, those combined with HHP at around 100 MPa will not show any acceleration of spore inactivation.

In the meantime, the germination of the *B. coagulans* spores is not easily induced by pressure as are other kinds of spores.[54] This will probably lead to difficulty in the inactivation in the temperature range of 50 to 90°C, even under 400 MPa, and also might be the reason that the shape of survival curves did not become a downward convex as in the cases of *B. subtilis* and *B. stearothermophilus* spores. On the contrary, it is reported that when the *B. coagulans* spore is pressurized at 30°C, the spore population remains at the initial level for 5 min and thereafter declines in line with the shape of the downward convex survival curves.[39]

17.6.4 Death Behaviors of *B. stearothermophilus* Spores

The survival curves of *B. stearothermophilus* at 113°C in the pressure range of 0.1 to 400 MPa are shown in Figure 17.18. The shape of each survival curve again proved to be a downward convex. In the case of 200 to 400 MPa, the survival curves were steep for the first 5 to 10 min and thereafter flattened out. One of the reasons is that the first 5 min is when the temperature is rising and the spores are efficiently killed after germinating, as previously reported.[22,23] After the first 5-min period, the spore suspension reaches the heating temperature at

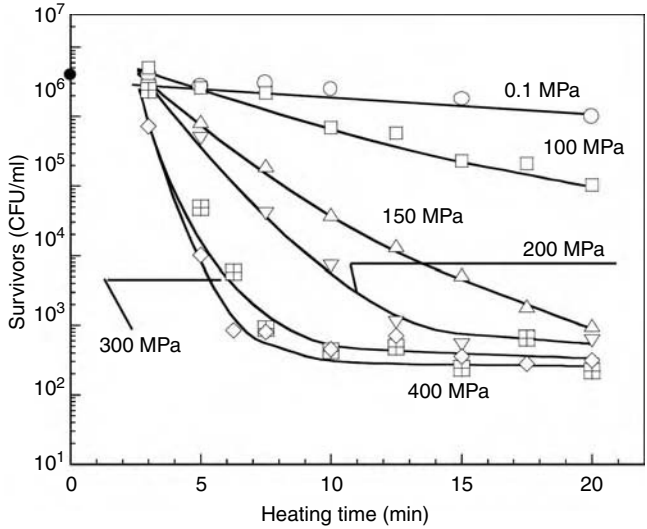

FIGURE 17.18 Survival curves of *B. stearothermophilus* spores by thermal treatments (113°C) combined with pressure in a pressure range of 0.1 to 400 MPa. ●, initial spore number.

113°C. In the case of temperatures of >95°C and pressures of >100 MPa, it is considered that the spores are not inactivated after germinating, but inactivated by bypassing the germination process.[23] In Figure 17.18, 2 ~ 3 log cycle spores were maintained at 300 and 400 MPa for 20 min after the first 5 min. This indicates no germination at 113°C at pressures of 300 to 400 MPa.

The survival curves in a temperature range of 50 to 120°C under 0.1, 200, and 400 MPa are shown in Figure 17.19a to c, respectively. At atmospheric pressure, it was most difficult to kill the spores at temperatures lower than 100°C. When pressurized at 400 MPa, the spores were not significantly inactivated at temperatures lower than 50°C, but began to be inactivated from the relatively low temperature of 60°C. The shape of the survival curves became a downward convex, particularly in the range of 70 to 90°C. However, the change in the convex shape was likely to terminate within 10 min in the temperature range of 100 to 120°C. Thereafter, the spore populations remained at the value of about 10^2 CFU/ ml for 50 min (Figure 17.19c). At 200 MPa, the spore inactivation did not progress up to the same degree as that at 400 MPa, but the tendency of the death behavior was similar to that of 400 MPa (Figure 17.19b).

In general, this sort of microorganism spore possesses high heat resistance. The inactivation of the spores below 100°C is related to their germination, since pressure is known to induce the germination of spores in a temperature range of 35 to 100°C,[42] especially at 70 to 95°C.[23] On the contrary, at temperatures lower than 60°C, the germinative effect of pressure is weak,[23] so that pressurization at 50°C hardly inactivates the spores, and at temperatures higher than 60°C, it begins killing some of the spores, as shown in Figure 17.19b and c.

The survival curves of *B. stearothermophilus* spores by thermal treatment at 120°C under 200 and 400 MPa are compared with that under 0.1 MPa in Figure 17.20. The survival curve obtained, when the pressure was released from 200 to 0.2 MPa after a 10-min treatment, is also shown. The results clearly show that HHP at 200 MPa was not able to fully inactivate the spores even at 120°C, whereas when the pressure was released to 0.2 MPa, the spores died exponentially. This indicates that pressure probably enhances the heat resistance of spores. The survival curve at 200 MPa was, in the meantime, somewhat different from that at 400 MPa. The curve of 400 MPa remained at 10^2 CFU/ml from 5 to 50 min, whereas that of 200 MPa declined gradually in the same period, and finally, the population decreased by approximately 10^1 CFU/ml. This result might suggest that higher pressure enhances the heat resistance of the spores more effectively. It is reported that pressure suppresses thermal denaturation of *B. subtilis* DNA, and the effect increases from 1200 to 1600 atm.[45] Enhancing heat resistance of the spores by pressure might be related to the same phenomenon reported above.

17.6.5 Death Behaviors of *C. sporogenes* Spores

Figure 17.21 shows the survival curves of *C. sporogenes* spores under pressures ranging from 0.1 to 400 MPa at 110°C. Each curve under pressure became almost

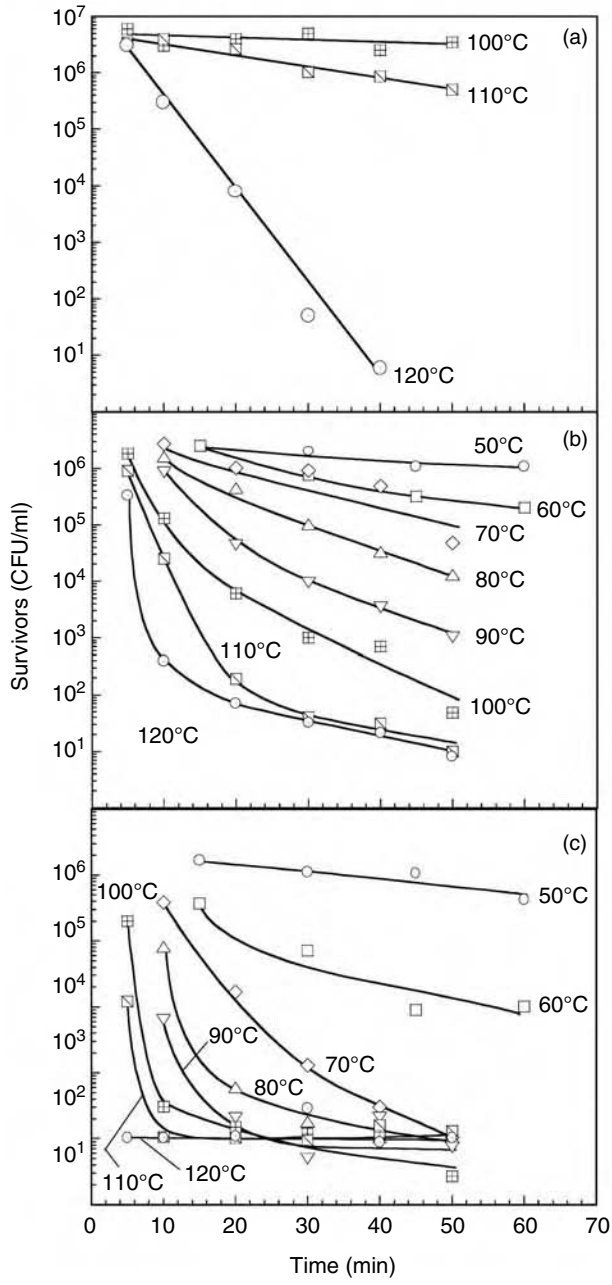

FIGURE 17.19 Survival curves of *B. stearothermophilus* spores by thermal treatment in a temperature range of 50 to 120°C combined with pressure. (a) 0.1 MPa, (b) 200 MPa, (c) 400 MPa.

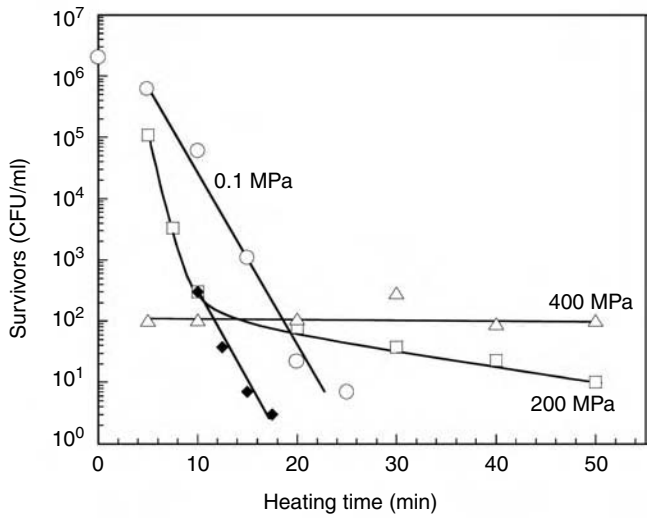

FIGURE 17.20 Comparison of survival curves by thermal treatment (120°C) combined with pressure. ◆, Pressure was released to 0.1 MPa after the 10-min thermal treatment combined with 200 MPa.

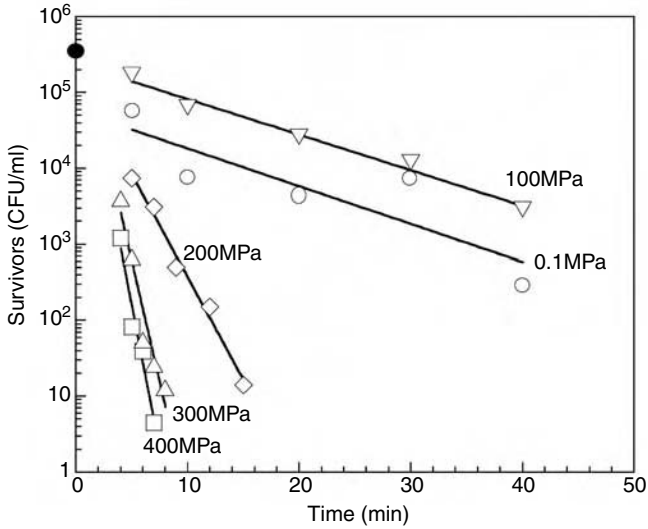

FIGURE 17.21 Survival curves of *C. sporogenes* spores under pressure ranging from 0.1 to 400 MPa at 110°C.

linear, and their slopes became steeper with increases in pressure, except for 100 MPa. This result is similar to that of *B. coagulans*. In addition, the initial numbers of spores (3.5×10^5 spores/ml) were reduced to $1 \times 10^3 \sim 10^4$ spores/ml during the first 5 min of treatment. This reduction is similar to that of *B. subtilis* spores (Figure 17.13), but the temperature range is higher. The *D* values calculated from each survival curve are shown in Table 17.12. The *D* values at 200 and 400 MPa were 5 and 13 times larger than that at 0.1 MPa, respectively. Accordingly, the sterilization at pressures higher than 200 MPa can assist the inactivation of the spores; however, the effect of inactivating the spores around 100 MPa is almost the same as that at 0.1 MPa or less.

The survival curve of the same microbe spores is also shown to be a downward convex at 600 to 700 MPa at 80°C in phosphate buffer and consommé.[40] This sort of microbe spore is important for the safety of foods made through thermal treatment, so that a lot of information to inactivate them by thermal treatment combined with HHP must be accumulated in the future.

17.7 PRESSURE COMBINED WITH MILD HEATING

The thermal treatments combined with pressure and their interesting phenomena and abilities for food processing were discussed in previous sections. These studies have been conducted exclusively in the area of pressure higher than 100 MPa. On the contrary, Okami[46] suggested that pressurization at less than 100 MPa also has potential for use in practice. In fact, there are a few innovative pressure techniques previously used at pressures relatively lower than 100 MPa.[7,19] In this section, two combination treatments of relatively low pressurization (below 100 MPa) and mild heating (40 to 60°C) for food processing will be discussed.

17.7.1 Shucking of Oyster by Pressure

At the beginning of the 1990s, an innovative way of shucking the shells of oyster was patented in Japan.[18] This method involved the pressurization at 100 to 400 MPa to smoothly separate the bond between the adductor and the shells without cutting. However, in Japan the new method was not practiced, because the cost of the pressure machine for shucking oysters was too high. In contrast, this method was afterwards reported in the U.S. too, and the innovative way of shucking oysters by pressurization was used in the U.S. The quality of pressure-shucked oysters has been reported.[20]

In the meantime, in Japan, pressurization combined with mild heating was investigated again. The appropriate conditions for shucking oyster shells have been described.[19,47] Figure 17.22 shows a photograph of the shucking oyster machine used in the tests. The shucking occurs after 5 min at 80 MPa and 42°C. The denaturation of the oyster itself seems not to take place, and the oyster is efficiently separated from the shells (Figure 17.23). The strongest point is that the pressurization combined with mild heating diminished the magnitude of pressure to approximately one fifth of the pressure (400 MPa).[18,20] Furthermore, it is reported that the oysters shucked by pressure are not distinguishable from those shucked by hand in both taste and appearance,

FIGURE 17.22 Photograph of a machine shucking oysters for testing.

and the microbe population declined by about one tenth of those shucked by hand.[47] Another benefit is that shucking oysters by pressure can diminish the risk that some fragments of shell might mix with them. Oysters shucked by pressure have been sold in the Japanese market.

17.7.2 Autolysis under Pressure and Mild Heating

It is known that the growth of microorganisms is generally inhibited under pressures higher than 60 MPa,[9] while enzymes like proteinases were inactivated at 200 MPa

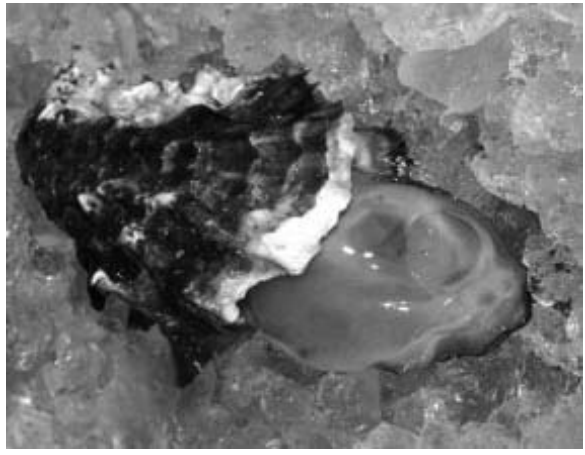

FIGURE 17.23 Photograph of an oyster shucked by pressure combined with warming.

(50°C) and 400 MPa (25°C).[48,49] Therefore, certain pressure conditions, at which microorganisms cannot grow and proteinases are not inactivated, probably exist in a range of 60 to 400 MPa at 25 to 50°C. If raw fish are kept under this pressure condition at the optimal temperature, proteinase will act rapidly without the growth of microbes. Fish sauce, one of the traditional seasonings in Southeast Asia, makes use of the autolysis of fish, and a large quantity of salt (over 20%) is added to it to prevent its rancidity. The authors have tried to produce fish sauce without any addition of salt,[7,50–52] using the idea of autolysis by pressure treatment combined with mild heating.

17.7.2.1 Inhibition of Microorganism Growth by Pressurization

The growth of microorganisms is inhibited by pressure, and the pressure magnitude is higher than 60 MPa.[10] However, this finding was reported in 1948, and much more information on the growth inhibition due to pressurization is not mentioned in the report. Thus, the investigation of growth inhibition by pressurization was tested again.[54]

Pressurization at 40 MPa prevented *yeast* (*Saccharomyces cerevisiae* and *Zygosaccharomyces rouxii*) from growing. The growth inhibition of lactic acid bacteria (*Lactobacillus lactice*, *Lactobacillus plantarum*, and *Tetragenococcus halophilus*) was needed to pressurize at 70 MPa. *Escherichia coli* and vegetative cells of *Bacillus. subtilis*, and bacterial spores (*Bacillus subtilis*, *Bacillus coagulans*, *Bacillus stearothermophilus*, and *Clostridium sporogenes*) were suppressed by pressurization at 60 and 50 MPa, respectively. From these results, it is necessary to pressurize at 70 MPa to stop growth of lactic acid bacteria, at 60 MPa to prevent growth of *Escherichia coli*, and at 50 MPa to stop growth of bacterial spores. In addition to those, microorganisms that mainly cause rancidity during autolytic processing at 50°C were isolated from anchovy, and they were also suppressed by pressurization at pressures higher than 50 MPa (Figure 17.24).[50] From these results, pressurization at pressure higher than 60 MPa probably prevents the growth of almost all the microorganisms that potentially can grow during the autolytic processing of fish at 50°C.

17.2.2.2 Autolytic Condition under Pressure

In order to find out the best autolytic condition under pressurization, anchovy was autolyzed for 24 h in the pressure range of 50 to 250 MPa at 50°C or in the temperature range of 20 to 70°C at 60 MPa. The autolysis progressed well on every magnitude of pressure,[7] but it is important to autolyze fish at low pressures for practical purposes. In addition, it is necessary to adopt pressure conditions without the growth of any microbes. With these considerations, the magnitude of pressure was set to 60 MPa, at which autolysis would proceed without rancidity.[7,50] Next, the optimal temperature for autolysis under pressure was set to 50°C.[7,51] At temperatures higher or lower than 50°C, the progress of autolysis

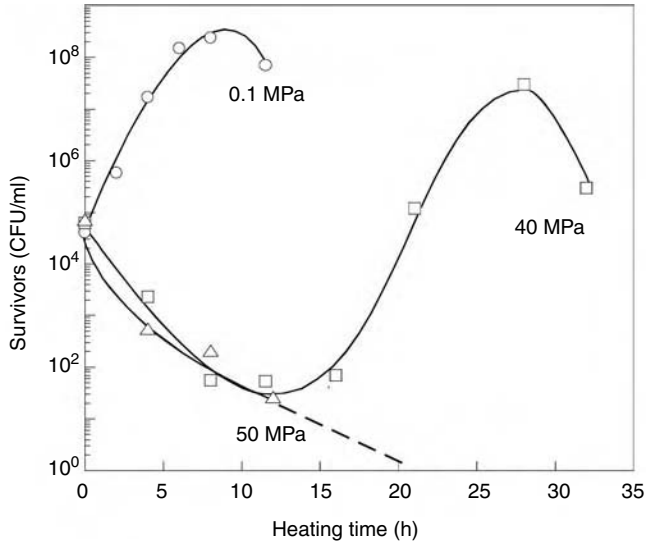

FIGURE 17.24 Effect of pressure on growth inhibition of *Clostridium* sp. isolated from a rancid anchovy at 50°C.

becomes slow. From these results, the condition of autolysis under pressure was finally set at 60 MPa and 50°C for 24 to 48 h.

17.2.2.3 Quality of Pressure Autolytic Extract

The extract produced by the autolysis of fish without the addition of salt is quite different from traditional fish sauce, in the view of flavor and taste. Therefore, this extract is called the *pressure autolytic extract* (PAE).[7] This PAE contains 0.6% NaCl that is originally contained in the fish, 2.6% total nitrogen, and 11.6% free amino acids, which consists of Glu 1.5%, Leu 1.3%, Lys 1.2%, Ala 1.0%, Asp 0.9%, and so on, by weight (Table 17.13). These contents are higher than those of commercially available fish sauce and soy sauce. Glu, Ala, and Asp are known to be taste-active amino acids, so that this PAE is expected to have a good taste. In contrast, nucleotides (adenosine monophosphate, inosine monophosphate, and guanosine monophosphate) are not detected in the PAE.

When evaluated for saltiness, PAE tasted significantly less salty than fish sauce ($p < 0.05$). PAE has a favorable odor like cooked fish, which is stronger than fish sauce ($p < 0.05$). In addition, the amount of cheesy and rancid odor in the PAE is significantly less than that of fish sauce ($p < 0.05$).

Therefore, this autolytic technique under pressurization combined with mild heating could be a new method for producing a good-quality autolytic extract like fish sauce without any addition of salt in an extremely short period. The autolytic extract produced by the innovative way has been launched in the Japanese market.

TABLE 17.13
Chemical and free amino acid components of pressure autolytic extract (PAE), fish sauce (Nampla) and soy sauce

	PAE	Nampla	Soy sauce
pH	6.6	5.4	5.4
NaCl (%)	0.6	20.9	13.6
T-N (%)	2.62	1.74	1.41
F-N (%)	1.42	1.06	0.74
F-N/T-N	0.54	0.61	0.45
Amino acids (%)			
Glu	1.47	1.22	1.23
Ala	1.00	0.78	0.79
Asp	0.88	0.84	0.19
Leu	1.27	0.67	0.72
Lys	1.24	0.87	0.30

17.8 CONCLUSIONS

The softening of vegetables and browning occurring during thermal processing were suppressed by pressure. Pressure might also have the capability of inhibiting an off-flavor and discoloration, and reducing viscosity during thermal treatment. Another important function of thermal treatment is pasteurization and sterilization of foods to provide consumer safety. It is, however, difficult to kill microorganisms by pressure, because some microorganisms survived at pressures above 500 MPa, while others died below 300 MPa. Bacterial spores were considerably inactivated by thermal treatment combined with pressure, though a few spores survived. Thus, the use of pressure for inactivating microorganisms is effective, but there are still some problems to resolve. Finally, two innovative techniques of pressure treatment combined with mild heating were introduced. One is to use the combination of pressurization at 80 MPa and mild heating at 42°C to allow easy shucking of oysters without the need of hands. A key to shucking oysters is temperature. The other is the autolysis of unsalted fish protein under pressurization. This technique can be a new way for producing a good-quality autolytic extract in an extremely short period without any addition of salt.

ACKNOWLEDGMENTS

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NOMENCLATURE

A	Absorbance of pectin solution (nm)
A_0	Initial absorbance of pectin solution (nm)
A_e	Equilibrium value of pectin solution (nm)
dV	Activation volume ($mm^3 \cdot mol^{-1}$)
k	Rate constant (sec^{-1})
P	Pressure (MPa)
R	Gas constant (8314 $mm^3 \cdot MPa/(K \cdot mol)$)
t	Time (sec)
T	Absolute temperature (K)
X_p	Decomposition ratio of pectin

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18 pH-Assisted Thermal Processing

Alfredo Palop and Antonio Martínez

CONTENTS

18.1 INTRODUCTION

Heat sterilization ensures food safety and preservability through bacterial destruction, but it also involves the application of intense treatments that cause additional food quality losses. In many cases, bacterial destruction is not necessary for food preservation, and bacterial growth can be inhibited by controlling environmental factors that affect viability. In this case, microbes will not be destroyed, but they will not be able to grow, and the preservation techniques used, which are much less intense, will affect food quality much less.

Acid pH has the advantage, over other environmental factors that affect microbial viability, that it also decreases microbial heat resistance. Hence, acidified foods can be heat treated at lower temperatures, keeping the same levels of microbial destruction. Moreover, acid pHs hamper the recovery and growth of the survivors to the heat treatment. Microorganisms show their maximum heat resistance at neutral pH, decreasing with the increase in acidification. The extent of the effect of acid pH on heat resistance depends on the microorganism being tested and the heating temperature. It is also influenced by the type of acid and its concentration.

The inhibitory effect of acid pH on microbial growth has long been used to preserve foods from spoilage. Indeed, acidification has been used as a food preservation technique through thousands of years in human history, naturally by

fermentation or artificially by adding weak acids. Fermented milks were produced for the first time a long time ago. Probably when humans started to tame dairy species and use their milk did lactic bacteria from soil or plants accidentally contaminate the milk, expanding to the recipients used to collect and preserve it and eventually installing on them. The mechanism of action of this preservation technique, though unknown by our ancestors, was simply a microbial lactic fermentation that reduced the pH value of the milk and was able to extend itself to the preservation of milk. This accidental growth of lactic bacteria probably did not lead to the production of homogeneous fermented milks with stable and defined flavors, but had the undeniable advantage of preventing the development of pathogen microorganisms.

Later, Romans used vinegar regularly to preserve their foods. Romans were very interested in agriculture and livestock farming, but also in food processing and preservation. To supply a large city such as Rome with food was not easy, and vinegar, together with other preserving agents such as brines or ice, was used regularly to preserve foods because of its acidifying effect.

Heat treatments were applied extensively to preserve foods much later in human history. Nicolas Appert showed at the beginning of the 19th century that the application of a thermal treatment to foods contained in tightly closed cans preserved them from spoilage, but about 50 years later it was Pasteur who made sense to this procedure by discovering that microbes were responsible for the deterioration of foods and heat acted to kill them, hence preserving foods. Pasteur used heat for the first time with the purpose of inactivating the spoilage microorganisms of wine and beer. The technique was rapidly extended to other liquid foods such as milk and was developed in the actual pasteurization treatments. Bigelow and Esty[1] studied in 1920 the heat inactivation kinetics of microorganisms and stated the basis for the modern food sterilization processes. Soon after this, Esty and Meyer[2] investigated the effect of acid pH on heat resistance, showing that acid pHs lowered the *D* values of microorganisms. Some years later, Sognefest et al.[3] corroborated the important influence of pH on bacterial heat resistance. All these findings led to the introduction in the food canning industries of an acidification step, prior to the thermal treatment.

Customers nowadays are demanding high-quality products combined with food safety. To meet this demand, the industry has developed minimally processed food products using a combination of different technologies in order to reduce the impact of severe heat treatments, which guarantee food safety, but produce a negative effect on the sensory and nutritional properties of the product. Acidification of the food allows reduction of the intensity of thermal treatments and is one of the most frequent procedures used. On the other hand, acidification does not seem to reduce consumer acceptability of canned foods.[4]

Present objectives of acidification of canned foods are to inhibit growth of *Clostridium botulinum* in order to ensure food safety and to sensitize spoilage microorganisms to heat, especially bacterial spores.

This chapter will start with a short discussion on the heat treatments that are applied to canned foods, attending to their pH. Afterwards, the chapter will focus

on the data related to the heat resistance of bacteria, especially bacterial spores, which are the target of heat sterilization treatments, and paying attention to recent relevant data. In Section 18.3, the inhibitory effect of acid pH on bacterial growth will be exposed, as an introduction to its destructive effect at high (heating) temperatures, which will be dealt with in Section 18.4. The effect of the type of acid on bacterial heat resistance will be described in Section 18.5, and the effect of pH on the recovery of the survivors to the heat treatment in Section 18.6. In Section 18.7 the theories that try to explain the increased sensitization of bacteria to heat when it is applied at acid pHs will be discussed. Finally, Section 18.8 will show the existing models, databases, and software developed to predict bacterial behavior at acid heat treatments.

18.2 CANNED FOODS AND pH

In their natural form, many foods, such as meat, fish, and vegetables, are slightly acidic. Most of the fruits are rather acidic, and only a few foods like egg whites are alkaline.

For canned foods, the distinctive pH value is 4.6, which is the minimum pH of growth for *C. botulinum*, the most heat resistant of the food pathogen microorganisms.[5]

Low-acid canned foods (with pH values higher than 4.6) have to be exposed at least to a heat treatment able to reduce *C. botulinum* spore counts in 12 log cycles (2.52 min at 121°C or an equivalent combination of time and temperature), which is known as the botulinum cook.[6] Acid or acidified canned foods (with pH values lower than 4.6) can be heat treated at temperatures around 100°C for a few minutes at atmospheric pressure without the need of usage of retorts to apply the treatments. Such a simplification in the way to apply these treatments has minimized the efforts invested in the technology, which is essentially the same that was used initially, i.e., open water baths heated at 100°C or lower temperatures.

Acid or acidified foods with pH values between 4.0 and 4.5 are usually heat treated to reach acceptable levels of risk of flat sour spoilage caused by *Bacillus coagulans*. Below pH 4, the risk of bacterial spore spoilage disappears and sterilization treatments are not necessary.[7]

However, in the last few years several spoilage incidents related to acid foods, such as heat-treated fruit juice products, have been reported.[8–11] In most of the cases, the microorganism responsible for the spoilage has been an acidophilic sporulated bacterium, belonging to a species of the genus *Alicyclobacillus*, such as *A. acidoterrestris.* These microorganisms are able to grow at pHs as low as 2.5 in spite of being sporuled bacteria.[10]

Moreover, it has been postulated that the growth of some mesophilic bacili that are able to grow at pH values close to 4.5 could lead to local increases of the pH of the food that would allow for the development of *C. botulinum*.[12,13] Furthermore, it has been observed that the minimum pH at which *C. botulinum* develops and synthesizes toxin depends on the anaerobic conditions[14] and on the acidulant used to lower the pH.[15]

Odlaug and Pflug[6] consider that for a canned food with a pH lower than 4.6 to be at risk of having the botulinic toxin, the following four situations should occur simultaneously: (1) food with high numbers of *C. botulinum* spores, (2) concurrence of other microorganisms because of poor processing or posttreatment contamination, (3) food composition and storage conditions that enable growth of *C. botulinum* and toxin formation, and (4) growth of other microorganisms that create favorable conditions for growth and toxin formation. Fortunately, in the opinion of the same authors,[6] the coincidence of the four situations happens very rarely.

The appropriate pH in the cans is obtained by the use of brines with known acid concentrations or tablets of known acid composition that are added to cans of specified volumes. The contents of the cans must then be conveniently stirred to ensure that the pH is below 4.6 in the center of all the food particles.[5]

Acids used in canning to lower the pH below 4.6 are usually citric, lactic, and malic, but also glucono-δ-lactone.[16] Dall'Aglio et al.[17] stated that while citric and other acids gave an acid taste (or other characteristic tastes related to the acid) to the food product, glucono-δ-lactone could be added to the brine to decrease the pH at the desired level without giving such an acid taste to the preserve. However, in most cases, the choice of acidulant used to decrease the pH is based on economics and convenience (ease to apply) criteria, more than on solid scientific data.

18.3 EFFECT OF pH ON BACTERIAL GROWTH

When the pH is shifted from the optimum for growth for a specific microorganism, the growth rate decreases, reaching a value where growth stops completely. Moderately acid pHs cause an increase in the duration of the lag phase, a lower growth rate during the exponential growth phase, and a lower maximum population density.

Bacteria deal with wide-ranging changes in the pHs of their growth medium by maintaining their internal pH near a fixed optimal value. The proton, more than any other ion, is involved in almost every physicochemical as well as biochemical reaction. The difference in proton concentration across the cytoplasmic membrane (proton electrochemical gradient) together with the difference in electrical charge at both sides (membrane potential) create a form of potential energy called proton motive force, which cells can use for a variety of purposes, including active transport, maintenance of cell's turgor, maintenance of cell's internal pH, turning flagella, and driving a reverse flow of electrons through the respiratory chain to produce reducing power, such as reduced nicotinamide adenine dinucleotide (NADH) or generation of adenosine triphosphate (ATP). However, extreme environmental pH values cause dysfunction of this system, leading to an acidification or alkalinization of the bacterial cytoplasm, blockage of the metabolic pathways, and finally growth prevention and even cell death.[18]

Typically, bacteria are more sensitive to an environmental stress when they are under the influence of other stresses; i.e., the minimum pH for growth will be higher if cells are cultured on a medium containing high concentrations of sodium chloride.

While much of the effect of acid pH can be accounted for by pH, it is well known that different organic acids vary considerably in their inhibitory effects.

Apart from the free proton concentration itself (that is, the pH value), microorganisms are affected by the concentration of nondissociated weak acid, which is also dependent on the pH value. It has been shown that both the ionized and the nonionized forms of an organic acid can contribute to its inhibitory effect, although the undissociated form is generally more inhibitory.[19]

Some weak acids (acetic and lactic acids, for example) are lipophilic in their undissociated form and pass readily through the plasma membrane, entering the bacterial cell. In the cytoplasm at a pH of approximately 7, the acid molecules dissociate, releasing protons that cannot pass across the lipid bilayer (only by active transport) and accumulate in the cytoplasm, thus lowering the internal pH.[5] Acidified cytoplasm in turn inhibits metabolism and consequently growth. Moreover, the dissociated form of these acids may have inhibitory effects for the cell at high concentrations. Other weak acids do not pass through the bacterial membrane, and hence do not acidify the cytoplasm, or as proposed for, sorbic acid[20] could act as membrane-active compounds. The mechanism for strong acids, such as hydrochloric or phosphoric, is to decrease considerably the external pH, providing a high environmental concentration of protons that determines the acidification of the cytoplasm of the cell.

Some acids are very effective inhibitors of microbial growth and are intentionally added to many foods as preservatives. This is the case of benzoic and sorbic acids.[16] Others, such as acetic, fumaric, propionic, or lactic, simply prevent or delay the growth of pathogenic and spoilage bacteria.[16]

Hsiao and Siebert,[21] after studying 11 physical and chemical properties of 17 organic acids commonly found in food systems, attributed the differences in their inhibitory effect to fundamental properties of them, including polar groups, number of double bonds, molecular size, and solubility in nonpolar solvents. However, these same authors found different patterns of acid resistance when studying the effects of the same acids on six test bacteria. This could mean that although the effect of different acids can be predictable for some known bacterial species (in function of their molecular properties), the susceptibility of a new bacteria should have to be investigated before any conjecture can be established.

Still, acetic followed by lactic acids are commonly found as the most inhibitory acids for many bacteria,[15,22–24] and this could be related to their low molecular weight and high dissociation constant (pK_a) values. Probably, these are the most important properties of weak acids,[25] because they determine the capability of acids to enter bacterial cells in an undissociated form. Acids are only able to enter the cell when they are in the undissociated form. Once inside the cell, they can dissociate and play their roles inside.[26] The amount of undissociated acid present in a system depends on its pH, the pK_a of the acid, and its concentration. At a given pH value, acids with the higher pK_a would show the higher proportion of undissociated acid.[25] When an acid has several acid groups, the values of $pK_{a1} \ldots pK_{an}$ are the dissociation constants of the protons and the value pK_{a1} (the lowest pK_a value) corresponds to the first proton, that is, to the balance of undissociated (the form in which the acid may enter the cell)/dissociated acid. Acids with a higher pK_{a1} value, such as acetic or lactic, would have higher proportions of the undissociated molecule at higher pH values, hence being more effective.

Prior exposure of bacterial cells to an acidic environment renders them more resistant to acid. More injury has been observed in unadapted cells of *Sighella flexneri* and *Escherichia coli* O157:H7 than in acid-adapted or acid-shocked cells.[27,28] The tolerance to an acid environment was shown to be dependent on the *type of acid* used, and *E. coli* O157:H7 acid-adapted and acid-shocked cells were more tolerant than unadapted cells to culture medium acidified with lactic acid, but all three types of cells behaved similarly in medium acidified with acetic acid.[28] Indeed, cellular changes have been described in yeast and in enteric bacteria as a function of stress adaptation to weak organic acids.[29,30] The involvement of a multidrug resistance pump has been established in yeast for the resistance development against weak organic acids.[29] Holyoak et al.[31] showed that this pump transports preservatives, sorbic acid, benzoic acid, and acetic acid from the cytosol to the extracellular environment. Enteric bacteria show an orchestrated response to proton stress by partially overlapping arrays of acid stress response proteins.[30]

Bacterial cells surviving exposure to acid stress may exhibit increased resistance to an unrelated stress that is subsequently applied.[27] Cross-protection against heat as a result of acid stress has been documented for *E. coli* O157:H7,[28] *Salmonella typhimurium*,[32] *Listeria monocytogenes*,[33,34] and *S. flexneri*.[27]

Cells of the different bacterial species show different sensitivities to internal acidification and different permeability to acids, which results in different sensitivity to the accumulation of dissociated weak acids. Molds, yeasts, and lactobacilli are frequently selected by their ability to grow at low pH values.

Probably, *C. botulinum* has been the microorganism that more attention has attracted, because of safety implications. Previdi and Gola[35] showed that *C. botulinum* grew more slowly when the growth medium was acidified with citric acid than with hydrochloric or glucono-δ-lactone, although the minimum pH for growth was the same for all three acidulants. Smelt et al.[15] found that lactic and acetic acids were more inhibitory for *C. botulinum* than citric or hydrochloric acids. Yamamoto et al.[36] found that adipic acid inhibited growth of several species of *Clostridium* more than citric or hydrochloric.

Lactobacillus brevis was able to grow in buffered peptone water up to pH 3 when it was acidified with citric, hydrochloric, phosphoric, or tartaric acids, but only to pH 3.7 with lactic acid and pH 4 when acetic acid was used.[23] Other studies have focused their attention on the effect of different acids on *L. monocytogenes*,[37–39] *Listeria innocua*,[40,41] *S. flexneri*,[42] *E. coli*,[24,43,44] and *Salmonella*.[22] On the other hand, the inactivation of *S. flexneri* at low pH depended on temperature and was enhanced with an increase in incubation temperature.[27]

In the case of bacterial spores, the picture is more complicated, as they have first to germinate and then to outgrow. Acid pHs are known to activate spores,[45] stimulating them to germinate. However, then the germinating spore will need an adequate pH to proceed with outgrowth.

After vegetative growth, when spore-forming bacteria find nutrient depletion in the medium, they undergo the process of sporulation.[46] However, for this process to occur successfully, sporulating bacteria need adequate conditions in the medium. Usually, these conditions are similar to those during growth, but

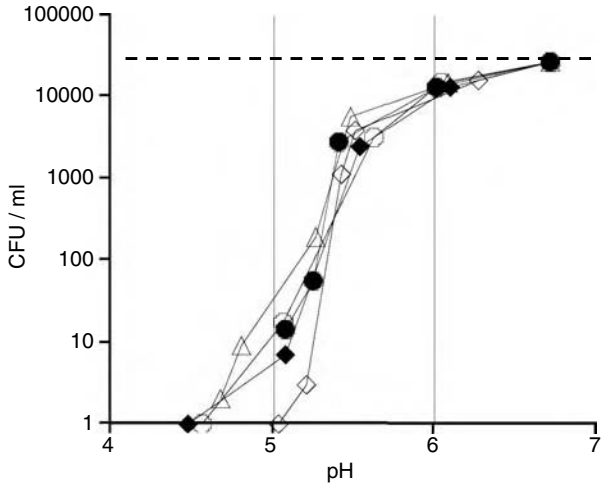

FIGURE 18.1 Growth of *B. coagulans* STCC 4522 spores plated on nutrient agar acidified to various pHs with different acids: acetic (◇), citric (●), lactic (♦), malic (△), hydrochloric (○). The dashed line represents the concentration of the inoculum.

with narrower margins for the different parameters of growth, such as temperature and pH.[46] Moreover, these conditions during sporulation influence strongly the subsequent heat resistance of the developing spores.[47,48] For example, the *D* values of several *B. cereus* strains dropped clearly with sporulation pH, decreasing by about 65% per pH unit.[49] *z* values were not significantly modified.

As an example of the effect of pH on bacterial growth, Figure 18.1 shows the behavior of a population of *B. coagulans* STCC 4522 spores plated on agar acidified at different levels with different acids. The same behavior can be seen with all acids: all the spores germinated and grew at neutral pH and almost all of them at pH 6, but at pH 5.5 and lower the level of inhibition increased dramatically. At pH 6 and higher no differences could be detected between the different acids, but at lower pH values some differences started to show, although still not significant. Acetic acid appeared to have the stronger inhibitory effect as it inhibited growth at a pH as high as 5. The other acids allowed growth of this microorganism at a pH value of around 4.5. Once more, the stronger inhibitory effect of acetic acid on bacterial growth is shown.

18.4 EFFECT OF pH ON BACTERIAL HEAT RESISTANCE

The heating medium pH has a great influence on the heat resistance of bacteria, and at present, it is considered the most important factor determining heat resistance, not only because of its effects, but also because it is easily applicable at an industrial level.

The influence of the pH of the heating medium has been widely investigated. Acid pH lowers in general the heat resistance of bacteria. Soon after discovering the kinetics of inactivation of bacteria exposed to heat,[1] Esty and Meyer[2] observed in 1922 that *C. botulinum* showed its maximum heat resistance at pHs between 6.3 and 6.9, and Williams[50] gave in 1929 the highest heat resistance values for *Bacillus subtilis* between pH 6.8 and 7.67. Sognefest et al.[3] found that between pH 4.5 and 9 the sterilizing treatment required was less the lower the pH. Other authors, however, have found no effect of pH on the heat resistance of *Clostridium sporogenes*,[51] although the pH range was narrow, and more recently on different species of the genus *Alicyclobacillus*.[52–54] And still others have found that *Clostridium perfringens*[46] and some strains of *Salmonella*[55] were most heat resistant at pH 5, and Morton et al.[56] have published more recently that toxigenic strains of *Clostridium butyricum* were most heat resistant at pH 4.4, although nontoxigenic strains of this same species were less heat resistant at progressively more acid pH values.

For the majority of the researchers, maximum heat resistance is shown at neutral pHs,[57] and an acidification of the heating medium leads to a decrease in the heat resistance of the spores of the genera *Bacillus*[26,57–72] and *Clostridium*,[25,59–62,73–78] as well as ascospores of fungi[79] and vegetative cells of bacteria.[80–84]

Different authors have found different relationships between the log *D* value of microorganisms and the pH of the heating medium. Several researchers have found linear relationships: Jordan and Jacobs[85] with *E. coli*; Cerny[57] with *B. subtilis* and *Bacillus stearothermophilus*; Pirone et al.[86] with *C. butyricum*; Mazas et al.[87] with *B. cereus*; Fernández et al.[88] with *B. stearothermophilus* and *C. sporogenes*; and Palop et al.[71] with *Bacillus licheniformis.* Other authors found a pH interval that was more effective in decreasing heat resistance. For example, Montville and Sapers[63] found that the greater effect of pH was from 4 to 5.5, while Xezones and Hutchings[73] and Cook and Gilbert[58] placed this range between 5 and 6. The range of minimum influence is usually located at pH values close to neutrality.[62,63,73,76]

Similar findings led other researchers to draw quadratic polynomial equations to adjust their data: Davey et al.[89] with *C. botulinum*; Mafart and Leguérinel[90] with *C. botulinum*, *C. sporogenes*, and *B. stearothermophilus*; Couvert et al.[91] with *B. cereus*; and Mañas et al.[84] with *S. typhimurium*. Mafart et al.[92] compared all these models used to describe the effect of pH on heat resistance (*D* values) with data obtained by other authors for *B. stearothermophilus*, *C. botulinum*, and *C. sporogenes* spores, concluding that linear models fit better at low heating temperatures and low pHs, while quadratic models would fit better at high temperatures and moderately acidic media. Actually, changes of the pH range of maximum influence on heat resistance, related to the temperature of treatment, were already described for *B. stearothermophilus* spores.[61]

Probably, differences in species behavior are also important in determining the overall magnitude of the effect of pH on heat resistance. These differences include the absence of effect in *Alicyclobacillus acidocaldarius* in a pH interval from 7 to 4,[54] small differences such as the one found in *C. sporogenes*,[76] which reduced its D_{110} value only by one third (from 15.9 to 10.6 min) in the pH interval from 7 to 5 and, probably the greatest effect described in literature for *B. stearothermophilus*

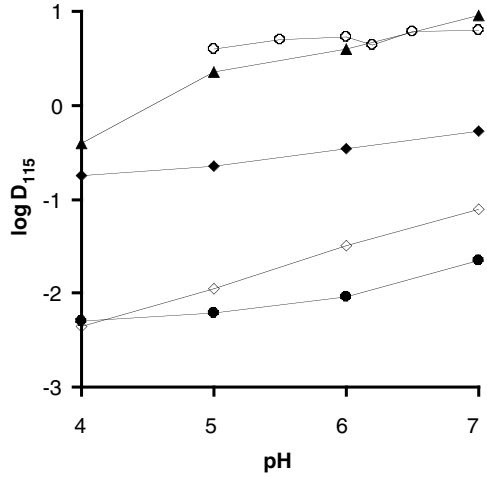

FIGURE 18.2 D_{115} values of different species of spore-forming bacteria in function of the pH of the heating phosphate buffer. *B. licheniformis* (●), *B. coagulans* (♦), *C. sporogenes* (○), *B. stearothermophilus* (▲), *B. subtilis* (◊). (Data taken from Palop, A. et al., *Int. J. Food Microbiol.*, 29, 1–10, 1996; Palop, A. et al., *Int. J. Food Microbiol.*, 46, 243–249, 1999; Cameron, M.S., *Appl. Environ. Microbiol.*, 39, 943–949, 1980; López, M., *Int. J. Food Microbiol.*, 28, 405–410, 1996; Palop, A., Estudio de la influencia de diversos factores ambientales sobre la resistencia de *Bacillus subtilis*, *B. licheniformis* y *B. coagulans*, Ph.D. dissertation, Universidad de Zaragoza, Zaragoza, Spain, 1995.)

ATCC 15952,[93] by more than 20 times in D_{115}. As a summary of all these results, Figure 18.2 shows D_{115} values of these and other bacterial spore-forming species in function of the pH of the phosphate buffer used as a heating medium.

Perhaps the smaller effect of acid pH on the heat resistance of *B. coagulans* spores, when compared to other *Bacillus* and *Clostridium* spores, could explain why this is one of the species more frequently isolated from acid or low-acid canned foods.[94]

One remarkable exception to the generalized decrease in heat resistance caused by acid pHs is the thermoacidophile *A. acidocaldarius*, which shows the same heat resistance in both pH 4 and pH 7 heating media.[54] This microorganism is affected by neither the pH nor other characteristics of the heating medium,[54] and has a quite unusual range of pH for growth (2.5 to 6) for a spore-forming bacterium.[10] Again, this lack of effect could account for the frequent isolation of *Alicyclobacillus* species in heat-treated fruit juices.[11]

Finally, to complicate the picture even more, the magnitude of the effect of the pH depends not only on the bacterial species,[59,66,71,72] but also on the crop.[61]

Other factors apart from the bacterial species and crop, such as the sporulation temperature, usually not taken into account by researchers, could be of importance in this regard. Sala et al.[70] found that the range of pH that influenced most of the

heat resistance of *B. subtilis* STCC 4524 spores was different when the sporulation temperature was 32 or 52°C.

The effect of pH can also be influenced by the overacting effects of other factors, such as sodium chloride or water activity of the heating medium. Hutton et al.[95] with *C. sporogenes* and *C. botulinum* and Periago et al.[96] with *B. stearothermophilus* spores found interacting effects of pH and NaCl concentration in the sense of decreasing heat resistance. Even the food composition itself may have its effect, although in Brown and Thorpe's[62] opinion this last effect could always be attributable to modifications in the pH or the water activity. There are, however, many data in literature[51,72,76,78,97] that seem to show that the heat resistance of microorganisms in foods is different from the one they show in a buffer, even when of the same pH. Hence, the most generalized opinion[55,67,98] is that heat resistance determinations developed in order to fix thermal treatments for canned foods should be performed in the same foods that are going to be sterilized.

As a consequence, in spite of the high number of investigations carried out to show the effect of the pH on the heat resistance, at present only a few number of general conclusions can be drawn and many aspects still remain unexplained.[25] The variety of strains studied, the diversity of methods used to estimate heat resistance, and the possible influence of uncontrolled factors make it difficult to discern whether the differences found in heat resistance are genetically determined or can be attributed to interferences caused by the methodology. To this respect, it is important to point out that pH varies with temperature, and moreover in a different way for each food produce.[4,61,67,99] Hence. the pH determined at room temperature may differ largely from the actual pH at the temperature of treatment. This variation may be in some cases as big as 0.6 pH units (at 130°C).[99] However, most of the work on the influence of the pH on heat resistance has been done measuring the pH at room temperature, without any knowledge of the pH at the actual temperature of treatment, assuming a constant pH value at all temperatures. This pH variation during heating could be responsible for some of the contradictions found in literature.

Condón et al.[99] developed a thermoresistometer able to measure pH at the heating temperature, up to 130°C. With this instrument, Palop et al.[71,72] found that when *B. licheniformis* and *B. coagulans* spores were heat treated in tomato or asparagus adjusted to different pHs (at the temperature of treatment), their behavior was almost similar to that which they showed in buffer of the same pHs.

The inactivation of non-spore-forming pathogen microorganisms by a heat treatment is essential for the safe preparation of many foods. Since *E. coli* O157:H7 was isolated from apple cider responsible from an outbreak,[100] the study of the heat resistance of this microorganism at an acid pH has become of interest for many researchers. Splittstoesser et al.[101] found that an acidification of apple cider reduced the heat resistance of this strain. Dock et al.[102] and Steenstrup and Floros[103] found synergistic effects of the combination of sorbate and benzoate with acidification with malic acid in the heat resistance of this strain in apple cider. The maximum heat resistance of salmonellae was obtained at slightly acidic conditions, around pH 6,[84,104] with a decrease of

more than 50% when the pH was reduced to 4.[84] Similar decreases were observed for *L. monocytogenes*[105] and *Yersinia enterocolitica*.[83]

The growth temperature of vegetative bacteria seems to influence the effect of pH of the heating medium on heat resistance. Hence, the magnitude of the influence of pH on heat resistance increases as the growth temperature increases.[83,84] Moreover, the pH of maximum heat resistance for *Y. enterocolitica* changed from 7 for cells grown at 37°C to 5 for cells grown at 4°C.[83] Pagán et al.[83] found that the outer membrane of the cells grown at higher temperatures was more easily disrupted than for cells grown at lower temperatures.

The pH of the heating medium also influences the z values of bacteria, and it is precisely this effect around which most controversy has arisen. Some authors have found an increase in z value at acid pHs,[57,62,71,72,106] which means that at high temperatures pH may even have no effect on heat resistance.[61,78] However, other authors found a decrease,[65,76,77,107] and still others were unable to find any effect.[64,66,73–75,93,108]

Figure 18.3 shows z values of different bacterial spore-forming species in function of the pH of the buffer used as a heating medium. As it can be seen, the z value remained approximately constant for *B. subtilis* spores ($z = 9$°C) and for *A. acidocaldarius* ($z = 7$°C). It increased from 7.8 to 9.6°C for *B. stearothermophilus* spores, from 8.9 to 10.5°C for *B. coagulans* spores, and from 7 to 11°C

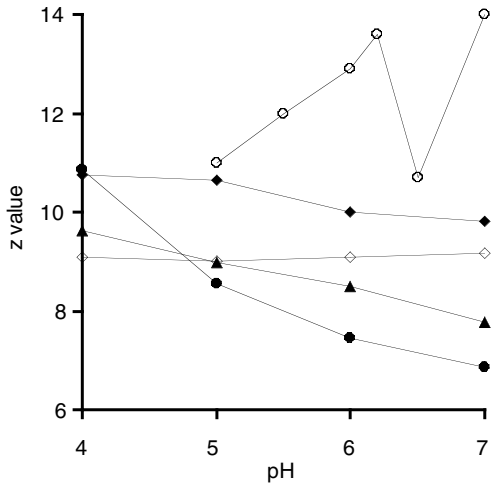

FIGURE 18.3 z values of different species of spore-forming bacteria in function of the pH of the heating phosphate buffer. *B. licheniformis* (●), *B. coagulans* (♦), *C. sporogenes* (○), *B. stearothermophilus* (▲), *B. subtilis* (◊). (Data taken from Palop, A. et al., *Int. J. Food Microbiol.*, 29, 1–10, 1996; Palop, A. et al., *Int. J. Food Microbiol.*, 46, 243–249, 1999; Cameron, M.S., *Appl. Environ. Microbiol.*, 39, 943–949, 1980; López, M., *Int. J. Food Microbiol.*, 28, 405–410, 1996; Palop, A., Estudio de la influencia de diversos factores ambientales sobre la resistencia de *Bacillus subtilis*, *B. licheniformis* y *B. coagulans*, Ph.D. dissertation, Universidad de Zaragoza, Zaragoza, Spain, 1995.)

for *B. licheniformis* spores when acidifying from pH 7 to 4. A decrease from 14 to 11°C was observed for *C. sporogenes* PA3679, with a rather odd peak at pH 6.5.

Although the differences in the effect of pH on z values could be related to the genetics of the microorganisms, i.e., different species would show different behaviors, it has also been proposed that the temperature at which spores were formed could play an important role in their behavior.[70] In their experiments, Sala et al.[70] found that z values of a spore suspension of *B. subtilis* sporulated at 32°C did not change in the pH range 4 to 7, while those of other spore suspensions of the same strain, but sporulated at 52°C, increased significantly when the heating medium was acidified in the same pH range.

The sporulation temperature is known to play a key role in the heat resistance of bacterial spores.[109] Spores sporulated at higher temperatures are more heat resistant,[110–112] and Sala et al.[70] showed that sporulation temperature was also related to the effect of pH on z values.

Also, the medium in which the spores are heat treated can be important for z values. In this regard, Condón and Sala[67] found that the z value of *B. subtilis* increased as the pH of the buffer was heated, but was approximately constant in different foods.

Regarding vegetative cells, Steenstrup and Floros[103] also found an important increase in z values of *E. coli* O157:H7 when apple cider was acidified with malic acid. However, Condón et al.[81] did not find any change in z value of *Aeromonas hydrophila* related to the pH of the menstruum in which the microorganism was heated. Neither Pagán et al.[83] with *Y. enterocolitica* nor Mañas et al.[84] with *S. typhimurium* found that pH caused any change in the heat resistance with treatment temperature.

18.5 EFFECT OF TYPE OF ACID ON BACTERIAL HEAT RESISTANCE

The type of acid used to decrease the pH also affects bacterial heat resistance. Leguérinel and Mafart[113] found a relationship between the lowest pK_a value of nine weak organic acids (acetic, L-glutamic, adipic, citric, glucono-δ-lactone, lactic, malic, malonic, and succinic acids) and their effects on the heat resistance of *B. cereus* spores in tryptone salt broth. These authors measured the influence of these acids by creating a new parameter, the z_{pH} value, which is the distance of pH from a reference pH (usually pH 7) that leads to a 10-fold reduction of the D value. The relationship was fitted according to a linear regression with a high coefficient of correlation (r_0) ($z_{pH} = -3.37pK_a + 21.23$; $r_0 = 0.965$). It was an inverse relationship between the z_{pH} and the lowest pK_a value of the acid (in case of acids with several acid groups), confirming that higher pK_a led to a higher effect on decreasing heat resistance. The sorted relation of acids (in terms of higher z_{pH} value) was as follows: L-glutamic > malonic > malic > citric > glucono-δ-lactone > lactic > adicpic > succinic > acetic.

These results are in agreement with those of other authors,[4,26,114,115] which showed that lactic and acetic acids are slightly more effective in reducing heat

resistance than other acids. The magnitude of this effect was the same regardless of the temperature of treatment.[4]

However, other authors did not find differences in the heat resistance of their bacterial strains when they were heated in the presence of different acidulants. This is the case of Brown and Martínez,[116] who found that *C. botulinum* showed the same heat resistance in mushrooms acidified with citric acid or glucono-δ-lactone. Neither did Ocio et al.[78] find any effect on *C. sporogenes* spores heated in the same medium with the same acidulants, although the same microorganism was less heat resistant in asparagus acidified with citric acid, but at low heating temperatures.[106] Fernández et al.[98] again found no effects with *B. stearothermophilus* spores.

Palop et al.[115] related the influence of the type of acid used to lower the pH of the heating medium with the sporulation temperature, showing that spores of *B. subtilis* and *B. coagulans* sporulated at high temperatures (52°C) were less heat resistant in asparagus and tomato acidified with lactic or acetic acid than with citric or hydrochloric acid, while the same spores sporulated at 35°C showed a similar heat resistance with all acids. The effect was constant along all heating temperatures tested. Hence, an interesting effect similar to that of the sporulation temperature on the pH on z values,[70] mentioned above, was also shown for the type of acid.[115] Both effects together show the relevance of sporulation temperature in determining the heat resistance of bacterial spores.

Most of these data have been obtained in foods requiring a low concentration of acidulants to adjust the pH at the required value because of their natural low pHs. Hence, when determining heat resistance, small differences among acidulants could be undetected because of the small amount of acidulant used. For example, Lynch and Potter[26] were unable to find any influence of the acidulant on the heat resistance of *B. coagulans* and *B. stearothermophilus* when a frankfurter emulsion slurry was adjusted to pH 4.5, but there was such an influence when the pH was adjusted to pH 4.2.

Supporting these findings, Palop[117] showed different degrees of sensitization to heat when at a constant pH value (pH 4) the concentration of different acids was increased. Figure 18.4 shows the D_{99} values of *B. coagulans* STCC 4522 heat treated in 1% peptone water acidified to pH 4 with increasing concentrations of different acids. The change in heat resistance caused by an increase in acid concentration depended on the type of acid used. D_{99} decreased significantly when lactic and acetic acid concentrations were increased (from 0.77 to 0.18, more than four times, when the concentration of acetic acid increased from 0.085 to 1 *M*), and also increased significantly when the concentration of hydrochloric acid was increased. The concentrations of all other acids tested did not seem to have an important effect on heat resistance, although there was a trend to increase heat resistance at increasing concentrations of glucono-δ-lactone and to decrease heat resistance with malic acid. The effects were also shown for *B. subtilis* and *B. licheniformis* spores.[117]

Again, these findings would point out that high pK_a values lead to lower heat resistances, and that pK_a, together with acid concentration, is an important parameter,

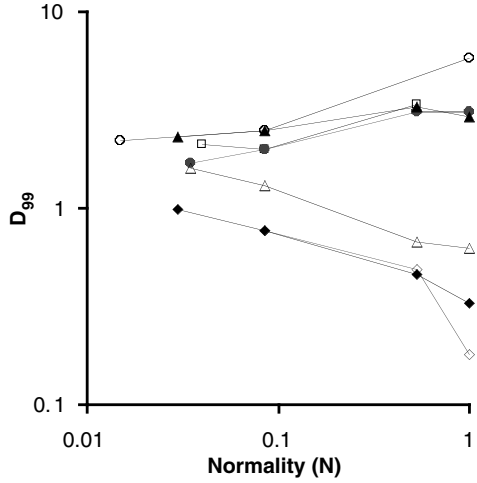

FIGURE 18.4 Heat resistance (D_{99} values) of *B. coagulans* STCC 4522 spores heat treated in 1% peptone water acidified to pH 4 with increasing concentrations of different acids: acetic (◊), ascorbic (□), citric (●), lactic (♦), malic (△), hydrochloric (○), and glucono-δ-lactone (▲).

not only to determine bacterial growth (see Section 18.3), but also for heat resistance. The surprisingly great increase in heat resistance caused by the increase in concentration of hydrochloric acid could be related to the protective effect that would cause the addition of salt (sodium chloride) to the heating medium,[55] because NaOH was used in all cases to adjust the pH to 4.

However, Leguérinel and Mafart[113] showed that at neutral pH the heat resistance of *B. cereus* spores was the lowest at the lowest acetic acid concentration (0.01 *M*), while there were no differences in heat resistance at lower pH values (up to pH 4.35) caused by the acid concentration. The authors attributed this protective effect of the acid concentration at neutral pH to the dissociated form of the acid, which accounts for 99.4% of the total concentration of the acid at pH 7, but only 29.1% at pH 4.35. Perhaps at pH 4 the lower proportion of dissociated acid present (that would leave spores unprotected) could account for the opposite effect found by Palop[117] using acetic acid at this pH.

18.6 EFFECT OF pH ON THE RECOVERY OF SURVIVORS TO HEAT TREATMENT

After a heat treatment, microorganisms are more sensitive to the environmental stresses. Heat causes injuries of different severity, before the microbial cell is irreversibly inactivated. Some of the damages can be repaired by the cells, depending mainly on the severity of heat injury and on recovery conditions.[118] These conditions include the temperature of incubation after heat treatment[119,120] and

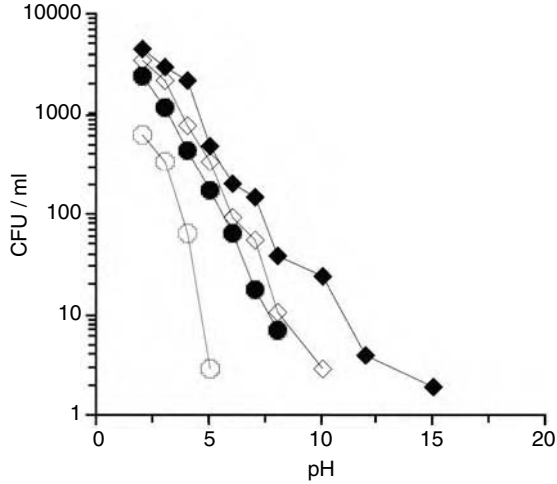

FIGURE 18.5 Survival curves of *B. coagulans* STCC 4522 heat treated at 108°C in pH 7 McIlvaine buffer and incubated for 24 h at 37°C in agar acidified to pHs of 6.22 (♦), 5.98 (◊), 5.85 (●), and 5.52 (○).

the physicochemical characteristics of the recovery medium.[95,121,122] In this regard, the pH is a very important factor.

Microbial heat resistance is estimated from the number of survivors of the heat treatment. Hence, any factor influencing cell damage and repair mechanisms might also influence the estimated heat resistance values. Figure 18.5 shows survival curves of *B. coagulans* STCC 4522 spores heat treated at 108°C in pH 7 McIlvaine buffer, plated on nutrient agar acidified to different pH values, and incubated for 24 h at 37°C. The heat treatment was exactly the same in all cases, but spores cultured on acid media appeared less heat resistant. $D_{108°C}$ decreased from 3.2 min when spores were incubated at pH 6.22 to 1.3 min when incubated at pH 5.52, and at this pH there was growth only in the plates corresponding to the first times of treatment, that is, when thermal injury was not important. At pH 5.05 no growth was observed at any of the heating times. However, as shown in Figure 18.1, the same microorganism was able to grow up to pH 4.5 before any heat treatment was applied, depending also on the type of acid used. It was also observed that the time needed for the colonies to develop was longer at acid pHs and at longer heating times.

Similar results have been shown by Leguérinel et al.[123] with *B. cereus* spores, and by Cook and Brown,[124] Cook and Gilbert,[125] Mallidis and Scholefield,[126] López et al.,[127] and Fernández et al.[128] with *B. stearothermophilus* spores. The last authors[128] did not find differences when the recovery medium was acidified with citric acid or with glucono-δ-lactone.

Other parameters of the recovery medium that have an influence on the apparent heat resistance of microorganisms are the sodium chloride concentration

and the anaerobic conditions.[121] An increase in the salt concentration has been shown to decrease the apparent heat resistance of bacterial spores.[121,123,129] Leguérinel et al.[123] found that there were no interactions between the sodium chloride concentration and the pH of the recovery medium in the apparent heat resistance of *B. cereus* spores, so that their effects could be modeled separately. However, Periago et al.[130] found that the effects of both factors were interacting in the heat resistance of *B. stearothermophilus.* A possible explanation for this controversy, apart from the different bacterial species used in both investigations, could be that the later authors[130] were combining the effects of the heating and of the recovery medium in their study.

The level of inhibition of bacterial growth in an acid medium depends also on the thermal history of the culture. Oscroft et al.[131] found that the efficacy of different acids for preventing growth of several species of *Bacillus* depended on the intensity of the previous thermal treatment, but always citric acid was less effective. Palop et al.[132] reported that a heat treatment as mild as 10 sec at 100°C led to an increase of almost 1 unit in the minimum pH required for *B. coagulans* spores to grow: peptone water acidified to pH 5.2 prevented growth of heat-treated *B. coagulans* spores, but it was necessary to decrease the pH to 4.4 to prevent growth of unheated spores. The minimum pH required for heated spores to be able to grow increased with the intensity of heat treatment: even pH 5.6 was able to prevent growth of spores after a heat treatment of 2 min at 100°C.

It has been shown through this chapter that acid pH hampers microbial growth and decreases microbial heat resistance; however, the most interesting and somehow unexplored advantage of pH probably comes from the combination of both inhibitory effects. Figure 18.6 shows the D_{95} values of *B. licheniformis* STCC 4523 spores heat treated in 1% peptone water acidified to pH values from 7 to 5.5 with citric acid, and then incubated in nutrient agar acidified to different pHs also with citric acid. *D* values reduced from 9 to 4 min when the heating medium pH was reduced from 7 to 5.5 and the recovery medium pH was kept constant at pH 7. A decrease of D_{95} from 9 to 3 min was observed when the recovery medium pH was decreased from 7 to 5.5 and the heating medium pH was kept constant at pH 7. At lower pHs of the recovery medium no survivors were found. However, when both heating and recovery medium pHs were reduced simultaneously from 7 to 5.5, an important synergistic effect was observed: the D_{95} value was decreased almost 30 times from 9 to 0.34 min. The effects of the acid pH on the heating medium and those of the acid pH in the recovery medium act together in reducing the heat resistance of bacteria, so that microorganisms heat treated at acid pH and recovered in an acid medium will show even lower *D* values.

The combination of heat treatments with acid pHs has been long used by the food canning industry and offers important advantages to the food processor. In the food industry the heating medium and the recovery medium are obviously the same. Thus, the intensity of heat treatments can be reduced as heat resistance of bacteria is lower at acid pHs. Moreover, the pH minimum for growth after heat treatment is higher.[132]

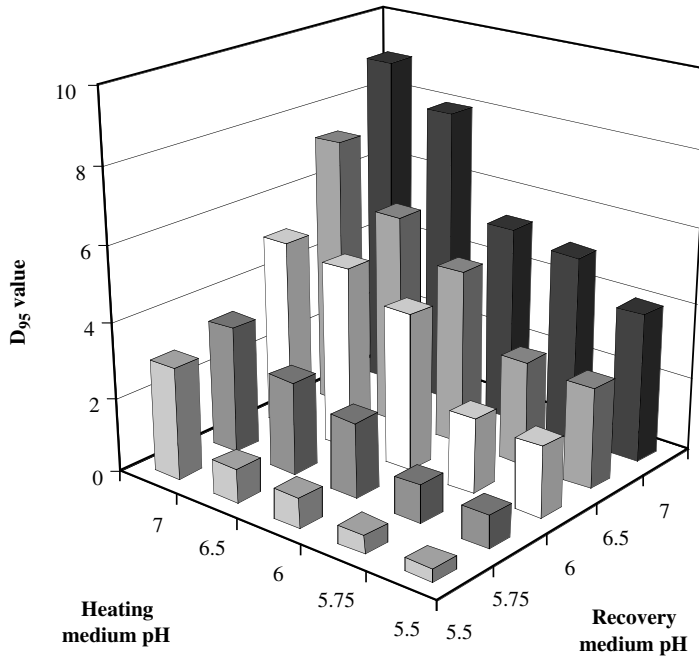

FIGURE 18.6 Effect of heating medium pH and recovery medium pH on the heat resistance (D_{95} value) of *B. licheniformis* STCC 4523 spores.

18.7 MECHANISM OF ACTION OF ACID pH AT HIGH TEMPERATURES

The mechanisms that make bacteria and especially bacterial spores resistant to heat are not fully known, and so mechanisms of sensitization of bacterial spores to acid pH at high temperatures still remain unrevealed. It has been proposed that there are three main factors that determine the heat resistance of bacterial spores: mineralization, protoplast dehydration, and sporulation temperature.[109] Minerals play a key role in the stabilization of proteins and other heat-sensitive structures of the spore. It is suggested that minerals, especially calcium, would replace water in the dehydrated protoplast of the spore, contributing to reaching a high degree of immobilization of the molecules and structures contained in it.[133] In this way, they would be less sensitive to heat. Sporulation temperature would be implicated by determining changes in the degree of mineralization of the spores: it has been found that spores obtained at higher temperatures were more mineralized and also more dehydrated.[109]

Gould and Dring[134] tried to explain the decrease in heat resistance of bacterial spores heated in acid media by means of a protonization of carboxyl groups of the cortex that would lead to its collapse and to the subsequent protoplast rehydration,

and thus to heat sensitization. Supporting this hypothesis, Okereke et al.[135] observed through electron microscopy that heating led to a decrease in the thickness of the cortex and to an increase in the protoplast volume. However, in the opinion of Warth,[136] should the cortex collapse by protonization, bacterial spores would be extremely unstable. Warth[136] proposed that the osmotic pressure created by the cortex is caused not only by carboxyl groups, but also by the whole structure, which includes divalent cations.[137,138]

It has also been proposed that the lower heat resistance of bacterial spores at acid pHs could be a consequence of a demineralization process taking place during heat treatment.[139,140] Marquis and Bender[141] showed that acidity in the heating medium led to an exchange of the divalent cations of the spore by protons of the medium, and hence to a protonization of spore proteins, which would be more sensitive to heat denaturation. This hypothesis matches the observation that calcium bonds are easily and quickly broken by changes in environmental conditions,[142] as well as other observations of different researchers,[94,109,143,144] who have seen that spores exposed to demineralization treatments partially lose their heat resistance.

If this is the case, demineralized spores, which are already devoid of most of their minerals, would show the same heat resistance in acid or in neutral heating media. However, Palop et al.[94] showed that demineralized spores, although much less heat resistant than native spores, were still less heat resistant when heated at acid pH.

Even more difficult to explain is the change in z values with acidification. If heating at acid pH values causes an exchange of the divalent cations of the spore by the protons of the heating medium,[139–141] it could happen that at higher temperatures the inactivation process would speed up relatively more than the exchange process. This would explain the decreasing effect of acidification at high temperatures, that is, the increase in z values with acidification. Indeed, it has been shown that demineralization speed is different for the different bacterial species,[141] that this process is more efficient at temperatures around 60°C than at room temperature,[139] and that it needs time to be completed but is not always successful.[145] However, other situations, such as the decrease in z values, still remain unexplained, and it should not be disregarded that changes in z value could simply reflect changes in the activation energy of the denaturation reaction of the molecules responsible for the death of the microorganism as a consequence of the acidification of the heating medium. In this regard, it is assumed that DNA denaturation leads to cell death,[146] but denaturation of DNA is not easy, and before it occurs, other cellular structures are damaged, impairing microbial growth. At present, mechanisms responsible for inactivation are not fully understood, but several target structures, such as some enzymes[147] or the germination system,[148] could be implicated.

18.8 MODELING THE EFFECT OF pH ON HEAT RESISTANCE OF BACTERIA

Predictive microbiology is gaining interest as a tool used to guarantee the production of safe foodstuffs. One of the main objectives in this area is to build, estimate, assess, and validate mathematical or probabilistic models with which it is possible

to describe the behavior (growth or inactivation) of food-borne microbes in specific environmental conditions (including factors as NaCl, pH, a_w, or temperature). The successful application of predictive microbiology depends on the development and validation of appropriate models.[149] Predictive models quantify the effects of interactions between two or more factors and allow interpolation of combinations that have not been tested explicitly.[150] Mathematical and probabilistic models are very useful, not only for hazard analysis and critical control points, but also for making decisions in scenarios when there is uncertainty.

As indicated in previous sections, pH reduces the thermal resistance of microorganisms, and the prediction of the effect of changes of pH during the production process or in formulation on the thermal resistance parameters (*D* value), or on the number of surviving microorganisms, is important. Some models have been developed using thermal resistance data as affected by variations in pH of the food. According to Reichart and Mohacsi-Farkas,[151] Fernandez et al.,[88] and Periago et al.,[96] second-order polynomial models give good descriptions of the thermal destruction parameter in vegetative and sporulated bacteria. Davey et al.[89] developed a model based on a quadratic polynomial equation to describe the joint effect of pH and temperature on *D* values. Mafart and Leguérinel[90] proposed an extension of Bigelow's equation and developed a linear regression model with temperature and the square of the pH. Various other models have been developed relating to pH and temperature on the heat resistance of microorganisms.[82,84,152,153]

In many cases, the models developed only account for the combined effect of two factors: temperature and pH. However, few studies in which various environmental factors are involved have been carried out. Gaillard et al.[154] developed a model that considered the combined effect of temperature, pH, and water activity on the *D* values of *Bacillus cereus* spores. This model is an extension of the first version of Mafart and Leguérinel's model.[90]

Periago et al.[96] proposed a quadratic response surface model represented by a polynomial to describe the combined effect of pH, NaCl, and temperature on the *D* value of *B. stearothermophilus* spores. This model had 10 coefficients, and predictions derived from the model were close, compared with *D* values published in the scientific literature. Nevertheless, in some cases significant differences were found, indicating the need to obtain models for specific foods. This model was improved by Tejadillos et al.[155] by using statistics regression techniques. The new model used only three predictor factors, and the variables could be easily computed from the basic variables of pH, temperature, and NaCl concentration.

All these models have the common fact that they use *D* or *k* parameters as kinetic rates, assuming a logarithmic linear relationship between the number of microorganism survivors and time after heat treatment. Nevertheless, in most cases, this assumption is not valid because of the presence of shoulders and tails in the survivor curve. To overcome this inconvenience, Fernández et al.[156] developed a model based on the Weibull distribution function. This function has been used before by diverse authors to describe the death of a microorganism that

undergoes an inactivation treatment when the survivor curve does not follow first-order inactivation kinetics.[157] The authors[156] concluded that Weibull parameters can be used to describe the effect of external factors on heat resistance. The overall model developed can describe the combined effect of pH and temperature with a low number of parameters.

All the information generated through recent years to predict the behavior of microorganisms under different environmental conditions has been used to build huge *databases* and computer programs that facilitate its usage. Some of these programs are free, while others are commercial and need to be registered before use. As an example of a free available program, the Pathogen Modeling Program (www.arserrc.gov/mfs/PMP6_Start.htm) was created by the U.S. Department of Agriculture. This predictive microbiology application was designed as a research and instructional tool for estimating the effects of multiple variables on the growth, inactivation, or survival of food-borne pathogens. As an example of a commercial program, the Food Micromodel (www.arrowscientific.com.au/predictive_micro_sw.html) offers the advantage that it has been validated in foods. This is a software package that will predict the growth, survival, and thermal death of the major food pathogens and food-spoilage organisms in a wide range of foods. It is the result of a research project, initiated and funded by the Ministry of Agriculture, Fisheries, and Food of the U.K.

These two independent data sets constitute thousands of microbial growth and survival curves that are the basis for numerous microbial models used by the industry, academia, and government regulatory agencies.

Ultimately, all these data sets have been unified in a common database, publicly and freely available, known as ComBase (wyndmoor.arserrc.gov/combase), following a structure developed by the Institute of Food Research of the U.K. Many European Union institutions are also adding their data to ComBase. By the end of 2003, ComBase contained up to 20,000 full bacterial growth and survival curves and some 8000 records containing growth/survival rate parameters.

In all these data sets, factors such as pH, NaCl, and a_w can be entered as independent variables to obtain the variation in the dependent variable, usually the inactivation or growth kinetics parameter.

18.9 CONCLUSIONS

Heat treatments have been applied successfully in food canning factories for several decades. Although the mechanisms that make bacteria less heat resistant remain somehow unknown, the knowledge acquired in the last few years regarding the behavior of bacteria in acid media has allowed for the combination of moderately acid pHs with low-intensity heat treatments, which results in foods of higher quality with the same level of safety.

Technical innovations regarding pH-assisted thermal processes are rather few, and acid foods (with pH values below 4.6) are still heat treated at temperatures close to 100°C in open water baths.

At present it is well known that the majority of the microorganisms show their maximum heat resistance at neutral pHs, decreasing with an increase in acidification. The magnitude of the effect of pH will depend on the microbial species and other factors, such as food composition, type and concentration of acid, or even the sporulation temperature in the case of bacterial spores.

pH influences not only heat resistance, but also bacterial growth, and most importantly, it influences very much the growth of the survivors to a heat treatment. Hence, the combined effect of the pHs of the heating medium and recovery medium may lead to synergistic reductions of the viability of microbes.

The huge amount of data on the effect of pH on microbial growth and heat resistance has allowed for the development of large databases and mathematical models that enable prediction of the behavior of microorganisms under certain conditions. These data sets are available for food microbiologists, manufacturers, risk assessors, and legislative officers.

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19 Time–Temperature Integrators for Thermal Process Evaluation

Antonio Martínez, D. Rodrigo, P.S. Fernández, and M. J. Ocio

CONTENTS

19.1 INTRODUCTION

Consumer demand for new and higher-quality foods has forced the food industry to develop new sterilization and pasteurization systems and to optimize current practices so that such demands can be satisfied without any negative impact on food safety. One of the main areas of current investigation is related to the use of heat in food preservation; the main objective is the application of the minimum heat levels to destroy or inhibit the development of the pathogen and spoiling microorganisms and to provide food with a longer shelf life. Technological developments such as treatment with high temperatures for short times (HTST) (or ultrahigh temperature (UHT)) and the aseptic processing of food containing particles are very interesting because of the potential advantages that they offer from the point of view of nutritive and organoleptic food quality. With the objective of guaranteeing the microbiological safety of food preserved by heat, a strict evaluation of the thermal process is necessary. However, the conventional validation methods of these preservation processes are not always appropriate due to the way in which the food is produced and thermally processed. The time–temperature integrators (TTIs) offer an alternative to the thermocouples and the conventional microbiological methods used to quantify the impact of thermal treatment on the microorganisms and other food components, such as vitamins or enzymes. In this chapter a historical perspective is given on the systems used in the evaluation of the thermal processes, and the development and use of TTI as a tool for ensuring the safety of thermally processed foods is described.

19.2 CALCULATION AND EVALUATION OF STERILIZATION PROCESSES

The thermal treatment of foods is one of the oldest and most used industrial methods to prolong the shelf life of foodstuffs. Today, its use as a preservation technology in its different applications represents a very significant percentage of all processed or manufactured foods. Apart from the heating system used and the way in which the heat is generated, an evaluation of the impact of the heat on the safety (inactivation of microorganisms and analysis of risks) and on the quality (nutritive value and acceptability for the consumer) is essential. Although there is no universal model system to predict the exact number of surviving spores after thermal treatment, the impact of the thermal processes has traditionally been evaluated in four different ways: (1) the method *in situ*, (2) the physico-mathematics approach, (3) the inoculated experimental packs, and (4) the use of time–temperature integrators. Traditionally, the first three methods have

been used to evaluate the thermal processes, while the time–temperature integrator is a more recent development.

19.2.1 *In Situ* Method

The *in situ* method is based on the evaluation of certain food quality indexes before and after the thermal treatment. Some of the analyzed parameters are the loss of vitamins,[1] sensory appreciation of taste, texture, and the physical evaluation of the color.[2] Using a first-order model for thermal inactivation of these quality indexes, the effect of thermal treatment process can be quantitatively expressed in terms of cooking values, C_T, or lethality values, F_T. These thermal inactivation values are established from the initial and final concentrations of the target property in the food and the D_T value (time of decimal reduction), which is defined as the time taken to reduce the level of a thermolabile element of the food by 90% at a constant temperature.

The main advantage of this method is that in some cases, the impact of the thermal process on the chosen parameter can be directly measured and with acceptable accuracy. The disadvantages associated with this methodology are (1) the concentration of the target element, which exists naturally in the food, may be outside the detection limits of the commonly utilized analytic methods after the thermal process has been applied, and (2) the analyses of the studied parameter cannot be applied with routine analysis due to its complexity and high cost.

19.2.2 Physico-Mathematical Methods

An alternative to the *in situ* method for the evaluation of the thermal processes is the physico-mathematical methods developed in recent years. With these methods, the time–temperature history of the food obtained by means of mathematical models, under well-known sterilization conditions, is combined with kinetics models, allowing us to determine the thermal impact of the treatment on the target element. Stoforos and Merson[3] proposed mathematical solutions for the heating systems for canned solid/liquid products. Models have also been developed for liquid products that contain solid particles in suspension.[4,5] The difficulty of measuring under certain conditions, the required physical parameters, such as viscosity values and conductivity at high temperatures, the coefficient of heat transfer, and the distribution of the residence times of particles in a continuous process mean that the mathematical models do not always accurately predict the time–temperature evolution inside the food, which is necessary to establish the required thermal treatment. In addition, these models must be microbiologically validated.

19.2.3 Inoculated Experimental Packs

Another way that has been used to validate thermal processes is to perform laborious inoculation tests, i.e., inoculated experimental packs.[6] Rodrigo and Martínez[7] used this methodology to evaluate mathematically obtained sterilization conditions for low-acid artichoke hearts (Table 19.1). The methodology consists

TABLE 19.1
Inoculated Experimental Pack Data for Artichoke Hearts

	Spoiled Cans/Sterilized		
Total Heating Time (min)	Inoculated	Confidence Limits ($p = 0.95$)	Nonheated (Controls)
5.0	18/50	11.4–25.8	6/6
10.0	17/50	10.7–25.7	6/6
18.0	0/50	0.0–7.0	6/6
21.5	0/50	0.0–7.0	6/6
35.0	0/50	0.0–7.0	6/6

Source: Extracted from A. Martínez, Optimizacion de las condiciones de fratamiento termico en dos nuevas conservas de distinta acidez, en base a la termorresistencia de los microorganismos y a los principales factores de calidad. Ph.D. thesis, Valenci University, Spain, 1988.

of inoculating groups of 50 containers with the reference microorganism (i.e., PA 3679). Each group of 50 containers undergoes different thermal treatment conditions based on the mathematical model. When the sterilization process is finished, the containers are stored at an optimum incubation temperature in order to allow the growth of the inoculated microorganism. The cans are regularly inspected, and those that show spoilage symptoms are enumerated. These data allow us to determine if the mathematically derived sterilization conditions were enough to guarantee the microbiological safety of the food.

Yawger[8] developed a method to evaluate the sterilizing effect of a process determining the reduction in viable spores in a group of inoculated cans (*Bacillus stearothermophilus* or *Bacillus coagulans*). This system is a specific application of the technique of inoculated experimental packs to evaluate the lethality of a thermal process. It differs from the inoculated experimental packs in that it measures the lethality of the process in each inoculated container and not an alteration percentage.

The lethality determined by this system is interpreted as an integrated sterilization value IS, which is the equivalent of the lethal value of a process in terms of minutes to the reference temperature in the whole content of the container and not at a single point.

19.2.4 Time–Temperature Integrators

The development of the time–temperature integrators relates to both consumer demand for high-quality convenience products and the food processing companies that need to save energy and achieve better control of the thermal process. Consequently, efforts have been made to optimize the existing systems and develop new heating technologies, such as continuous processing retorts, heat exchangers, aseptic processing, microwave or ohmic heating, and combined

processes. Because these evaluation methods have serious limitations when applied with these new technologies, a considerable effort has been made to develop time–temperature integrators capable of accurately measuring the impact of thermal treatment on food in terms of quality and safety. In general, these devices are artificial particles made of alginate, plastic, or another carrier, containing a sensor element (microorganism or enzyme) homogenously distributed inside them. The response of the sensor element is proportional to the intensity of the given thermal process. These devices can be introduced in HTST or UHT systems as well as in cans or retorts.

19.2.5 Biological Lethality and Physical Lethality Relationship

The lethality of the preservation process by heat can be determined by physical measures, using thermocouples that record the temperature history of the food during the heat treatment, and by biological measures, using bacterial spores, or another sensor, inmobilized in a time–temperature integrator. The sterilization values physically and biologically calculated are named physical lethality (F.PHY) and biological lethality (F.BIO) values, respectively. In general, the value of F.BIO is based on the reduction in the number of viable spores after thermal treatment, and it is determined by using a previously established relationship (curve of calibration or equation) among the number of surviving spores (N_F) and the equivalent in minutes of heating (F) at a given temperature.[8–12] Since the spores are sensitive to environmental changes, and there are differences between spores of the same strain, the reduction of the number of viable spores is not constant for the same treatment. However, the value of F.BIO should be constant for a given thermal treatment, since the differences between spore cultures, species of spores, and environmental conditions (different from the heating environment) do not affect the value of an F.BIO that is correctly determined.

The value of F.PHY is calculated by using an appropiate mathematical model and the acquired temperature measurements by using a thermocouple inserted in a cold point of the product (point of the slowest heating), which usually coincides with its geometric center.

Both the F.BIO and F.PHY values should be identical for the same reference temperature. However, several studies mentioned in the literature show differences between both values.[13–17] There are several reasons that could explain these differences. The F.BIO values may be erroneous due to the incorrect use of the TTI, which depends on the biological system and the associated analytic procedures, and the F.PHY values may be erroneous due to the incorrect determination of the required parameters' time–temperature history and spore thermal resistance data. Some explanations that may account for the discrepancies among the F.BIO, using a TTI system and the associated analytic procedures, and the F.PHY value, determined by the general method,[18] are mentioned in the following sections.

19.2.5.1 Possible Errors in the Determination of the F.BIO Value

1. Use of a badly calibrated curve
2. Differences between the conditions used to obtain the calibration curve and those used to evaluate the thermal treatment
3. The use of an incorrect lag factor when obtaining the calibration data where the temperature is reached instantly
4. Alteration of the thermal properties of the spores when introducing them in a carrier system
5. Differences between the number of survivors recovered after the calibration experiments and after the nonisothermal treatments
6. Incorrect conversion of the F.BIO values to F_o.BIO values

19.2.5.2 Possible Errors in the Determination of the F.PHY Values by Means of the General Method

1. Errors in the temperature measurements
2. Alteration of the heat transfer characteristics of the product as a consequence of the use of thermocouples as measuring devices
3. Errors in the calculation of the z values
4. Supposition of constant z values in the whole interval of temperature
5. Inexact calculations by means of the Ball formula method

19.2.5.3 Explanations for the Discrepancies between the F.BIO and F.PHY Values

1. The experimental variations can cause differences between the F.BIO and F.PHY. Quite frequently the thermocouple and the time–temperature integrator are not located in the same container. Consequently, these values are subject to variations in the heating and cooling rates. Also, each thermocouple and each indicator exercises its influence on the results; therefore, it is necessary to get sufficient repetitions for the same experiment.
2. The discrepancy can be caused by the differences in the measurement point inside the same container, in which the bioindicator (TTI) is not exposed to a uniform temperature, while the temperature around the thermocouple is uniform.
3. The use of inactivation kinetics obtained by isothermal processes may make inexact predictions in complex systems, such as the biological ones in which the temperature changes.[19] Johnson[20] observed an unexpected second inactivation phase in the spores of *Bacillus cereus* during cooling from 50 to 40°C after being heated to 90°C, and he concluded that the inactivation data generated at constant temperatures cannot

always be used to predict the response of the bacterial spores to changes of temperature. On the contrary, the F.PHY values do not consider the changes in the relationship between the temperature and the rate of inactivation of the spores. Nevertheless, experiments have been done that show that a good correlation can be obtained between the F.BIO and F.PHY values. Secrist and Stumbo[21] used containers inoculated with spores of PA 3679 and found a good correlation between the predicted and experimental values. Rodriguez et al.[22] obtained a good correlation in the predicted and experimental numbers of survivors after nonisothermal treatment, using spores of *Bacillus subtilis*. Sastry et al.[23] inoculated spores of *B. stearothermophilus* in mushrooms using alginate gels. Good correlations were obtained in the preliminary studies sterilizing mushrooms in metallic containers.

With the introduction of aseptic processing, a significant change in the sterilization, in comparison with the traditional preservation technologies, took place. In this process the food is pumped through a plate, tubular, or scraped-surface heat exchanger according to the characteristics of the food; it is then cooled and put into aseptic sterile containers. This process is utilized for liquid foods, such as juices, milk, etc., but because of the difficulty in ensuring the lethality reached by the food particle in the sterilization process, it is not often used for foods containing particles larger than 10 mm. On the contrary, as happens in the sterilization process of a container (can or retort pouch), there are no physical methods to determine the temperature reached in the center of the food particle (meat or vegetable pieces) aseptically processed in a heat exchanger. Before authorizing a treatment, the Food and Drug Administration (FDA) requires a demonstration of the sterility reached in the center of the food particle, that is, the cold point of the process. Therefore, mathematical simulation models and validation by means of biological methods (TTI) should be used. At present, some mathematical models have been developed[24,25] that simulate the penetration of heat in the particle. However, for high-temperature short-time treatments, the discrepancies between the F.PHY and F.BIO can be greater because of the difficulty in establishing times of residence, temperature transference, etc., which are necessary in order to develop an effective mathematical model.

19.3 GENERAL ASPECTS OF THE TIME–TEMPERATURE INTEGRATORS

A time–temperature integrator can be defined as a small device that shows some irreversible changes with the time–temperature, which is measurable in an easy, exact, and precise way that mimics the changes produced in a temperature-sensible factor (microorganism, enzyme, etc.) contained in a foodstuff that suffers the same treatment at variable temperature.

The main advantage of a time–temperature integrator is its ability to quantify the integrated impact of the time and the temperature in the target attribute without the need for any information on the history of the product's real temperature.[26]

In accordance with the given definition, a time–temperature integrator should fulfill some requirements for its structure, behavior, and use:

1. The integrator should contain a calibrated and resistant sensor element for the thermal treatment, and it should experience the same evolution of temperature as the real food.
2. The size of the integrator and its geometry should be similar to the real food, with the sensor element homogeneously distributed in its interior.
3. The carrier should efficiently retain the sensor element so that losses do not take place during the sterilization process.
4. The integrator should be incorporated in the product so that it does not produce distortions during the heat transfer, neither should it modify the time–temperature profile of the food.
5. The integrator should be cheap, easy, and quick in its preparation, and easy to analyze and recover.
6. The integrator should be stable and capable of long-term storage without any loss of functionality.
7. The integrator should be physically resistant enough to support the heating process without disintegrating.

Besides these requirements, there are some kinetic aspects that an integrator should satisfy. When the sterilizing value of the process is chosen as a concept to express the integrated impact of the time and temperature, the TTI should fulfill the following equation:

$$(F^{z}_{Tref})_{indicator} = (F^{z}_{Tref})_{TTI} \tag{19.1}$$

That is to say, the lethality reached in the integrator should be similar to the response of lethality of the factor used as the indicator (microorganism, enzyme, etc.). It is also easy to understand that a system will work as a TTI if its activation energy (E_a) or the z value is the same or similar to that of the factor considered to be the indicator.

19.4 CLASSIFICATION OF THE TIME–TEMPERATURE INTEGRATOR BY CONSIDERING THE SENSOR ELEMENT

The time–temperature integrators can be divided into the following groups:[26] (1) chemical systems, (2) physical systems, and (3) biological systems. The biological systems are further divided into microbiological, enzymatic, and nonenzymatic systems. In general, the sensor element of the TTI can be introduced in a carrier

system and located in a defined position inside the food, or it can be dispersed in the food, as in an inoculated experimental pack validation process. When a physical contact does not exist between the sensor element and the food, the inactivation kinetics of this sensor can be determined independently of the food type and the local conditions. When the sensor element is immobilized in a device, thermophysical properties of the carrier system should be similar to the thermophysical properties of the food to ensure that the transfer of heat of the carrier is similar to that in the food, and in this case, the inactivation kinetics of the sensor should be determined in its own device. If the sensor element is dispersed in the food, it is necessary to keep in mind that the new chemical atmosphere in which the sensor is immersed requires that kinetic calibration may have to be carried out.

19.4.1 Chemical TTI

Chemical TTIs are based on the detection of chemical reactions to quantify the impact of a thermal process. Hendrickx et al.[27] described a detailed revision on the chemical reactions that can be used as time–temperature integrators. Different chemical systems, such as thiamine heat inactivation[1,28,29] and color changes produced by sugar and amino groups reduction,[30] have been used. Methylmethionine sulfonate (MMS) thermal degradation between 121.1 and 132°C in a citrate buffer (pH 4 to 6) has been correlated to the reduction of microorganisms in thermally treated liquid foods.[31] Under certain process conditions it is possible to compare the decrease in *B. stearothermophilus* spores with the reduction of the MMS concentration. Sugar hydrolysis has also been used as an indicator of thermal treatments by Kim and Taub.[32] Measurements of this chemical marker have been correlated to the inactivation of *Clostridium botulinum* spores.

In spite of the important role that chemical TTIs seem to have in carrying out the valuation of thermal processes, there is an important disadvantage associated with them. The high value of z (20 to 50°C) or the low values of its activation energy (E_a = 60-160 kJ/mol) make them unable to guarantee microbiological safety in the interval of sterilization temperatures. However, the inclusion of sensors in carrier systems that diminish the z value and make it closer to that of the microorganism has been an object of investigation.

19.4.2 Physical TTI

Physical time–temperature integrators are based on diffusion phenomena. The system described by Witousky[33] consists of a colored chemical substance that can melt and be absorbed in wick paper under the effect of humid heat (steam). The TTI response is calculated by measuring the distance reached by the melted compound. Its use as an indicator of thermal processes was established by Bunn and Sykes.[34] However, this TTI presents the disadvantage that it cannot be used in thermal processes where dry heat is applied; neither can it be included inside the product because the TTI is activated by steam.

Another system proposed by Swartzel et al.[35] is based on the ionic diffusion and capacity of a semiconductor metal. The diffusion distance can be exactly calculated by measuring the cellular capacitance change before and after a thermal treatment. These systems use several ionic carriers with at least two different activation energies, from which sterilizing values can be calculated by means of the equivalent point method.[36] However, Maesmans et al.[37] have demonstrated that this method can lead to serious errors.

19.4.3 Biological TTI

19.4.3.1 Protein-Based TTI: Enzymatic and Nonenzymatic (Inmunochemical)

Thermal treatment can produce irreversible changes in the tertiary structure of proteins. In enzymes, this can affect their activity. Enzymatic systems use this activity loss to measure the impact of thermal processes. Proteins with thermostabilities at different temperature intervals and with different activation energies have been used. This can cover a wide range of food safety and food quality attributes. Two types of TTI can be defined based on the detection methods to measure protein activity:

1. Enzymatic TTI, where the enzyme residual activity is a direct response of the protein to the thermal impact. Recently, a TTI has been calibrated based on the use of the peroxidase enzyme in an organic solvent.[27,38] De Cordt et al.[39,40] proposed the use of the *Bacillus licheniformis* enzyme amylase as a time–temperature integrator. TTI systems have been developed with the -galactosidase, lipase, and nitrate reductase enzymes encapsulated in alginate.
2. Immunochemical methods based on the specific interaction of antigen antibody. The thermal treatment of proteins can affect binding sites so that the antibody does not join the protein. Kinetics of antigenic capacity loss differ between different proteins and, in some cases, between different binding sites within the same protein. These immunologic techniques (competitive and noncompetitive enzyme-linked immunosorbent assay (ELISA)) have been used by Brown[41] to study the antigenic inactivation after the thermal treatment.

Although these protein systems can provide quick and accurate enough detection measures, they present inconveniences because enzymes become inactive well before reaching the treatment temperature in HTST systems. It is therefore necessary to increase their thermostability so that they can work properly at high temperatures. The necessary manipulations to increase thermostability, adjusting the values of the activation energy (E_a) or the rate constant (k), imply changes in the environmental conditions, stability, and immobilization of enzymes that cannot always be carried out.

19.4.3.2 Microbiological TTI

The use of microbiological systems to control the efficiency of the sterilization processes constitutes one of the main objectives of the food and pharmaceutical industry. A microbiological TTI consists of a carrier system inoculated with a microorganism (essentially bacterial spores) of well-known thermal resistance and concentration under the specific sterilization conditions to assess. The inactivation level of the microbiological integrator in the sterilization treatment gives an idea of the magnitude of the process, and therefore of the level of sterility achieved in it.[42] A microbiological integrator should complete the following general requirements:

1. The microorganism should be stable in number and thermal resistance. Results should be reproducible and of low variability.[43]
2. The microbiological system (microorganisms, carrier system, and procedures used) should be calibrated under the specific conditions of sterilization to be assessed.[44]
3. Relations between the microbiological integrator and the natural microbiological load of the product should be known so that the validity of the sterilization can be ensured.[12]

The selection of microorganisms that can be used as biological indicators for sterilization treatments depends on the specific applications for which they have been designed.[44] The strains of the most resistant species are generally used for the valuation of the sterilization processes, although under certain conditions microorganisms less resistant but quite similar to the natural microflora of the product or easier to detect are used instead. *B. stearothermophilus* spores are commonly used as biological indicators in processes of sterilization by wet heat.[45] Spores of *Bacillus subtilis* have been used for treatments with dry heat and in processes with ethylene oxide, while spores of *Bacillus pumilus* are used for sterilization by means of ionic radiations.[42]

z values of spores used to control food microbiological security are similar to the z value of *C. botulinum* (z = 10°C), which is used as a reference in the sterilization of canned products with low acidity. For these foods, spores of *B. stearothermophilus*, *B. subtilis* 5230, *B. coagulans*, and *Clostridium sporogenes* have been used as microbiological indicators in sterilization by wet heat.[43,44] To determine the impact of the thermal treatment, it is necessary to use spores previously calibrated and validated against well-known physical parameters.

Microbiological control systems are divided into (1) qualitative systems that integrate time–temperature evolution and indicate whether the process has reached the established value (negative or positive growth), for which no conclusions can be derived about the extension of the thermal treatment, and (2) quantitative systems that estimate the count reduction and intensity of the process, which can be determined by a plate count of the survivors.

19.5 SUPPORTS USED IN THE DEVELOPMENT OF TIME–TEMPERATURE INTEGRATORS

To immobilize the sensing element (enzymes, microorganisms, etc.), different carriers or supports have been used.

Pflug[46] developed a hollow plastic bar into which he introduced *B. stearothermophilus* endospores to validate sterilization processes of a great variety of foods, like green beans,[47] corn, and peas.[48] Rodriguez and Texeira[49] proposed using an aluminum tube with better heat transfer and mechanical resistance than plastic, as a support to evaluate sterilization processes of low-viscosity and quickly heated foods. Another method used is the inoculation of a small glass bulb with an endospore suspension, which is placed in the center of a food piece subject to the conditions of the process.[50] All these methods have one particular disadvantage: the chemical environment of endospores is not that of food. Strips of filter paper impregnated with an established quantity of bacterial endospores in foods heated in conventional systems have also been used.[51,52] The evaluation of the continuous sterilization processes has required the development of another type of integrator, since integrators with a plastic, metallic, or glass support did not suffer the same temperature dragging or evolution as real foods. In this sense, Segner et al.[53] inoculated the food piece with bacterial endospores. However, the endospores were not homogeneously distributed within the whole piece of food, so it did not fulfill one of the necessary requirements for a TTI. Another alternative that has turned out to be the most appropriate is the elaboration of artificial devices that simulate real foods and that contain homogeneously distributed endospores inside.[16,23,54–56]

For the simulation of real foods, the devices used are prepared in a gelificable support; therefore, this technique is also known as immobilization in gel. It involves adding some type of pureed gel to the food in the mixture, of which the sensor (microorganism, enzyme, etc.) can be immobilized, and so-called artificial particles similar in size and shape to those of real foods can be made. This makes it possible to ensure that conditions in the sensing element are as close as possible to the pieces or particles of the real food to be treated, with regards to its chemical environment, particle dynamics during the process, heat penetration, density, etc.[57] Another advantage of this method is that as microorganisms are homogenously distributed in the artificial particle, the result of the thermal treatment will be an integrated sterilization value.

Different types of gelificable supports have been used, such as albumin gels,[58] carrageenan gels,[59,60] and polyacrylamide gels.[55,61] However, the most commonly used gels are *alginate gels*.[56]

Dallyn et al.[62] described the use of an integrator consisting of the immobilization of bacterial endospores in alginate pellets. This TTI had enough mechanical strength to be used in scratch-surface heat exchangers. Later on, Bean et al.[54] inoculated endospores of *B. stearothermophilus* in 1.6- to 3.2-mm-diameter alginate pearls and observed that the size of the beads was too small to evaluate sterilization processes of foods that contained large pieces. Other, larger (8 to 24 mm) and

cube-shaped alginate artificial particles were developed by Brown et al.,[16] who observed discrepancies between the experimental sterilizing values and those calculated by means of a mathematical model of temperature transfer. Another approach was carried out by Sastry et al.,[23] who developed an indicator inoculating bacterial endospores suspended in an alginate gel and introducing it inside a mushroom. The lack of homogeneity in the distribution of endospores observed in this integrator hindered the interpretation of results, and in some cases, the mushroom stalk came off the cap during the heating process.

Other problems present in TTIs developed in an alginate matrix are that some devices cannot be stored for long[16] and the endospores can get lost by lixiviation during the heating. Ocio[56] developed a TTI with alginate and mushroom puree to which she added 4% starch. She observed that this allowed for the freezing of the particle for a long period, and its later defrosting, while maintaining mechanical characteristics similar to those of the particle that did not contain starch and that had been stored for 7 days in refrigeration. Later on, Rodrigo[63] used an integrator similar to the one developed by Ocio[56] to evaluate a thermal process under pilot plant conditions. This author[63] did not find significant differences at a 5% level of significance between the experimental lethality values and those calculated by a mathematical model.

19.6 ALGINATE TTI ELABORATION

Alginate and food puree TTIs containing immobilized microorganisms are probably the most versatile and the ones that approach best the physicochemical characteristics of a real food particle (Figure 19.1). Therefore, the production of this type of artificial particle is described below in further detail. A time–temperature integrator based on alginate with immobilized spores inside requires a series of previous studies related to the calibration of the sensor (microorganism, enzyme, etc.) and the stability of the support or carrier (mechanical resistance, capacity of retention of the sensing element inside, etc.).

19.6.1 Thermoresistance of the Sensor Element

Based on the example of the *B. stearothermophilus* spores or microbiological — amylase, which are much used in this type of TTI, it is first necessary to consider the *thermoresistance* characteristics of the microorganisms in the medium that will act as carrier.

An important aspect in heat inactivation kinetic studies is the form of heating and the method used for analyzing experimental data. Thermobacteriology studies have conventionally been carried out in isothermal conditions. Determination of kinetic parameters in these conditions is relatively simple, and it produces conservative sterilization or pasteurization processes. However, during heat treatment microorganisms are subjected to conditions that often differ substantially from isothermal experimental conditions. An alternative is to apply nonisothermal heating methods. These methods offer the advantage of subjecting the spores to

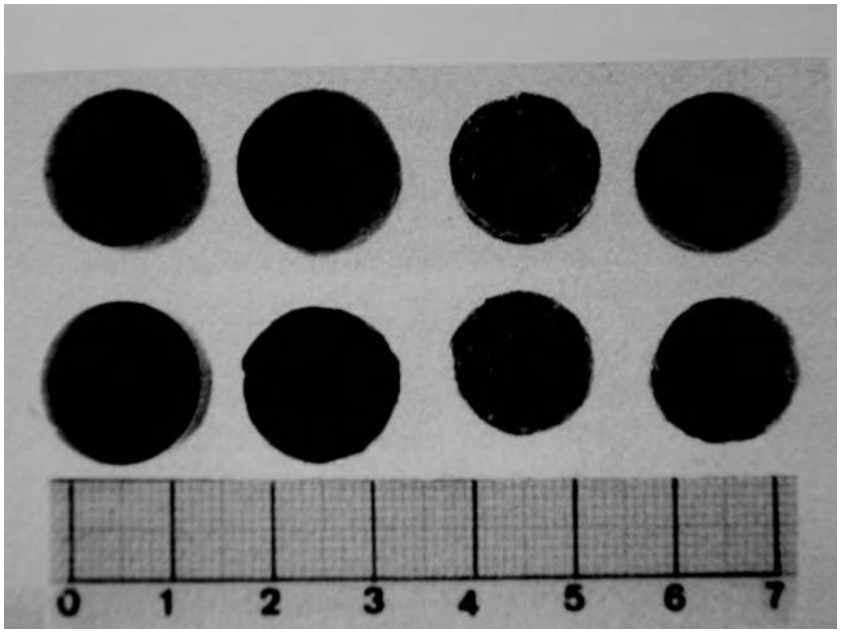

FIGURE 19.1 Alginate–mushroom–starch particles.

dynamic temperature conditions, such as those that occur in real thermal sterilization processes. Tucker[64] reviewed the various nonisothermal methodologies used in accelerated methods for the stability study of pharmaceutical products. These methods can also be used for microbial inactivation studies. Tucker[64] discussed the following temperature increase programs: (1) uncontrolled temperature increase, (2) linear program, (3) linear program followed by an isothermal period, (4) polynomial program, and (5) hyperbolic program.

With nonisothermal heating processes it is possible to obtain much information (experimental data) with a single experiment, with consequent savings in material, time, and labor costs. Moreover, nonisothermal studies provide a wealth of data for subsequent development of predictive models.

Experimental data in microorganism inactivation studies are generally analyzed by means of two successive linear regressions. In the first, the logarithm of the concentration of the thermolabile factor remaining after heat treatment is plotted against time, giving the D_T value. In the second regression, the logarithm of D_T is plotted against treatment temperature, giving the z value. This methodology generally provides high confidence ranges, due to the small number of degrees of freedom[65] Arabshahi and Lund[66] presented a method for analyzing kinetic data for inactivation of thiamine that provided smaller confidence ranges than those obtained by using two linear regressions. To do this, they calculated the activation energy, E_a, from the original experimental data by applying nonlinear

regressions in a single step. A possible drawback of this methodology is the high correlation that may exist between the parameters estimated, D_T and z, or k_T and E_a, causing convergence and accuracy problems. Nevertheless, the convergence can be improved if the equations are transformed by taking natural logarithms or reparameterizing.

Inactivation predictive models can be an excellent tool for ensuring the microbiological safety of the thermal process. There is growing interest in predictive microbiology because of its many potential applications, such as estimating the effect of changes or errors in estimating specific microorganism parameters,[67] for example, D_T or z. The successful application of these models depends on developing and validating them in real conditions.[68]

The parameters that define the inactivation of microorganisms by heat in nonisothermal conditions by analyzing experimental data obtained in real substrates by means of single-step nonlinear regressions are of great value for the development of inactivation models that relate the D_T value to environmental factors of importance in the canning industry, such as pH, sodium chloride concentration, anaerobiosis, or water activity. These models can be incorporated into a hazard analysis and critical control point plan, to safeguard the sterilization process against any eventuality during the manufacturing process that might affect the D_T value of the microorganisms, potentially causing spoilage of the food product.

19.6.2 Preparation of the Carrier

A desirable characteristic that an integrator should satisfy is its mechanical and storage stability. Alginate has been frequently used as a carrier to immobilize bacterial spores. Alginate is obtained from a marine alga, and its molecules are composed by two monomers: manuronic and guluronic acids (Figure 19.2). Rodrigo[63] prepared an alginate–mushroom–starch mixture to produce cylindrical devices that support the liophilization process without losses of mechanical properties or microorganisms spores. The mixture must be gelified (Figure 19.3 and Figure 19.4). For this, two procedures can be used:

1. Internal gelification. In this method a salt is added to the alginate solution. The salt liberates the calcium in controlled quantities, since a quick contact would cause a precipitation of the gel and the cationic diffusion in it would not be good. Sulfate, carbonate, and calcium orthophosphate acid are the salts that are most commonly used for this purpose.
2. Gelification by diffusion. In this technique the alginate solution contacts a calcium ion solution. The contact of both solutions can take place in two ways: directly between them or through dialysis membranes (Figure 19.5). Particles formed by alginate gelification are the most interesting particles for the evaluation of thermal processes of real foods containing particles.

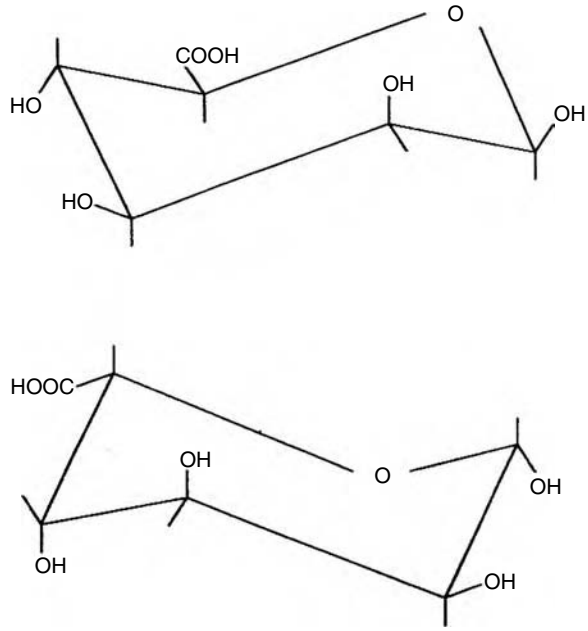

FIGURE 19.2 Structure of manuronic (above) and guluronic (bottom) acids.

19.6.3 Recovering of Sensor Element and Calculating Impact of the Process

After its use, spores immobilized inside the gelified alginate particle must be recovered in order to quantify the thermal treatment impact. For that, devices are introduced in sterile masticator bags containing sodium citrate and -amylase. After 7 min of treatment, serial dilutions are made and spores are plated in duplicate in a suitable culture medium. Counts are made after several hours of

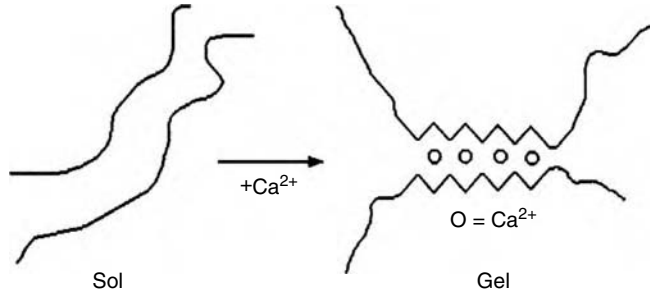

FIGURE 19.3 Gelification process.

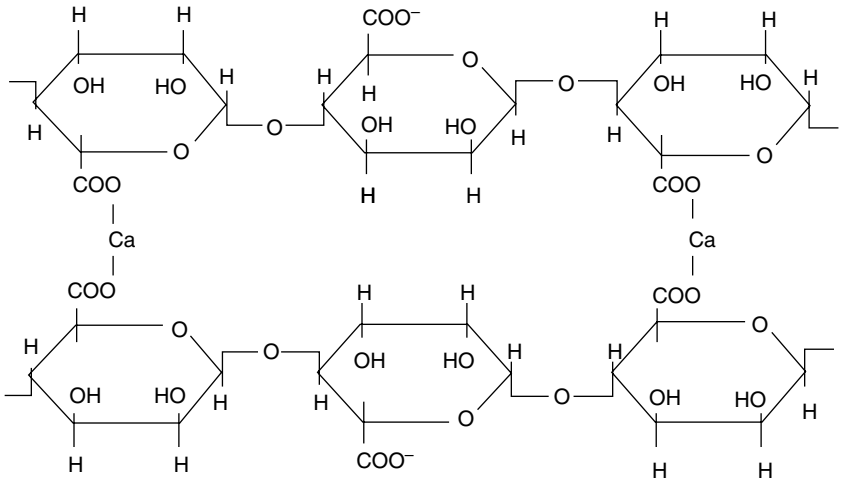

FIGURE 19.4 Structure of the calcium–alginate molecule.

incubation at an optimum temperature, depending on the microorganisms. When the sensor is other than a microorganism, the same procedure could be followed, but the analytical methodology can vary as a function of the sensor element.

Table 19.2 shows that there is a good distribution of spores inside the gelified particle and that the extraction procedure is reproducible.

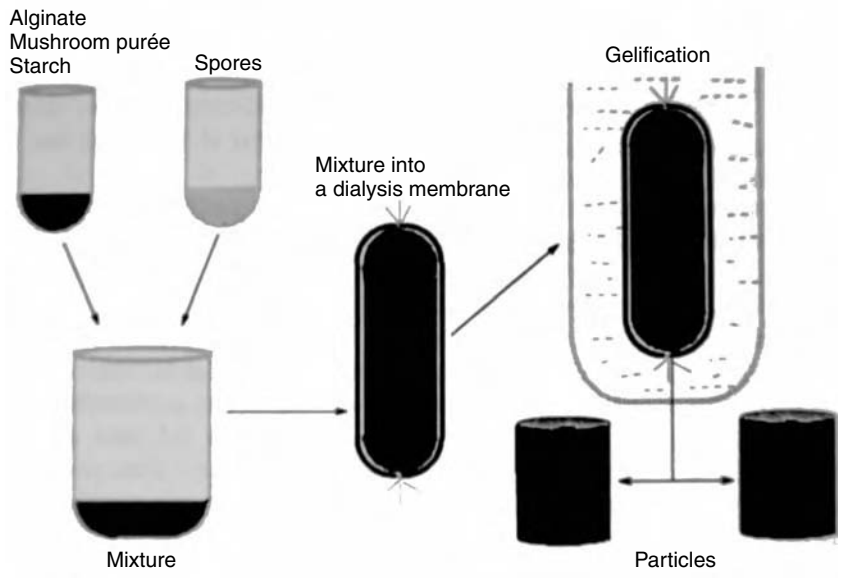

FIGURE 19.5 Gelification process using a dialysis membrane.

TABLE 19.2
***B. stearothermophilus* Spore Counts in Three Different Particles Coming from Five Gelified Pieces**

	Counts (FCU/TTI)		
Gelified Piece	**TTI 1**	**TTI 2**	**TTI 3**
1	5.55×10^6	6.40×10^6	5.85×10^6
2	5.75×10^6	5.25×10^6	5.90×10^6
3	4.35×10^6	5.35×10^6	6.65×10^6
4	4.90×10^6	4.30×10^6	4.35×10^6
5	4.35×10^6	6.85×10^6	6.30×10^6

19.7 APPLICATION EXAMPLES OF TTI

From a food safety evaluation point of view, thermal process design should be based on the heat impact achieved in the coldest spot (or slowest-heating point) of the food. Time–temperature integrators can be used as wireless instruments to follow and identify those slow-heating points inside a can or jar when other systems are not adequate. They can also be used to establish variability in lethality among different parts inside a retort. This would be a measure of heating heterogeneity, and therefore a way to identify potential risks for food safety.

Van Loey et al.[26] used sylicon beads with an elastomer containing 10 mg/ml immobilized BSA (*B. subtilis* -amilase) to determine the coldest point in a model (a particulate food system) and to identify the coldest spot in a retort. Results indicated that these TTIs were sensitive enough to distinguish variations of the lethal impact achieved in each container due to their situation in the retort. This allows one to find the coldest point inside the container in an easy, reliable, and fast way, which is very useful for design or evaluation of a continuous heat treatment.

When beads were used to identify the coldest part of the retort, the distribution of lethalities showed that the coldest area where the test was performed was located in the central, lowest part of the box containing the product. According to this study, the lowest layer should be used as a reference for the development and evaluation of the sterilization process.

TTIs containing *B. stearothermophilus* spores as a sensor element have also been used. Tejedor[69] developed a TTI with alginate and food puree as supporting elements to establish sterilization conditions for a food containing vegetables and tuna fish. The integrator was appropriate to validate the level of safety achieved with the thermal processes in this substrate. The integrated lethalities calculated with a mathematical model of temperature transference and those obtained empirically using the TTI were very similar (Table 19.3).

Tucker[70] used a *Bacillus amyloliquefaciens -amylase* time–temperature integrator injected in the center of silicone devices to validate pasteurization processes of products containing large particles. A feasibility study was conducted on an

TABLE 19.3
Comparison between Experimental and Calculated *B. stearothermophilus* Counts in TTI

Retort Temperature	F_o (min)	Time (min)	TTI Counts	
			Experimental	Calculated
112	0	0	3.95×10^7	3.95×10^7
	1.10	33.6	9.76×10^6	8.09×10^6
	2.58	44.4	1.96×10^5	1.52×10^5
	3.89	53.2	3.81×10^3	5.74×10^3
115	0	0	4.57×10^7	4.57×10^7
	1.17	25.8	1.33×10^7	2.15×10^6
	2.58	35.4	3.18×10^4	6.11×10^4
	4.44	40.6	2.40×10^3	5.86×10^3

industrial ohmic plant using 10- to 12-mm whole strawberries as the yogfruit product. The technique developed and demonstrated on continuous pasteurization processes can be applied to almost any process for foods that contain solid particles. Furthermore, Lambourne and Tucker[71] developed *B. amyloliquefaciens* and *B. licheniformis* -amylase time–temperature integrators encapsulated in silicone tubes and in silicone cube particles. Another form of encapsulation was also employed using polytetrafluoroethylene (PTFE) tubes. The PTFE tubes produced some problems with leakage. Devices were employed in the validation of different pasteurization processes. Those devices were found to be a reliable and alternative method for measuring the thermal process delivered to products where conventional probe-based validation techniques were not suitable. The industrial application trials using *B. amyloliquefaciens* and *B. licheniformis* -amylases were successfull in all cases and showed that the pasteurization treatments being applied were in general substantial, and overprocessing was taking place in most cases.

Fernández et al.[72] performed a study to evaluate the lethalities achieved in glass jars containing baby food in a static industrial retort as a function of their position in the crates, distribution within the retort, and variability within the jar. As the sensor element, highly heat resistant spores of *Bacillus sporothermodurans* were used (personal communication), which were suspended in spheric alginate beads of 4 mm diameter. The following experimental design was used: 10 inoculated alginate beads were mixed within the content of each glass jar, and over 20 jars containing beads were distributed in the 4 crates of the retort, at different heights and positions (central or corners) within each crate. After the sterilization process, the number of survivors in each individual bead was obtained and a statistical study was performed.

Results indicated that one of the crates presented a significantly lower level of inactivation than the other ones, and that the bottom part of this crate was the coldest spot of the retort. No significant differences were found between the

central part and the corners of each crate or within jars. These data allowed an efficient establishment of the variability of inactivation within the product, the coldest spot of each crate, and the coldest spot of the whole retort.

19.8 CONCLUSIONS

Thermal processing of food remains one of the most widely used methods of food preservation. Consumer pressure for more convenient and nutritional foods and the need of saving energy in the industry has been the engine driving the development of new heating and filling systems (heat exchangers, heaters, and aseptic processing). The main inconvenience that arises with the development of these new heating technologies for low-acid particulated foods is the difficulty to establish a *sterilization process* that ensures food safety against pathogenic organisms, e.g., *C. botulinum*. Time–temperature integrators can help in developing safe sterilization or pasteurization processes and are essential for their validation. Those systems allow a fast, easy, and correct quantification of the thermal processes' impacts in terms of food safety without knowing the actual temperature history of the product. Time–temperature integrators (chemical, enzymatic, and microbiological) have also demonstrated their ability to validate processes that are carried out in conventional still retorts. In those cases, their usages overcome the need of performing heavy and expensive inoculated experimental packs. Nevertheless, a good knowledge of the heat resistance of the sensor element under isothermal and nonisothermal conditions is required, and a study to assess the mechanical properties of the carrier is advisable in order to ensure that the TTI behaves as the real food under the same treatment conditions.

NOMENCLATURE

A_W	Water activity
D_T	Decimal reduction coefficient at temperature T
E_a	Activation energy
F_o	Treatment time at 121.1°C needed to reach a preestablished number of decimal reductions in a microbial population with z = 10°C
$F_{T,}\,C_T$	Time at a given reference temperature that produces the same reduction in the thermolabile element (microorganism or chemical) during the temperature evolution that the food undergoes
F^z_{Tref}	Treatment time at reference temperature needed to reach a preestablished number of decimal reductions in a microbial population with a particular z value
k_T	First-order reaction constant at temperature T
TTI	Time–temperature integrator
z	Inverse negative of the slope of the thermal destruction curve

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Food Science and Technology

The challenge of maintaining both quality and safety in the thermal processing of foods results from the degradation of heat-sensitive quality attributes during processing. The editor of **Thermal Food Processing: New Technologies and Quality Issues** presents a comprehensive reference through authors who meet this challenge by explaining the latest developments and analyzing the latest trends in thermal food processing research and development.

The book is divided into three parts for easy reference. Part I, *Modeling of Thermal Food Processes*, discusses the thermal physical properties of foods, recent developments in heat and mass transfer, innovative modeling techniques including artificial neural network modeling, and computational fluid dynamics (CFD).

Part II, *Quality and Safety of Thermally Processed Food*, provides the latest research and development information used to maintain high quality and safety standards for certain types of food products including thermally processed meat, poultry, fishery products, dairy products, canned foods, and vegetables.

Part III, *Innovations in Thermal Food Processes*, details existing, alternative thermal processing technologies, outlining their potential, future application in the food industry. These innovations include the ohmic heating technique, radio frequency energies, infrared rays, the combination of pressure and pH with thermal processing, and time-temperature integrators used in evaluating and controlling thermal processes.

Features

- Provides an essential and complete reference on the modeling, quality, safety, and technologies associated with thermal food processing
- Discusses fundamental data and equations for thermal-physical properties used in modeling, deterministic model simulation, artificial neural network modeling, and computational fluid dynamics
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