Quality and Thermophysical Properties of Pressure Treated Foods

Dissertation

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of the Ohio State University

By

Loc Thai Nguyen, M.S.

Graduate Program in Food Science and Technology

The Ohio State University

2009

Dissertation Committee:

V.M. Balasubramaniam, Advisor

Sudhir K. Sastry

Ahmed E. Yousef

Luis E. Rodriguez-Saona

Abstract

High pressure processing (HPP; 100-700 MPa at temperatures $\leq$ 45^{o}C) and pressure-assisted thermal processing (PATP) (500-700 MPa; 90-120^{o}C) have been used to inactivate pathogenic and spoilage bacteria and produce high quality foods. The objectives of this dissertation were to evaluate the influence of various pressure-temperature combinations on quality, microbial lethality and thermophysical properties of selected foods.

Experiments were conducted to investigate the influence of process temperature (95-121^{o}C) at different pressures (0.1, 500-700 MPa) on carrot quality. Results indicated that under comparable process temperatures (up to 105^{o}C), pressure-assisted thermal processing (PATP) retained the carrot quality attributes such as color and carotene content better than thermal processing (TP). However, process and preprocess thermal history greatly influenced carrot textural change. Pressure protective effects on product hardness at elevated temperatures (110-121^{o}C) were less pronounced. Subsequently, experiments were conducted to evaluate the role of pressure during sequential (pressure pre-treatment at ambient temperature followed by TP) or simultaneous (PATP) treatment in preserving product quality attributes. To learn how different food matrices are influenced by various pressure-heat combinations, experiments were also carried out using carrot, jicama, red radish, zucchini, and apricot. Results showed that TP degraded

product texture severely but HPP followed by TP improved texture retention. In comparison to TP alone, PATP better retained texture and color. The beneficial effects of PATP may come from the densification of the tissue due to pressurization or biochemical changes of the pectic substances. Texture retention was product dependent, with jicama being the least influenced among the foods tested. An instrumental based crunchiness index (CI) was developed and validated using sensory data. CI was able to describe textural transformation of various processed products.

In-situ thermal conductivity (k), diffusivity (α), volumetric specific heat (ρCp) and isobaric specific heat (Cp) of tomato puree, soy protein isolate (10% W:V), soybean oil, guacamole, honey, cream cheese and sucrose solution (10% W:V) were measured up to 600 MPa at 25^{o}C by a dual needle probe adapted to elevated pressures. Increasing pressure linearly increased k values. Among the food materials tested, the maximum increase in k under pressure was observed for soybean oil (0.173 -0.256 W/m^{o}C), while k of honey had the least change (0.324 – 0.396 W/m^{o}C). Thermal diffusivity of the tested materials showed a positive pressure dependence and can be expressed as a second order polynomial function of pressure. Isobaric specific heat of food materials decreased with increase in pressure. The maximum combined uncertainty in the measurement of k, α, ρC_p and C_p were 3.1, 6.8, 6.6 and 6.9%, respectively.

A model was developed to calculate accumulated lethality during PATP. A differential equation that considered momentary inactivation rates as a function of

pressure and temperature was formulated and numerically solved using Rung-Kutta method. The model was experimentally validated under different process conditions. Predicted log-reduction computed by the model using n^{th} order kinetics was found to be in good agreement with experimental values. The ability of the model to predict microbial reduction was found to be satisfactory when evaluated under various process scenarios.

Dedication

Dedicated to my family

Acknowledgments

I'd like to express my sincere gratitude to Dr V.M. Balasubramaniam for his inspiring guidance, support and encouragement during my graduate studies at the Department of Food Science and Technology, The Ohio State University. I'd also be deeply grateful to Dr. Sudhir K. Sastry for giving me the opportunity to work in his lab and for his guidance, encouragement and very valuable scientific advices.

My sincere appreciation and gratitude are expressed to Dr. Ahmed E. Yousef and Dr. Luis E. Rodriguez-Saona for helpful discussions and service in my advisory committee.

I'm thankful to Brian Heskitt, Department of Food, Agricultural and Biological Engineering and the staff of Department of Food Science, The Ohio State University for their valuable assistance in experimental set-up and equipment maintenance.

I'm indebted to all colleagues and friends in my lab for their stimulating discussions and kind help in my experiments.

I owe my gratitude to my wife, Hong, and my son, Khang for their immense dedication, understanding and silent sacrifices during my long graduate studies.

I’d like to thanks supports for this research which were provided by USDA-CSREES-NRICGP grant 2005-35503-15365, Center for Advanced Processing and Packaging Studies (CAPPS), Kraft Foods and the Ohio Agricultural Research and Development Center (OARDC), The Ohio State University.

Vita

1997……B.S. Food Technology, Can Tho University, Vietnam

1998 – 2000 …...……Laboratory Supervisor, Cailan Oils & Fats Co., Vietnam

2000 – 2003 …….....Technical Manager, American Feeds Co., Vietnam

2005……M.S. Food Engineering and Bioprocess Technology, Asian Institute of Technology, Thailand

2005 to present…….....…Graduate Research Associate, Department of Food Science and Technology, The Ohio State University

Publications

Loc Thai Nguyen, Rastogi, N.K., & Balasubramaniam, V.M. (2007). Evaluation of the instrumental quality of pressure-assisted thermally processed carrots. *Journal of Food Science*, 72(5), E264-E270.

Rastogi, N.K., Nguyen, L.T., & Balasubramaniam, V.M. (2008). Effect of pretreatments on carrot texture after thermal and pressure-assisted thermal processing. *Journal of Food Engineering,* 88, 541-547.

Rastogi, N.K., Nguyen, L.T., Jiang, B., & Balasubramaniam, V.M. (2008). Improvement in texture of pressure-assisted thermally processed carrots by combined. pretreatment using response surface methodology. *Food and Bioprocess Technology*. doi:10.1007/s11947-008-0130-6.

Nguyen, L.T., & Balasubramaniam, V.M. (2009). Fundamentals of food processing using high pressure. In Handbook of nonthermal processing technologies for food. Zhang, H.Q., Barbosa-Carnovas, G.V., Balasubramaniam, V.M., Dunne, C.P, Farkas, D.F., Yuan, J.T.C. (Eds.). Blackwell Publishing. *In press*

Nguyen, L.T., Tay, A., Balasubramaniam, V.M., Legan, J.D., Turek, E.J., & Gupta, R. (2009). Evaluating the impact of thermal and pressure treatment in preserving textural quality of selected foods. *LWT-Food Science and Technology*. doi:10.1016/i.lwt.2009.09.022

Fields of Study

Major Field: Food Science and Technology

Table of Contents

List of Tables

List of Figures

Chapter 1: Introduction

Historical development of food preservation with high pressure processing began with pioneering work of Hite (1899) more than a century ago. He observed that the delay of microbial spoilage of milk by the application of high pressure at 600 MPa and room temperature for 1 h. Hite and his colleagues continued their investigation on a variety of foods. It took until 1980's for the technology to become commercially viable in the food industry. During 1980's, Japanese universities and industries pioneered the commercialization of value-added pressure pasteurized products such as jam, jelly, juice, etc. Subsequently continued research efforts in North America and Europe led to introduction of a number of value added pressure pasteurized commercial products. During 2007, the production of HPP products is estimated around 150,000 tons per year. High pressure pasteurized products are commercially available in North America (Canada, Mexico, USA), Europe (Germany, Italy, Spain, Portugal, UK) and Asia (including China, Japan, Korea). Guacamole, salsa, smoothies, deli meat, oysters, and cooked ham are examples of products in the market (Saiz et al., 2008). The current industrial interest on high pressure processing are primarily motivated by potential benefits offered by the technology in preserving natural, fresh-like product quality attributes, nutritional values while ensuring microbiological safety. Pressure

treatments can have pasteurization or sterilization effects depending on the intensity of pressure-temperature combination applied. Pressure treatment at around ambient temperature is effective against variety of pathogenic and spoilage bacteria, but have limited efficacy against bacterial spores.

Pressure assisted thermal processing (PATP), a combined elevated pressure-temperature treatment to a preheated food, has potential in producing shelf-stable foods due to its sterilizing effects. PATP can be effective in inactivating variety of bacterial spores. Advantages of PATP compared to traditional thermal processing (TP) include reduced thermal degradation of food quality due to compression heating during pressurization and rapid cooling during depressurization.

Most of the current published literature is mainly based on end points data and the role of pressure in preventing food quality degradation during combined pressure-temperature treatment is not well understood.

Thermophysical properties of food play a very important role in design of equipment, optimization of process and evaluation of quality degradation or microbial safety. In-situ measurement of food properties under pressure needs to overcome several technical challenges including developing sensors capable working under extreme conditions. The knowledge will also help understand the process uniformity and identify the least treated zone during PATP.

It is further desirable to develop a mathematical model to evaluate the process safety based on integrated lethality concept analogous to F-value concept in traditional thermal processing. However, introduction of pressure as third vector along temperature

and process time, deviation of microbial inactivation kinetics from first order model present considerable challenges.

In 2009, FDA approved filing of PATP for production of low acid foods. However, commercial products are not available in the markets yet. A number of questions of regulatory and industrial importance need to be addressed before successful introduction of PATP treated shelf-stable products in the market place.

Accordingly, this dissertation attempted to address the following research questions:

- What role does pressure play in protecting quality of PATP shelf-stable products?
- How the food properties such as thermal conductivity, specific heat change under pressure?
- Can the integrated process lethality models taking into account the contribution of both pressure and heat can be used to predict PATP process lethality?

Chapter 2: Fundamentals of Food Processing using High Pressure

2.1. Introduction

Most processed foods are treated with heat to kill harmful bacteria, a process that often diminishes product quality. Considered one of the most important innovations in food processing in 50 years (Dunne, 2005), high pressure processing (HPP) presents an alternative that retains food quality and natural freshness while extending microbiological shelf life (Farkas and Hoover, 2000). High pressure processing, also commonly referred to as "high-hydrostatic pressure" (HHP) processing or "ultra high pressure" (UHP) processing, uses elevated pressures, with or without the addition of external heat, to achieve microbial inactivation or to alter food attributes. The pressures used in HPP are almost ten times greater than in the deepest oceans on earth. Common pressure units are listed in Table 2.1.

Long used in the material and process engineering industry for sheet metal formation and isostatic pressing of advanced materials such as turbine components and ceramics, high pressure processing offers many advantages to food processors. Because HPP does not break covalent bonds, it preserves food freshness (Farkas and Hoover, 2000). The technology also provides food processors with an opportunity to process heat sensitive value-added foods with fewer additives and cleaner ingredient labels. Pressure

can be applied at ambient temperature, thereby eliminating thermally induced cooked off-flavors. Finally, this technology is efficient, as it can be used to process liquid foods in semi-continuous equipment and both liquid and solid foods in batch equipment. Table 2.2 summarizes some of the unique advantages of high pressure processing.

The applications and limitations of high pressure food processing have been reviewed extensively (Hayashi, 1991; Cheftel, 1995; Ledward et al., 1995; Ohlsson, 1996; Thakur and Nelson, 1998; Kunugi and Hayashi, 1998; Autio, 1998; Smelt, 1998; San Martin et al., 2002; Matser et al., 2004; Hogan et al., 2005; Torres and Velásquez, 2005; Rastogi et al., 2007). This chapter summarizes the basic process engineering principles related to high pressure processing of food materials and emphasizes the importance of thermal effects during this preservation process.

2.2. Basic principles governing high pressure processing

LeChatelier's principle

LeChatelier's principle states that the application of pressure shifts the system equilibrium towards the state that occupies the smallest volume (Farkas and Hoover, 2000). Thus, any phenomenon (phase transition, change in molecular configuration, chemical reaction) that is accompanied by a decrease in volume is enhanced by pressure (and vice versa). This means that pressure stimulates reactions that result in a decrease in volume but opposes reactions that involve an increase in volume.

For a simple chemical reaction, the kinetics of transition from A to B with intermediate state $A^{\#}$ can be expressed as (Pfister et al., 2001):

$$A \leftrightarrow A^{\neq} \leftrightarrow B \qquad (2.1)$$

For this reaction, the process pressure (P), temperature (T), system's free enthalphy (ΔG), thermal energy (ΔE), volume (ΔV) and entropy (ΔS) can be related by

$$\Delta G = \Delta E + p\Delta V - T\Delta S \qquad (2.2)$$

Under isothermal condition, the kinetics of this reaction can be described by Eq. 2.3

$$\Delta V^{\neq} = V^{\neq} - V_A = \left(\frac{\partial \Delta G^{\neq}}{\partial p}\right)_T = -RT\left(\frac{\partial \ln k}{\partial p}\right)_T \qquad (2.3)$$

where k is reaction rate constant and R is universal gas constant (R=8.314 J/mol.K). $\Delta G^{\neq}$ and $\Delta V^{\neq}$ relate the changes in free activation enthalphy and activation volume. $V^{\neq}$ represents the volume of the activated system while V_A represents the volume before activation (Pfister et al., 2001). A positive ΔV implies a shift toward the reactants at higher pressures. Depending upon the mechanism, some reactions may be accelerated or retarded by pressure.

Isostatic principle

It is generally believed that at the macroscopic level pressure is transmitted in a quasi-instantaneous manner throughout the sample volume (Pascal's principle). Thus, processing time during high pressure processing is often thought to be independent of product size and geometry (Cheftel, 1995).

However, care must be taken to understand the interdependence of pressure and temperature during the high pressure processing of food samples. Compression of the food sample results in a temperature increase (due to adiabatic heating). Water, carbohydrates, proteins, and fats are some of the basic building blocks of a complex food matrix and each of these may respond uniquely under physical compression

(Rasanayagam et al., 2003). The different rates of heating of each food matrix component under pressure may result in thermal gradients. Further, product near the vessel wall may lose heat to the environment.

Traditionally, the food industry has employed modest pressure treatment (3-30 MPa; 435-4351 psi) for the homogenization of liquid foods. During homogenization, the liquid is forced to flow under high- pressure through a narrow orifice. High product velocity and high shear characterize the homogenization process (Farkas and Hoover, 2000). Product heating can be expected. On the other hand, during HPP, the product is compressed isostatically (i.e., compressed in three dimensions), held, and then decompressed. Pressure reduces the volume of water by 10% at 300 MPa (43,500 psi) and by 17% at 600 MPa (87,000 psi) (Farkas and Hoover, 2000). Little product distortion occurs at the macroscopic level in food materials with high moisture. On the other hand, if the food materials contain a significant amounts of air (e.g., marshmallow, strawberry, leafy vegetable), the air will escape from the product after pressure treatment because of the difference in material compressibility. At HPP treatment pressures, gases in general, are liquefied, if not dissolved in the liquid fraction of the food. On decompression the gases expand and are released from the food matrix. Thus, products containing significant air may not be good candidates for pressure treatment. Similarly, dry solids form cake-like structures after pressure treatment. If food products do not contain sufficient moisture to maintain a water activity above 0.98, HPP may not provide effective microbial destruction.

2.3. Typical process description

High pressure processing of solid foods starts with removing as much as air as possible from the food and vacuum packaging the products in flexible, high-barrier containers. Air removal is essential to insure that a maximum number of containers can fill the pressure vessel during each cycle and that compression work will not be wasted on air in the system. The containers are loaded into a carrier basket or placed directly into the pressure vessel. Loading is similar in operation to a batch steam retort. Commercial batch vessel volumes range from 30 to 600 liters. A typical process cycle consists of loading the vessel with the pre-packaged product and filling the remaining vessel void space with water which acts as the pressure-transmitting fluid. The vessel is closed and the desired process pressure is achieved through addition of water deliveried by an intensifier. After holding the product for the desired time at the target pressure, the vessel is decompressed by releasing the water (Balasubramaniam et al., 2008).

Liquid foods can be processed in batch or semi-continuous mode. In the batch mode, the liquid product is pre-packaged and pressure-treated as described for packaged foods. Semi-continuous pressure equipment employs two or more pressure vessels with free-floating pistons arranged to compress the liquid foods. A low-pressure transfer pump is used to fill the pressure vessel with the liquid food. After filling, the pressure vessel inlet valve is closed, and the pressure-transmitting fluid (usually water) is introduced behind the free piston to compress the liquid food. After the appropriate holding time, releasing the pressure on the pressure-transmitting fluid decompresses the system. A pump is used to move the free piston towards the discharge port. The treated liquid food,

which is held in a sterile tank, can then be filled aseptically into sterile containers. Three batch vessels in a semi-continuous system can be connected such that while one vessel discharges the product, the second vessel is being compressed, and the third vessel is being loaded. In this way, the output is maintained in a continuous fashion (Balasubramaniam et al., 2008).

2.4. Packaging

The packaging requirement for the HPP process varies depending upon the type of equipment (batch or semi-continuous) used. Semi-continuous systems are used in the case of pumpable liquid products which are aseptically packaged after pressure treatment. On the other hand, flexible or semi-rigid packaging with at least one flexible interface, is best suited for batch processing. A variety of existing flexible packaging structures may be used (Balasubramaniam et al., 2004). Since high moisture foods compress by 15-20% in the range of 600 MPa (87,000 psi) at ambient temperature, HPP packaging materials must be able to accommodate these reductions in volume and then return to their original volume without loss of seal integrity or barrier properties. For this reason, metal cans are generally not suited for the process.

Package size and shape will influence the product loading efficiency within the pressure chamber. The package should be designed to achieve at least 75% loading for economical processing. Further, the mass ratio of product to void space water, and package size and shape can influence the heat exchange between the pressure treated product and the surroundings and may create thermal gradients within the food. As noted previously, the air present in the package headspace should be minimized to the extent

possible to further improve the loading factor. High-barrier packaging materials with oxygen- and light-impermeable properties may be desired for extended refrigerated product storage. This can also help preserve the fresh color and flavor attributes of many pressure treated products (Hogan et al., 2005).

2.5. Pressure-transmitting fluids

During HPP, a pressure transmitting fluid is used to transfer pressure to the pre-packaged foods uniformly and instantaneously. The choice of pressure-transmitting fluid is based on the materials used to fabricate the pressure chamber. To prevent corrosion, commercial pressure vessels use a stainless steel liner. This enables the use of water as the fluid of choice for HPP treatment of foods. It is worth noting that the compression-heating behavior of water is similar to that of most food materials. This can minimize thermal gradients between the food material and the compression fluid. Water has also emerged as the pressure-transmitting fluid of choice due to its availability, non-toxicity, and low cost.

Castor oil, silicone oil, solutions of glycol-water mix, and sodium benzoate solutions are among the list of other pressure- transmitting fluids used in laboratory pressure equipment (Balasubramanian and Balasubramaniam, 2003). Depending upon their thermal and physical properties (such as specific heat, viscosity, compressibility, etc.), each solution may have a different rate of compression heating. For example, the heat of compression of water under pressure is 3.0^{o}C per 100 MPa (14,500 psi) while that of silicone oil is about 20^{o}C per 100 MPa. These differences can influence the magnitude of heat transfer among the pressure-transmitting fluid, food product, and the environment.

The thermal gradient in the system subsequently could influence microbial inactivation and the quality of the processed foods (Balasubramanian and Balasubramaniam, 2003). If lab equipment (used for microbial or enzymatic kinetic studies) and commercial production equipment employ different pressure-transmitting fluids, the differences in respective heat transfer characteristics must be considered for reliable microbial challenge studies (Balasubramaniam et al., 2004).

2.6. Pressure-temperature response during processing

During HPP, the temperature of food materials increases, as an unavoidable thermodynamic effect of compression (Ting et al., 2002). Figure 2.1 presents the typical pressure-temperature curve for a food sample subjected to high pressure treatment. The temperature of the food sample increases because of physical compression (Figure 2.1 p_1-p_2).

The magnitude of temperature change (Figure 2.1, T_1-T_2) depends on the compressibility of the substance, thermal properties, initial temperature, and target pressure. For example, at 600 MPa (87,000 psi), the volume of a polar compound such as water is reduced by 17%. The maximum product temperature at the target process pressure is independent of the compression rate as long as heat transfer to the surroundings is negligible.

Pressure comeup time

The time (Figure 2.1, t_1-t_2) required to increase the pressure of the sample from atmospheric pressure to the target process pressure is often defined as “pressure come-up time” (Farkas and Hoover, 2000). The process come-up time is primarily a function of

the desired target pressure, the volume of the pressure vessel, and the horsepower of the pump-intensifier employed. Typical commercial scale high pressure equipment is designed to have a come-up time in the range of 2-3 min to reach 600 MPa (87,000 psi). Longer come-up times add to the total process time by reducing the hourly cycling rate. This affects product throughput. Variation in come-up time may also affect the inactivation kinetics of microorganisms. Therefore, consistency and awareness of these times are important in the process development of HPP (Farkas and Hoover 2000; Ting et al., 2002; Balasubramaniam et al., 2004).

Pressure holding time

Once the desired pressure is reached, and assuming there is no significant pressure drop in the system as a result of heat exchange with the surroundings, no more additional energy is added to the process. Thus, pressure holding time (Figure 2.1, t_2-t_3) can be defined as the interval between the end of compression and the beginning of decompression. The products are held at the target pressure and temperature (if specified) for a predetermined holding time to achieve the desired microbial inactivation and/or quality.

Short processing time (< 10 min) is often desired since process time has a significant effect on throughput (Balasubramaniam et al., 2004). Stability of product temperature during the holding time at pressure may depend upon the insulation characteristics of the pressure vessel. If the equipment is not properly insulated, the temperature of the product decreases from T_2 to T_3 (Figure 2.1) during pressure holding time (t_2 to t_3) due to thermal exchange through the pressure vessel walls.

Decompression time

The time (Figure 2.1, t_3-t_4) to bring a food sample from process pressure to near atmospheric pressure is often termed "decompression time." Most pressure equipment allows product to be decompressed in a few seconds. Certain food products may change their structure during decompression due to the very rapid expansion of dissolved or occluded gas. If structural changes are undesirable, a slower rate of decompression may be considered. The rate of decompression can be controlled by inserting a smaller venting line or by other throttling means, however, this will increase the cycle time.

During decompression, the product temperature drops towards T_4, which may be lower than its initial temperature value (T_1). The difference between the sample initial temperature and final temperature after decompression (T_1~T_4) can be indicative of the extent of heat loss from the product to the surroundings during processing (Ting et al., 2002).

Cycle time

The total time for loading, closing the vessel, compression, holding, and decompression and unloading is commonly referred to as the "cycle time." The cycle time and the volumetric efficiency (i.e. the percentage of the vessel volume occupied by the product) determine the system throughput and the cost of the HPP treatment.

Process pressure

"Process pressure" (Figure 2.1, $p_2 \sim p_3$) refers to the holding pressure during the sample treatment. The accuracy of the pressure reading should be identified along with the pressure indicated. The recommended level of accuracy both to control and record pressure is ±0.5% (electronic) or ±1.0% (dial display) (Farkas and Hoover, 2000). Most mechanical Bourdon tube-type gauges lack good reliability under heavy use at elevated pressures. Strain gauges on the pressure vessel or displacement transducers on the external frame can be effective and reliable methods to measure pressure. It is recommended that at least two methods be used to measure pressure and an appropriate periodic calibration program should be in place (Balasubramaniam et al., 2004). A reference sensor or gauge should be available for periodic calibration of process instrumentation.

Product initial temperature

The initial temperatures (T_1) of the product, the pressure-transmitting fluid, and the process vessel must be documented if the temperature is a specified condition for microbial inactivation during high pressure treatment. For heterogeneous food samples, additional time may be needed to achieve temperature equilibrium within the sample. The high pressures used in food processing do not influence the type-K thermocouple readings at temperatures below 500°C (Bundy, 1961). The reference thermocouple sensor should be located at a cold point or in an equivalent zone within the pressure vessel and calibrated to an accuracy of ±0.5°C (Farkas and Hoover, 2000). Standard methods and good laboratory practices regarding temperature measurement should be followed (e.g., Beckerath et al., 1998).

2.7. Treatment effects during high pressure processing

Depending upon the pressure-temperature regime and duration of exposure, high pressure processing can be used to deliver a variety of treatment effects on the food material. These include food pasteurization, sterilization, blanching, or freezing and thawing (Figure 2.2).

High pressure pasteurization

Pasteurization treatment typically employs pressures in the range of 600 MPa (87,000 psi) at or near ambient temperatures for a specific holding time (Cheftel, 1995; Farkas and Hoover, 2000). High pressure pasteurization treatments inactivate pathogenic and spoilage bacteria, yeasts, and molds, but have limited effectiveness against spores and enzymes (Figure 2.2). The extent of bacterial inactivation also depends on the type of microorganism, food composition, pH, and water activity. Gram-positive organisms are more resistant than gram negatives. Significant variations in pressure resistances can be seen among strains (Cheftel, 1995; Smelt, 1998). Water activity has a major influence on the rate of microbial inactivation.

Examples of high pressure pasteurized products commercially available in the United States, Europe, and Japan include smoothies, guacamole, deli meat slices, ready-meal components, poultry products, oysters, ham, fruit juices, and salsa (Dunne, 2005).

High pressure sterilization

Elevated pressures (500-900 MPa; 72,500-130,500 psi) can be combined with several minutes heat (90-120^{o}C) exposure to sterilize low-acid foods (Ahn et al., 2007; De Heij et al., 2003; Matser et al., 2004; Rajan et al., 2006). During typical pressure-

assisted thermal processing (PATP) (also referred to as "pressure-assisted thermal sterilization" or "PATS"), the food is subjected to a combination of elevated pressures and moderate heat for certain time. One of the unique advantages of PATP is its ability to provide a rapid and uniform increase in the temperature of treated food samples. Uniform compression heating and expansion cooling, on decompression, help reduce the severity of thermal effects encountered with conventional processing techniques. Inactivation of various bacterial spores by the combined pressure-temperature treatment is a topic of ongoing research. Prions are even more resistant than spores under combined pressure-temperature treatment. Limited studies evaluated PATP conditions under which prions can be inactivated. For example, Brown et al. (2003) reported that elevated temperatures (121 -137^{o}C) and pressures (690 – 1200 MPa) are required to inactivate prions.

Quality of pressure sterilized products

PATP technology reportedly reduces process time and preserves food quality, especially texture, color and flavor as compared to retorted products (Hoogland et al., 2001; Krebbers et al., 2002, 2003; Juliano et al., 2006) Preheating and subsequent heat transfer during combined pressure-thermal treatment can influence the quality of PATP samples (Nguyen et al., 2007). During 2009, the Food and Drug Administration approved a petition for pressure-assisted thermal sterilization of a low-acid product (Food Processing, 2009). Shelf-stable, low-acid foods processed by this technology are not yet commercially available. However the technology has the potential for sterilizing heat-sensitive products such as soups, egg products, coffee, tea, and mashed potatoes.

Pressure pulsing

Application of two or more pressure pulses (referred to as "pressure pulsing" or "oscillatory pressure treatments") has been shown to be more effective (Meyer et al., 2000) than single pulse treatments with an equivalent pressure holding time. Pulse treatment can be utilized for both food pasteurization and sterilization. The measure of improved inactivation by pulsed pressurization must be weighed against the design capabilities of the pressure unit, the added compression costs, added wear on the pressure unit, possible detrimental effects on the sensory quality of the product, and the additional time required for cycling.

Pressure applications during freezing and thawing

Conventional freezing at atmospheric pressure may cause structural damage due to the formation of larger ice crystals. Rapid freezing using cryogens can induce cracking, possibly due to the initial decrease of volume from cooling and the subsequent increase in volume from freezing (Kalichevsky et al., 1995). As per LeChatelier's principle, pressure opposes reactions associated with volume increase such as the state change that occurs during the transition from liquid water to ice. This provides new opportunities for pressure-assisted freezing and thawing, pressure-shift freezing, and pressure-induced thawing so that food material can be preserved under subzero temperatures without ice crystal formation (Figure 2.3) (Benet et al., 2004). During pressure-assisted freezing and thawing, the phase transition occurs under constant pressure (Figure 2.3, a-b-e-f or f-e-b-a). During pressure-shift freezing, the sample is cooled under pressure to below 0^{o}C, but kept in the liquid state. Once the desired temperature is reached in the product, the pressure is released (Figure 2.3, a-c-d-f). This results in super cooling and rapid ice

nucleation. Researchers demonstrated that this can reduce the freezing point and can promote rapid ice nucleation and growth throughout the sample thus producing small ice crystals. The process can result in a better preserved microstructure and texture and less drip losses than conventional frozen products (Otero et al., 2007). During pressure-induced thawing, a frozen product can be forced to the liquid state by applying pressure (Figure 2.3, pathway f-d-c-a). This facilitates faster thawing. Pressure-induced thawing is likely to have many applications in the food industry, especially for products in which significant sample deterioration occurs during thawing.

Pressure-assisted blanching

Eshtiaghi and Knorr (1993) reported that high pressure processing at or near ambient temperatures can be effectively used to blanch food products. This process is similar to hot water or steam blanching, but with much reduced thermal degradation. This can help minimize problems associated with water disposal. For example, the application of 400 MPa or 58,000 psi pressure at 20^{o}C for 15 min blanched potato samples and provided a four-log cycle reduction in microbial count while retaining 85% of the ascorbic acid. Complete inactivation of polyphenoloxidase was achieved when a 0.5% citric acid solution was used as the blanching medium. The addition of a 1% $CaCl_2$ solution to the medium also improved potato texture. The leaching of potassium from the high pressure treated sample was comparable with a three min hot water blanching treatment (Eshtiaghi and Knorr, 1993).

2.8. Properties of food materials under high pressure

High pressure processing requires knowledge of the pressure dependency of various thermal and physical properties such as thermal conductivity, specific heat, density, and viscosity of food materials to evaluate heat transfer within the processed volume. While pressure primarily affects the volume of the system, heat transfer can cause both volume and energy changes within the system. Knowledge of combined pressure-thermal effects on food properties can facilitate the understanding of the uniformity of pressure treatment on microbial safety and the quality of food material.

After the pioneering work of Bridgman (Bridgman, 1931), the properties of water under pressure were well documented. Data are available from the International Association for the Properties of Water and Steam (IAPWS). A software implementation of IAPWS work can be obtained from the U.S. National Institute of Standards and Technology (NIST) (Harvey et al., 1996). Very limited information is available on properties of food materials under pressure because of the practical challenges associated with the in-situ measurement of these properties at elevated pressures (Ramaswamy et al., 2005). The effect of pressure on density, viscosity and thermal conductivity of selected food materials are given in Figure 2.4. Density and thermal conductivity of material increase with an increase in pressure (Figure 2.4a and c). Water viscosity decreases from 0.1 to 200 MPa (14.5 to 29,000 psi), while the range of 300 – 600 MPa (43,500 to 87,000 psi) produces a slight increase of viscosity (Figure 2.4b). A further increase of pressure is associated with a drastic reduction in water viscosity.

Compressibility

During high pressure processing of food materials, the gross structure of the food material is compressed. Compressibility is an intrinsic property of the material and is defined by the balance between attractive and repulsive potentials. Compression of a liquid decreases the average intermolecular distance and tends to reduce rotational and translational motion. Food material (for example, orange juice) is considered to contain molecules that occupy space in excess of that needed for close packing. This excess is called "free volume," and it is this volume that is reduced in initial compression (Rasanayagam et al., 2003). At elevated pressures, when the free volume has largely disappeared, a reduction in the van der Waals dimensions may occur and the compressibility is greatly diminished. Isothermal compressibility (β) is defined as the relative change in volume (V) with pressure (P)

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad (2.4)$$

Very limited information is available on the compressibility of food materials under pressure. The temperature of the food substances also changes during physical compression (Ting et al., 2002) (Figure 2.1). This temperature change causes thermal expansion of the material. The thermal expansion coefficient (α) is another thermodynamic property that provides a measure of the amount by which the density changes in response to a change in temperature at constant pressure.

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad (2.5)$$

Denys et al. (2000a) reported the thermal expansion coefficient of apple sauce and tomato paste at different combinations of temperature and pressure. The values were lower than that of pure water under these process conditions.

Heat of compression

The instantaneous temperature change in materials during compression or decompression is often called the "heat of compression" (Otero et al., 2000; Rasanayagam et al., 2003; Ardia et al., 2004). The heat of compression can be estimated theoretically using the equation

$$\delta = \frac{dT}{dP} = \frac{T\alpha}{C_p \rho} \qquad (2.6)$$

where α, T, ρ and C_p represent the thermal expansion coefficient, temperature, density, and heat capacity at constant pressure, respectively. Eq. 2.6 is strictly applicable only to small pressure changes (Otero et al., 2000). An accurate estimation of volumes (Eq. 2.3) or thermal expansion (Eq. 2.4) under pressure is difficult to obtain due to challenges associated with developing reliable sensors and instrumentation that can withstand elevated pressure conditions. Alternatively, researchers often estimate the heat of compression values experimentally by directly monitoring temperature changes in the substance during compression or decompression (Otero et al., 2000; Rasanayagam et al., 2003; Patazca et al., 2007). Most foods exhibit a compression-heating behavior very similar to that of water, since water is usually their main ingredient. Among the food constituents, water, being a compact polar molecule, has the least heat of compression value under pressure (3^{o}C per 100 MPa at 25^{o}C) (Table 2.3). Non-polar fats and oils with

long-chain fatty acids have higher heat of compression values (up to 9°C per 100 MPa) (Table 2.4).

While for water, the heat of compression values increase with an increase in its initial temperature (Table 2.3), values of fats and oils are not much influenced by the initial temperature (Table 2.4). Proteins and carbohydrates have intermediate heat of compression values. The differences in the thermal response of water, fats, and oils can be attributed to their molecular structure and phase transition characteristics. If heats of compression values for various food constituents are known, the average temperature (T_2) of the test sample at the beginning of pressure holding time can be estimated using simple mixture rule shown in the following equation:

$$T_2 = T_1 + \left(\frac{\sum_i (\delta_m * M_f)}{M}\right)(\Delta P) + \Delta T_H \qquad (2.7)$$

In this equation, T_1 is the sample initial temperature, M is the total mass, M_f is the mass of individual constituents, and P is the applied pressure. ΔT_H is temperature gain (or lost) between the test sample and the surrounding during product loading within pressure chamber and pressurization. For example, if a product, consisting of several constituents at an initial temperature of 75°C, is compressed to 700 MPa (101,500 psi), and it could reach a maximum process temperature of approximately 106°C as a result of compression heating. This temperature will be the average of the combined heats of compression of the several constituents present in the sample. The above example only considers the temperature change in the product as a result of the heat of compression and assumes no heat exchange with the surroundings. However, in practice, heat exchange is likely to occur. Temperature changes resulting from heat transfer (ΔT_H) between the product and

external factors such as compression fluid, pressure vessel and the environment must be empirically determined by actual test. The time dependent heat transfer between the test sample and the surrounding factors during the product loading, compression, and holding phase must be considered. It is worth noting that measured ΔT_H values are likely influenced by the insulation characteristics of the pressure equipment used, operator skill, and process conditions employed. Once ΔT_H values are determined, the initial sample temperature can then be suitably adjusted to achieve the desired final product temperature (Nguyen et al., 2007).

Thermal conductivity

There are a limited number of studies reporting the thermal conductivity (*k*) of food materials under pressure. Denys and Hendrickx (1999) studied the *k* of tomato paste and apple pulp at pressures up to 400MPa (58,000 psi). Zhu et al. (2007) studied *k* values of potato and cheddar cheese at pressures up to 350 MPa (50,750 psi) at 5°C. These foods showed a thermal conductivity increase with an increase in pressure. The increase in thermal conductivity was influenced by the amount of moisture present in the food material. Ramaswamy et al. (2007) reported on the thermal conductivity of selected liquid foods under pressure. Water and water-like substances (apple juice) were found to have the highest *k* values (up to 0.82 W/ m^oC at 700 MPa (101,500 psi) and 25^oC), while fatty foods such as canola oil and clarified butter had the lowest values (0.29–0.40 W/m^oC, respectively at 700 MPa and 25^oC). Honey and high-fructose corn syrup had intermediate values (Figure 2.4c). The estimated *k* values of all the food materials tested

under pressure were higher than the corresponding k values of materials under atmospheric pressure (Ramaswamy et al., 2007).

Specific heat

The specific heat of foods at atmospheric pressure is measured using techniques such as the method of mixtures or differential scanning calorimetry (DSC). However, there is very limited literature using these techniques for estimating specific heat values of food materials under high pressure process conditions. Data on the specific heat of pure water, as a function of elevated pressure and temperature, is readily available through the NIST data base (Harvey et al., 1996). These values are approximately ten percent lower than those estimated at ambient pressures. In the absence of experimental data, researchers often ignore the effect of pressure on specific heat in heat transfer calculations.

Density

When a food material is processed under pressure, there can be a significant decrease in the volume of the product. This decrease is due to a reduction in the "free volume" between molecules and the compacting of voids occupied by gases. These changes can, in turn, influence temperature process uniformity during HPP. The density of a material under pressure can be estimated by determining its change in volume under pressure and its mass. Density is then calculated as the ratio of mass to volume. The volume change of a material under pressure can be estimated by using a linear velocity differential (LVD) transducer (Bridgman, 1931). Changes in sound velocity have also been used to measure density under pressure (Kovarskii, 1993). Denys et al. (2000 a,b)

estimated the density of food materials using a bulk volume displacement method. Density of selected food materials was measured by a variable piezometer at 25^{o}C up to 700 MPa (Min et al., 2009) (Figure 2.4a)

pH

During high pressure processing, the pH of food materials, in general, shifts towards a lower pH value as a function of applied pressure. The direction of pH shift and its magnitude depends on the food composition. For a simplified model, the dissociation of acid HA can be described by the equation:

$$HA \Leftrightarrow A^{-} + H^{+} \tag{2.8}$$

The dissociation of HA is accompanied by a reduction in volume due to the more compact packing of solvent around the charged ions as compared to the uncharged HA molecule. As per LeChatelier's principle, the dissociation of HA is favored by an increase of pressure and as a result, the pH of a solution is reduced. El'Yanov and Hamann (1975) developed a theory on the dependency of a dissociation constant on pressure. This dependency is given by the following equation:

$$pK_a = pK_a^0 + \frac{\Delta V_m^0 p}{2.303RT(1+bp)} \tag{2.9}$$

In this equation, pK_a is the dissociation constant, ΔV_m^0 is the molal volume change between associated and dissociated forms of buffering acid in solution, R is the universal gas constant(8.314 J/mol K), b is a universal constant(9.2 Pa^{-1}), p is pressure, and superscript 0 denote values at atmospheric pressure. Heremans (1995) reported apple pH decreased by 0.2 units with 100 MPa increase in pressure. For a neutral pH phosphate

buffer, a pressure of 68MPa (9,860 psi) results in a decrease of 0.4 pH units (Johnson et al., 1954). The prediction of pH change during HPP in various foods can be complicated by the composition and the unknown equilibrium constants. More research effort is needed in this area, and pH-measuring instruments that operate under pressure would aid these studies.

2.9. Process uniformity during high pressure processing

Combined pressure-heat treatment can provide either synergistic or antagonistic effects on the microbial safety and quality of the processed product. Thus, similar to traditional thermal processing, identification of the least processed volume ("cold-spot") during HPP will help ensure safety of the processed foods. Knowledge of the least processed volume within a pressure chamber is especially critical for high pressure sterilization of low-acid, shelf-stable, foods. Although both pressure and temperature can contribute to HPP process non-uniformity, for food processing calculations, pressure is assumed to be uniformly transmitted throughout the processed volume.

A number of factors can influence heat transfer-related process non-uniformity within a pressure chamber. These include the design of the pressure equipment as well as the geometry and insulation characteristics of the pressure chamber (Hartmann et al., 2004). The size of the pressure chamber will affect the rate of change of temperature gradients within the vessel. Larger size pressure vessels likely have slower temperature gradient changes.

The type of pressure-transmitting fluid used strongly influences temporal and spatial temperature distributions. During HPP, the temperature of the food material and

the pressure-transmitting fluid increases as a result of physical compression. Subsequently, transient heat exchange takes place among the sample, the pressure-transmitting fluid, and the pressure chamber walls. The resulting temperature gradient in the system can also lead to density differences within the pressure- transmitting fluid and, consequently, induce free convection (Hartmann, 2002; Otero et al., 2007). Redistribution of momentum and energy may then occur, and this fluid motion strongly influences the temporal and spatial distribution of temperature. Transient temperature and velocity fields also strongly influence each other. The viscosity of pressure-transmitting fluids is another important factor in process uniformity (Hartmann and Delgado, 2002). Fluid viscosity strongly affects the convective transport phenomenon, which contributes to the temporal and spatial distribution of temperature inside the pressure chamber.

The ratio of sample to vessel chamber volume, the size and shape of the package, and the insulation properties of the packaging material can influence the process uniformity due to temperature gradients during high pressure processing (Otero et al., 2007). The packaging material can act as a heat barrier to maintain an "adiabatic" condition of the packed foods (Hartmann and Delgado, 2003). Heat of compression of food material and other relevant thermophysical properties can also influence the process uniformity (Ramaswamy et al., 2005).

2.10. Modeling process uniformity

The determination of temporal and spatial temperature distributions within a high pressure chamber is dependent on the thermo-fluid dynamic effects. The process temperature and pressure gradient developed during high pressure processing can be

modeled by solving equations for conservation of mass, momentum, and energy. The treatment effect on the product can then be considered by including these gradient temperatures and pressures in relevant equations for microbial or enzymatic kinetics. Denys et al. (2000a) used residual enzyme activity and a numerical heat-transfer model for evaluating process uniformity in apple sauce and tomato paste. The residual enzyme activity distribution appeared to be dependant on the inactivation kinetics of the enzyme under consideration and the pressure–temperature combination considered. Hartmann et al. (2003) studied the influence of heat and mass transport effects on the uniformity of high pressure induced microbial inactivation. Their results showed that the effective inactivation rate increased with the increase in size of the high pressure vessel. However, more than one log variation in the residual surviving cell concentration could be observed, depending on the package material used, and the position and arrangement of the packages in the vessel. Hartmann et al. (2004) studied the thermo-fluid dynamics and process uniformity of HPP in a laboratory scale autoclave using experimental and numerical simulation techniques. Ghani and Farid (2007) proposed a simulation study of heat transfer during high pressure processing of food using computational fluid dynamics (CFD).

2.11. Approaches to minimize process non-uniformity

Several approaches have been proposed to minimize thermal non-uniformity during pressure treatment. Temperature control of the product, package, pressure-transmitting fluid and the pressure vessel for each cycle during high pressure processing is critical (Farkas and Hoover, 2000). It is also important to consider the heat of

compression of the various materials (food, pressure transmitting fluid, package, etc.) and target pressure. The initial temperature of the materials can then be adjusted to minimize thermal gradients during pressure holding time (Ting et al., 2002; Balasubramaniam et al., 2004). In addition, use of an external temperature control jacket for heating or cooling can help minimize temperature gradients within the system. Thermal insulation of the inner wall of the pressure chamber can also aid process uniformity (Hartmann et al., 2004). Finally, the selection of appropriate packaging materials can contribute to better thermal uniformity during high pressure processing. For example, a high degree of uniformity can be achieved when packaging materials with good insulating characteristics are used (Hartmann and Delgado, 2003, 2005).

2.12. Conclusions

High pressure processing of foods offers a commercially viable alternative for food processors to preserve a variety of food materials with reduced thermal impact. Depending upon the combination of pressure and temperature used, a variety of treatment effects, including freezing and thawing, pasteurization, sterilization, and blanching, are possible. The technology has been found to be effective for the control of a variety of pathogenic vegetative bacteria including *Salmonella*, *E. coli, and Listeria* at room or modest temperatures. Combined pressure-thermal treatment demonstrated that spores can be inactivated. Although more research is needed to evaluate process uniformity and estimate in-situ properties of food materials under pressure, high pressure processing has demonstrated a significant advance in the quality of preserved foods.

References

Ahn, J., Balasubramaniam, V.M., & Yousef, A.E. (2007). Inactivation kinetics of selected aerobic and anaerobic bacterial spores by pressure-assisted thermal processing. *International Journal of Food Microbiology*, 113(3), 321-329.

Ardia, A., Knorr, D., & Heinz, V. (2004). Adiabatic heat modeling for pressure build-up during high pressure treatment in liquid-food processing. *Transactions of Institution of Chemical Engineers (IChemE), Part C, Food Bioproduct Process*, *82* (C1), 89-95.

Autio, K. (Ed.). (1998). Fresh novel foods by high pressure. 1998. VTT Symposium 186. Valtion Teknillinen Tutkimuskeskus, VTT Biotechnology and Food Research, Food Technology Biologinkuja Finland.

Balasubramaniam, V.M., Farkas, D., & Turek, E. (2008). Preserving Foods through High-Pressure Processing. *Food Technology*, 62(11), 32-38.

Balasubramanian, S., & Balasubramaniam,V.M. (2003). Compression heating influence of pressure transmitting fluids on bacteria inactivation during high pressure processing. *Food Research International*, 36(7), 661-668.

Balasubramanian, V.M., Ting, E.Y., Stewart, C.M., & Robbins, J.A. (2004). Recommended laboratory practices for conducting high pressure microbial inactivation experiments. *Innovative Food Science and Emerging Technologies*, 5(3), 299–306.

Beckerath, A. V., Eberlein, A., Julien, H., Kersten, P., and Kreutzer, J. (1998). Pressure and temperature measurement. *WIKA handbook*. Atlanta: IPD Printing.

Benet, G.U., Schluter, O., & Knorr, D. (2004). High-pressure low temperature processing. Suggested definitions and terminology. *Innovative Food Science and Emerging Technologies*, 5(4), 413-427.

Bridgman, P.W. (1931). The physics of high pressure. London: G. Bells and Sons.

Brown, P., Meyer, R., Cardone, C., & Pocchiari, M. (2003). Ultra-high-pressure inactivation of prion infectivity in processed meat: A practical method to prevent human infection. *Proceeding of National Academy of Science U.S.A.*, *100* (10), 6093–6097.

Bundy, F.P. (1961). Effect of pressure on EMF of thermocouples. *Journal of Applied Physics*, *32*(3), 483-488.

Cheftel, J.C. (1995). Review: high pressure, microbial inactivation and food preservation. *Food Science and Technology International*, 1, 75–90.

De Heij, W.B.C., Van Schepdael, L.J.M.M., Moezelaar, R., Hoogland, H., Matser, A.M., & Van Den Berg, R.W. (2003). High-pressure sterilization: Maximizing the benefits of adiabatic heating. *Food Technology*, 57(3), 37-41.

Denys, S., & Hendrickx, M.E. (1999). Measurement of the thermal conductivity of Foods at high pressure. *Journal of Food Science*, 64(4), 709-713.

Denys, S., Van Loey, A.M., & Hendrickx, M.E. (2000a). A modeling approach for evaluating process uniformity during batch high hydrostatic pressure processing: Combination of numerical heat transfer model and enzyme inactivation kinetics. *Innovative Food Science and Emerging Technologies*, 1(1), 5-19.

Denys, S., Ludikhuyze, L.R., Van Loey, A.M, & Hendrickx, M.E. (2000b). Modelling conductive heat transfer and process uniformity during batch high-pressure processing of foods. *Biotechnology Progress*, 16, 92-102.

Denys, S., Schluter, O., Hendrickx, M.E., & Knorr, D. (2001). Effects of high pressure on water-ice transitions in foods. In Ultra high pressure treatments of foods, Hendrickx, M.E.G., and D. Knorr (Eds). New York: Kluwer Academic/Plenum Publishers. pp. 215-248.

Dunne, CP. (2005). Killing pathogens: high-pressure processing keeps food safe. http://www.military.com/soldiertech/ 0,14632,Soldiertech_Squeeze,,00.html (last accessed June 15, 2006).

Eshtiaghi, M.N., & Knorr, D. (1993). Potato cube response to water blanching and high hydrostatic pressure. *Journal of Food Science*, 58, 1371–1374.

El'yanov B.S., & Hamann, S.D. (1975). Some quantitative relationship for ionization reactions at high pressure. *Australian Journal of Chemistry*, 28, 945-954.

Farkas, D., & Hoover, D. (2000). High pressure processing. In Special supplement: Kinetics of Microbial Inactivation for Alternative Food processing Technologies. *Journal of Food Science Special Supplement*, 47-64.

Food Processing. (2009). Pressure-assisted thermal sterilization accepted by FDA. http://www.foodprocessing.com/articles/2009/032.html (accessed April 3, 2009).

Ghani, A.G.A., & Farid, M.M. (2007). Numerical simulation of solid–liquid food mixture in a high pressure processing unit using computational fluid dynamics. *Journal of Food Engineering*, 80(4), 1031–1042.

Hartmann, C. (2002). Numerical simulation of thermodynamic and fluid-dynamic processes during the high-pressure treatment of fluid food systems. *Innovative Food Science and Emerging Technologies*, 3, 11-18.

Hartmann, C., & Delgado, A. (2002). Numerical simulation of convective and diffusive transport effects on a high-pressure-induced inactivation process. *Biotechnology and Bioengineering*, 79(1), 94-104.

Hartmann, C., & Delgado, A. (2003). The influence of transport phenomena during high-pressure processing of packed food on the uniformity of enzyme inactivation. *Biotechnolgy and Bioengineering*, 82(6), 725-35.

Hartmann, C., & Delgado, A. (2005). Numerical simulation of thermal and fluiddynamical transport effects on a high pressure induced inactivation. *Simulation modeling Practice and theory,* 13, 109-18.

Hartmann, C., Delgado, A., & Szymczyk, Z., (2003). Convective and diffusive transport effects in a high pressure induced inactivation process of packed foods. *Journal of Food Engineering*, 59, 33-44.

Hartmann, C., Schuhholz, J.P., Kitsubun, P., Chapleau, N., Le Bail, A., & Degado, A. (2004). Experimental and numerical analysis of the thermo fluid dynamics in a high-pressure autoclave. *Innovative Food Science and Emerging Technologies*, 5, 399-411.

Harvey, A.H., Peskin, A.P., & Klein, S.A. (1996). NIST/ASME Standard Reference database 10, Version 2.2. Boulder, CO: National Institute of Standards and Technology.

Hayashi, R. (Ed). (1991). High Pressure Science for Food. Minamitaisumi-cho Katsura, Nishikyo-ku, Kyoto 615 Japan: San-Ei Publishing Co.

Heremans, K. (1995). High pressure effects on biomolecules. In High pressure processing of foods. Ledward, D.A., Johnston, D.E., Earnshaw, R.G., & Hasting, A.P.M. (Eds). Nottingham: Nottingham University Press.

Hogan, E., Kelly, A.L., & Sun, D.W. (2005). High pressure processing of foods: an overview. In *Emerging technologies for food processing*. Elsevier Academic press. pp. 1-32.

Hoogland, H., de Heij, W., & van Schepdael, L. (2001). High pressure sterilization: novel technology, new products, new opportunities. *New Food*, 4(1), 21-6.

Johnson, F.H., Eyring, F.H., & Polissar, M.J. (1954). The kinetics basis of molecular biology. New York: John Wiley and Son.

Juliano P., Toldrág M., Koutchma, T., Balasubramaniam, V.M., Clark, S., Mathews, J.W., Dunne, C.P., Sadlerand, G., & Barbosa-Cánovas, G.V. (2006). Texture and water retention improvement in high-pressure thermally treated scrambled egg patties. *Journal of Food Science*, 71(2), E52-61.

Kalichevsky, M.T., Knorr, D., & Lillford, P.J. (1995). Potential food applications of high-pressure effects on ice-water transitions. *Trends in Food Science and Technology*, 6, 253–259.

Kovarskii, A.L. (1993). High-pressure chemistry and physics of polymers. Boca Raton, Florida: CRC press, Inc.

Krebbers, B., Matser, A.M., Koets, M., & Van Den Berg, R.W. (2002). Quality and storage stability of high-pressure preserved green beans. *Journal of Food Engineering*, *54*(1), 27–33.

Krebbers, B., Matser, A.M., Hoogerwerf, S.W., Moezelaar, R., Tomassen, M.M.M., van den Berg, R.W. (2003). Combined high-pressure and thermal treatments for processing of tomato puree: evaluation of microbial inactivation and quality parameters. *Innovative Food Science and Emerging Technologies*, 4(4), 377-85.

Kunugi, S., & Hayashi, R. (Ed.). (1998). High pressure biotechnology. San-Ei Publishing Co,. 30 Minamitaisumi-cho Katsura, Nishikyo-ku, Kyoto 615 Japan.

Ledward, D.A., Johnston, D.E., Earnshaw, R.G., & Hasting, A.P.M. (Eds). (1995). High pressure processing of foods. Sutton Bonington Campus, Loughborough, Leicestershire: Nottingham University Press.

Matser, A.M., Krebbers, B., van den Berg, R.W., & Bartels, P.V. (2004). Advantages of high pressure sterilization on quality of food products. *Trends in Food Science and Technology*, 15(2), 79-85.

Meyer, R.S., Cooper, K.L., Knorr, D., & Lelieveld, H.L.M. (2000). High pressure sterilization of foods. *Food Technology*, 54(11), 67, 68, 70, 72.

Min, S, Sastry, S., & Balasubramaniam, V.M. (2009). Variable volume piezometer for measurement of volumetric properties of materials under high pressure. *International Journal of High Pressure Research*, 29(2), 278-289.

Nguyen, L.T., Rastogi, N.K., & Balasubramaniam, V.M. (2007). Evaluation of the instrumental quality of pressure-assisted thermally processed carrots. *Journal of Food Science*, 72(5), E264-E270.

Ohlsson, T. (1996). High pressure processing of food and food components, a literature survey and bibliography. SIK, Box 5401, Gtoborg, Sweden.

Otero, L., Molina-Garcıa, A.D., & Sanz, P.D. (2000). Thermal effect in foods during quasi-adiabatic pressure treatments. *Innovative Food Science and Emerging Technologies*, 1, 119–126.

Otero, L., Ousegui, A., Benet, G.U., de Elvira, C., Havet, M., Le Bail, A., & Sanz, P.D. (2007). Modeling industrial scale high-pressure-low-temperature processes. *Journal of Food Engineering,* 83, 136-141.

Patazca, E., Koutchma, T., & Balasubramaniam, V.M. (2007). Quasi-adiabatic temperature increase during high pressure processing of selected foods. *Journal of Food Engineering*, 80(1), 199–205.

Pfister, M.K.H., Butz, P., Heinz, V., Dehne, L.I., Knorr, D., & Tauscher, B. (2001). Influence of high pressure treatment on chemical alterations in foods. A literature review. *Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin*, Tabellen, Berlin.

Rajan, S., Ahn, J., Balasubramaniam, V.M., & Yousef, A.E. (2006). Combined pressure-thermal inactivation kinetics of *Bacillus amyloliquefaciens* spores in egg patty mine. *Journal of Food Protection*, 69(4), 853-860.

Ramaswamy, R., Balasubramaniam, V.M., & Sastry, S.K. (2005). Properties of food materials during high pressure processing. In: Heldman, D. R., *Encyclopedia of Agricultural, Food, and Biological Engineering*. New York: Marcel Dekker Inc.

Ramaswamy, R., Balasubramaniam, V.M., & Sastry, S.K. (2007). Thermal conductivity of selected liquid foods at elevated pressures up to 700 MPa. *Journal of Food Engineering*, 83, 444-451.

Rasanayagam, V., Balasubramanaiam, V.M., Ting, E., Sizer, C.E., Bush, C., & Anderson, C. (2003). Compression heating of selected fatty food materials during high pressure processing. *Journal of Food Science*, 68(1), 254-259.

Rastogi, N.K., Rangarao, K.S.M.S., Balasubramaniam, V.M., Niranjan, K. & Knorr, D. (2007). Opportunities and challenges in high pressure processing of foods. *Critical Reviews in Food Science and Nutrition*, 47, 69–112

San Martin, M.F., Barbosa-Canovas, G.V., & Swanson, B.G. (2002). Food processing by high hydrostatic pressure. *Critical Reviews in Food Science and Nutrition* 42, 627-645.

Smelt, J.P.P.M. (1998). Recent advances in the microbiology of high pressure processing *Trends in Food Science and Technology*, 9, 152–158.

Thakur, B.R., & Nelson, P.E. (1998). High pressure processing and preservation of foods. *Food Reviews International*, 14(4), 427–447.

Ting, E., Balasubramaniam, V.M., & Raghubeer, E. (2002). Determining thermal effects in high-pressure processing. *Food Technology*, 56(2), 31–35.

Torres, J.A., & Velásquez, G. (2005). Commercial opportunities and research challenges in the high pressure processing of foods. *Journal of Food Engineering*, 67(1), 95-112

Zhu, S., Ramaswamy, H.S., Marcotte, M., Chen, C., Shao, Y., & Le Bail, A. (2007). Evaluation of thermal properties of food materials at high pressures using a dual-needle line-heat source method. *Journal of Food Science*, 72(2), E49-E56.

	Atmospheres	Bars	Megapascals	Pounds inch^{-2}
Atmospheres	1.000	0.987	9.901	0.068
Bars	1.013	1.000	10.000	0.069
Megapascals	0.101	0.100	1.000	0.00689
Pounds inch^{-2}	14.696	14.504	145.038	1.000

Table 2.1. Frequently used pressure units and conversion factors

Description	Advantage
Pressure	Rapid and uniform distribution throughout the sample
Thermal distribution	Reduced impact of thermal gradient
Physical compression	Instant temperature increase and subsequent cooling upon decompression
Product handling	Suitable for both particulate and pumpable foods
Process time	Less dependence on product shape and size
Functionality	Opportunities for new process/product development
Quality impact	Food may not undergo significant chemical changes.
Reaction rate	Pressure accelerates traditional thermal inactivation kinetics.

Table 2.2. Unique advantages of high pressure processing.

Initial sample temperature (°C)	Heat of compression factor (°C per 100 MPa)
0	1.6
15	2.5
30	3.0
45	3.5
60	4.0
75	4.6
90	5.3

[1]Estimated using NIST ASME software (Harvey, Peskin, & Klein, 1996)

Table 2.3. Estimated compression heating factors (°C per 100 MPa) of water at various initial temperatures[1].

Substance at 25˚C	Temperature change per 100 MPa
Juice, tomato salsa, 2% fat milk, cream cheese, and other water-like substances	3.0
Tofu	3.1
Egg Albumin	3.0
Mashed potato	3.0
Yoghurt	3.1
Honey	3.2
Salmon	3.2
Chicken fat	4.5
Water/Glycol (50/50)	From 4.8 to 3.7[1]
Beef fat	6.3
Olive oil	From 8.7 to 6.3[1]
Soy oil	From 9.1 to 6.2[1]

[1]While the initial temperature does not influence heat of compression values for fatty substances, the values increase with initial temperature for water-based foods (see also Table 2.3)
*Source: Otero and Sanz, 2000; Rasanayagam et al., 2003; Patazca et al., 2007

Table 2.4. Heat of compression for various foods pressure treated at 25˚C[*].

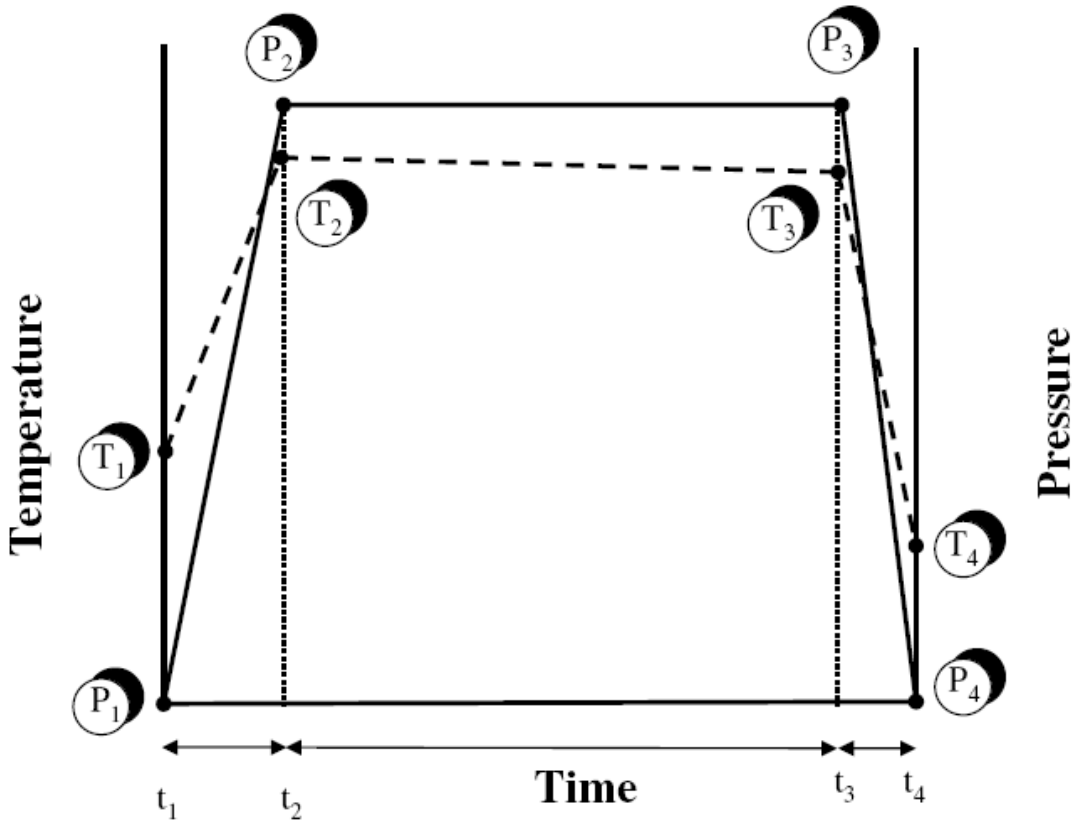


Figure 2.1. Typical pressure-temperature response of a water based food material undergoing high-pressure processing. Come-up time: t_1-t_2; holding time: t_2-t_3; decompression: t_3-t_4.

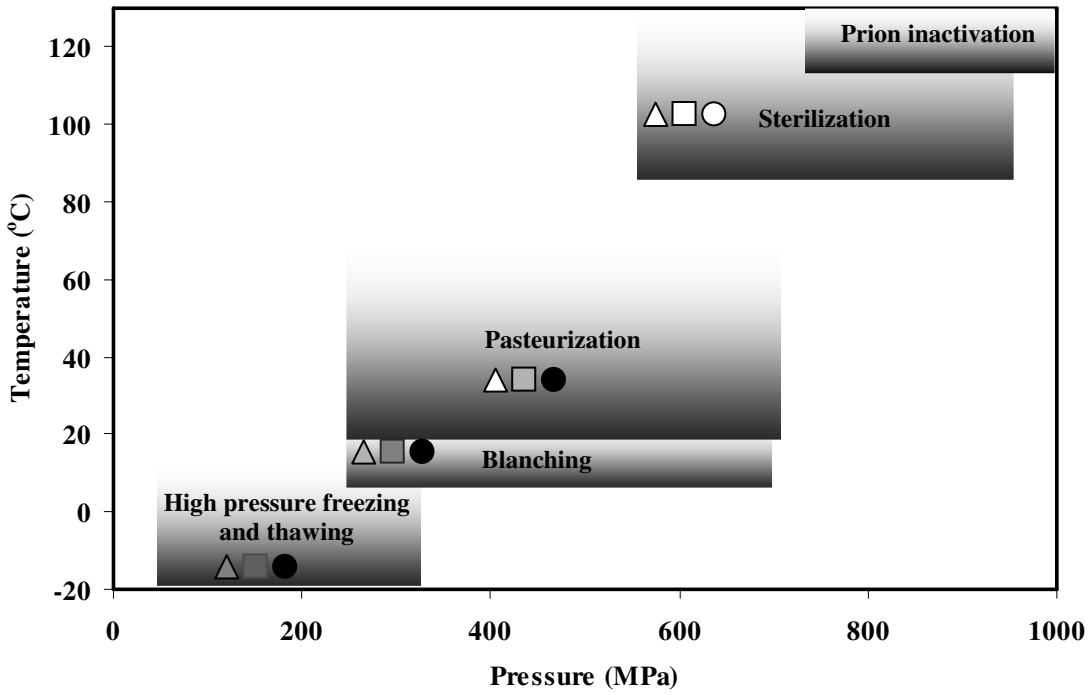


Figure 2.2. Different pressure-temperature regions yield different processing effects. Inactivation of vegetative bacteria, yeasts and molds (□), bacterial spores (○), and enzymes (Δ) are also shown. A filled symbol represents no effect, and an open symbol represents inactivation.

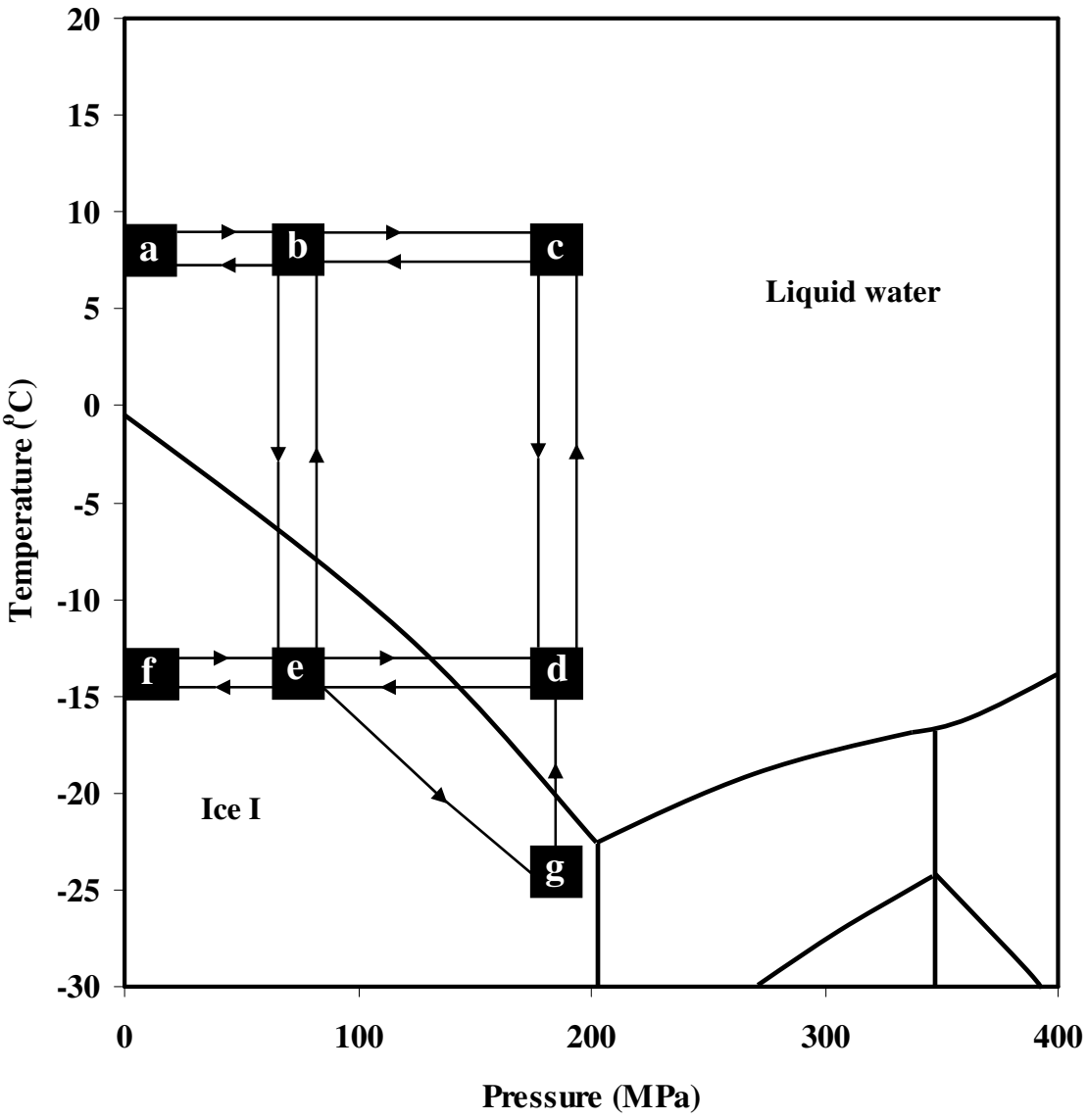
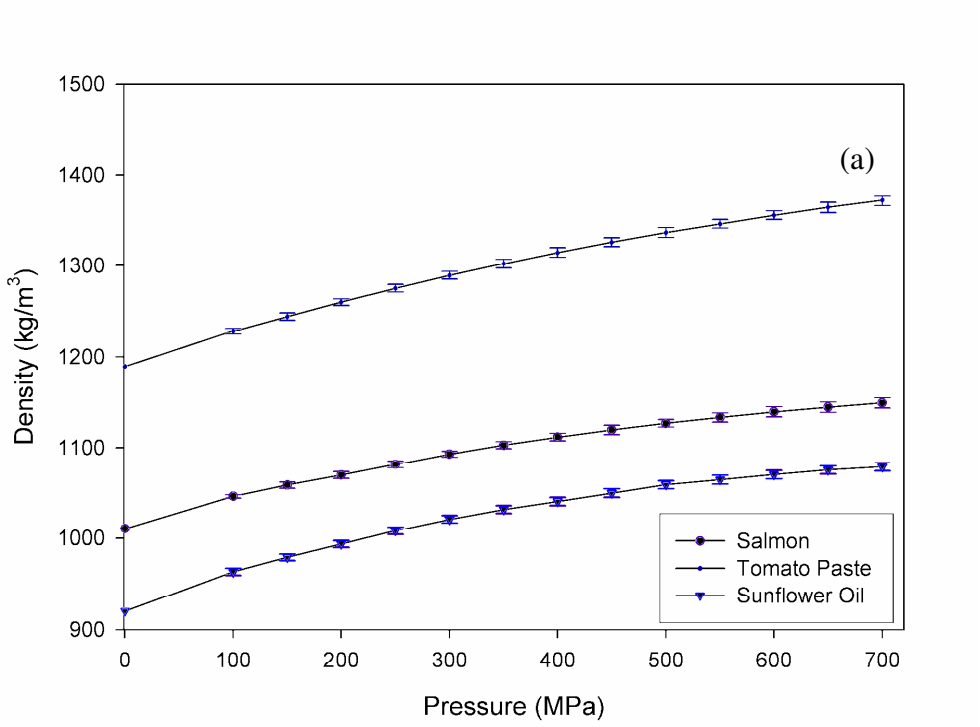


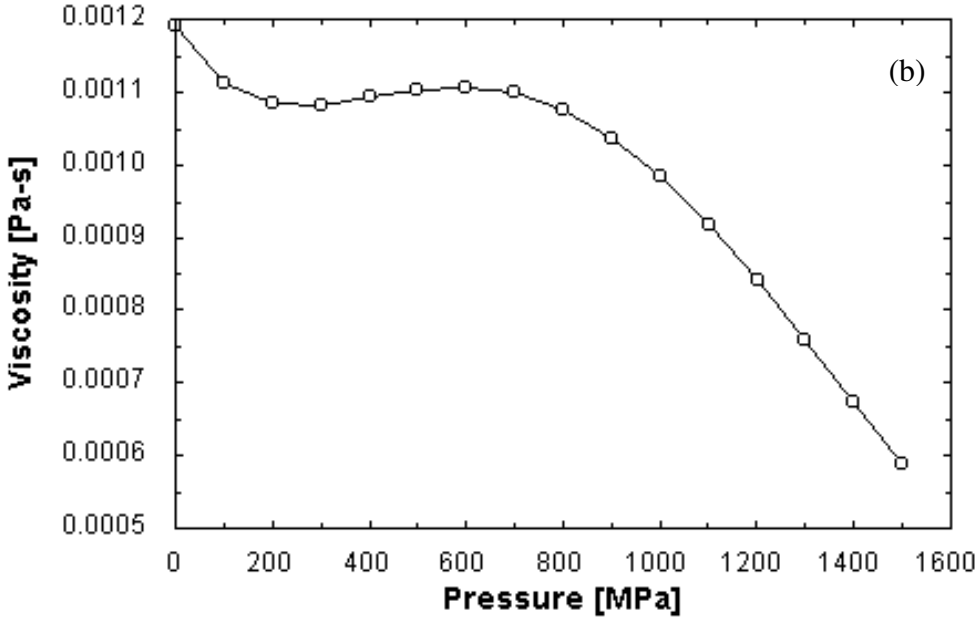
Figure 2.3. High-pressure application in freezing and thawing (Denys et al., 2001).

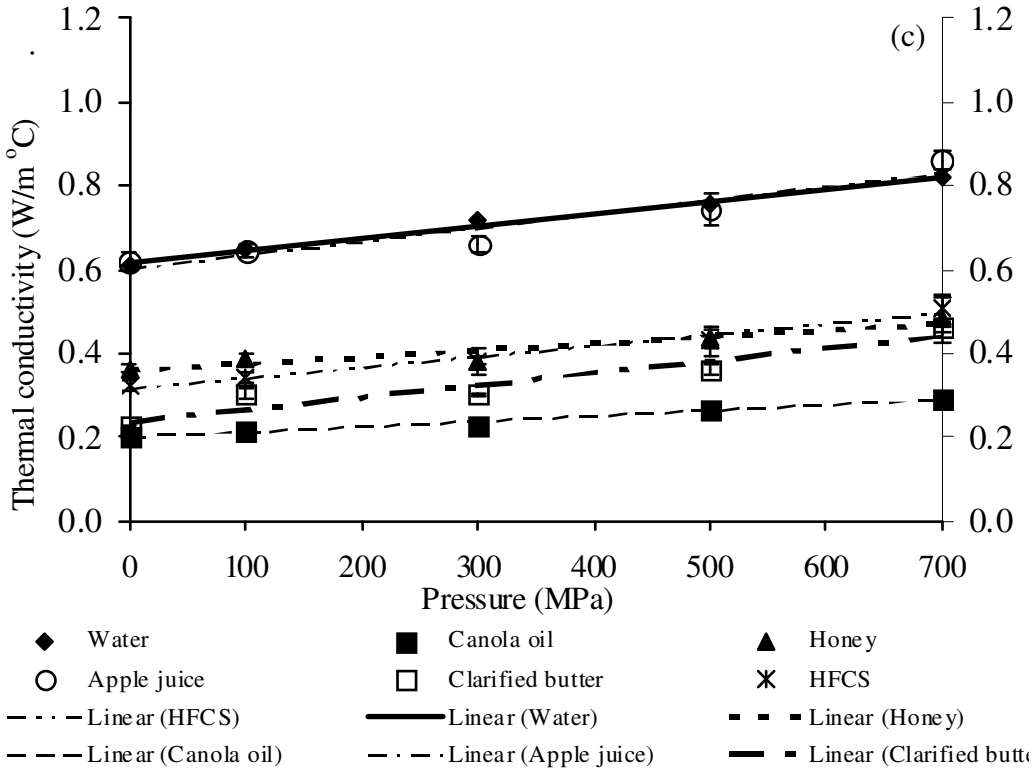


continued

Figure 2.4. Selected properties of food materials under pressure. (a) Density of salmon fillet, tomato paste, and sunflower oil as a function of pressure at 25˚C. Error bars represent uncertainty of density data (Min et al., 2009); (b) viscosity of water under elevated pressures at 25°C (Harvey et al., 1996). (c) thermal conductivity values of selected liquid foods under high pressure (data points with error bars indicate mean ± standard deviation (Ramaswamy et al., 2007).

Figure 2.4. continued





Chapter 3: Evaluation of Instrumental Quality of Pressure-Assisted Thermally Processed Carrots

Abstract

This study was conducted to compare the effectiveness of pressure-assisted thermal processing (PATP) in preserving the texture, color and carotene content of carrot cylinders in the pressure range of 500-700 MPa and the temperature range of 95-121°C. Effectiveness of PATP process was compared against that of conventional thermal processing (TP) by matching carrot pre-process temperature history. The results indicated that under comparable process temperatures (up to 105ºC), PATP retained the carrot quality attributes such as color and carotene content better than TP. However, process and pre-process thermal history at 121°C greatly influenced carrot textural change and pressure protective effects were less pronounced. This study demonstrated that PATP has the potential to produce low-acid foods with a relatively better quality than TP.

Key words: Pressure-assisted thermal processing, thermal processing, low-acid food, quality, carrots, texture, color

3.1. Introduction

Pressure-assisted thermal processing (PATP) generally involves simultaneous application of elevated pressures (500-900 MPa) and temperatures (90–120°C) to preheated foods (Matser et al., 2004; Rajan et al., 2006a) and has been reported to have the potential to preserve low-acid foods (Matser et al., 2004). Over the years, microbial inactivation efficacy of PATP technology has been widely reported (Gola et al., 1996; Rovere et al., 1998; Heinz and Knorr, 2001; Reddy et al., 2003; Margosch et al., 2004; Rajan et al., 2006 a, b; Ahn et al., 2007). Studies also indicated that PATP compression heating during pressurization and rapid cooling during depressurization could help to reduce the severity of thermal effects encountered in conventional thermal processing (Rasanayagam et al., 2003; Ting et al., 2002). For example, PATP technology reportedly reduced process time and preserved food quality, especially texture, color and flavor as compared to retorted products (Hoogland et al., 2001; Krebbers et al., 2002, 2003; Juliano et al., 2006). However, many of these studies made quality comparisons based on the end point data and little is known about the effect of combined pressure-thermal treatment on the kinetics of food quality. It is thus necessary to systematically evaluate the role of pressure in preserving product quality under comparable process temperatures, which can further help the food industry to make decisions about the commercial viability of PATP technology.

The objective of present work is to compare the effect of PATP and thermal process (TP) on the quality attributes of carrots such as texture, color, and carotene

content. The microbial inactivation efficiency and the microstructure change of samples under both treatments were also reported.

3.2. Materials and methods

3.2.1. Materials

Baby carrots were purchased from a local supermarket in large quantities, and stored at refrigerator temperature for up to a week. This minimized the quality variation of the raw materials. The carrots were cut into cylindrical pieces of 10 mm diameter and 10 mm height by using a cork borer (Fisher Scientific, Pittsburgh, PA) and a sharp knife. The pH of the carrot samples was 5.6. The carrots on an average had a wet basis moisture content of 86.5%, as determined by vacuum drying at 70 °C for 24 h (AOAC 1990).

3.2.2. Pressure-assisted thermal processing

A custom-made high-pressure kinetics tester (PT-1, Avure Technologies, Kent, WA) was used for the present work (Rajan et al., 2006a). The equipment has a 54-ml high-pressure chamber. The chamber was immersed in a temperature-controlled bath with propylene glycol (Avatar Corporation, University Park, IL) as the heating medium. Stable process temperature condition during pressure-holding time was maintained by setting the glycol bath at desired process temperature. The pressure was created by an intensifier (M-340 A, Flow International, Kent, WA). Propylene glycol was also used as the pressure-transmitting fluid. Before the pressure-transmitting fluid enterred into the pressure chamber, it passed through a high pressure tubing coil suspended within the glycol bath. This allowed preconditioning the temperature of the pressure-transmitting fluid to the surrounding glycol bath temperature. The rate of pressurization of the

equipment was 18.90 MPa/s. Depressurization usually took less than 4 s, regardless of holding pressure. The internal pressure chamber temperature was measured using a thermocouple (K-type, Model KMQSS-04OU-7, Omega Engineering, Stamford, CT) passed into the chamber through a high-pressure thermocouple assembly at the top closure. A pressure transducer (Model 3399 093 006, Tecsis, Frankfurt, Germany) measured process pressure. The pressure and temperature were recorded every 1 s using a data acquisition system (Model Daq-Board/2000, IOtech Inc. Cleveland, OH) and software (DasyLab 7.00.04; National Instruments Corp., Austin, TX).

Five cylindrical carrot samples (10 mm dia x 10 mm height) were placed in a high barrier pouch made from sterile filter bag (01-002-57, Fisher Scientific, Pittsburgh, PA). Samples were suspended in 1% isotonic NaCl solution to prevent the loss of nutrient or solids from carrot and aid in heat transfer during TP. The pouches were then heat sealed and placed inside a 10 ml polypropylene syringe (Model 309604, Becton Dickinson and Company, Franklin Lakes, NJ), which was insulated with two layers of insulating tape (Sport tape, CVS Pharmacy Inc., Woonsocket, RI) and served as a sample carrier. The gap between the syringe and pouch was filled with distilled water.

Carrot samples were preheated to the desired pre-heating temperature (T_1) in a water bath and then loaded into the pressure chamber. The pressurization started when the sample temperature reached a value T_2 (Figure 3.1), which was predetermined by using the following equation (Rasanayagam et al., 2003; Rajan et al., 2006a):

$$T_2 = T_3^{'} - \left(CH.\frac{\Delta P}{100} + \Delta T_H \right) \qquad (3.1)$$

where T'_3 is the target temperature, CH is the heat of compression value of the sample (defined as temperature increase per 100 MPa during sample pressurization) and ΔP is the process pressure. Due to its high moisture content, carrot's CH value assumed to follow that of water (Rasanayagam et al., 2003). ΔT_H is the temperature gain by the test sample from the surrounding glycol bath during pressure-come-up time and early stages of pressure-holding time (Figure 3.1). ΔT_H values were empirically determined for various pressure-temperature combinations through a set of preliminary experiments. Similarly, the temperature of pressure-transmitting fluid within the pressure chamber, temperature of water in the gap between syringe and sample pouch, temperature of water near carrot sample within pouch were also determined (Figure 3.1).

The carrot samples were processed over a range of temperatures (95 to 121^{o}C) and pressures (500 and 700 MPa) up to 15 min pressure-holding time. The pressure-holding time varied with the combination of temperature and pressure. The samples were withdrawn at specified intervals and immediately cooled in ice-water mixture, and analyzed within one hour after the treatment.

3.2.3. Matching pre-process time

To compare the quality attributes between the PATP and TP, the respective pre-process times were matched (Table 3.1), the effect of pressure can be clearly evaluated. The pre-process time (t_1) during TP was defined as a time to reach the thermal process temperature (Figure 3.1). PATP pre-process time included a (mild) preheating time (t') in water bath and pressure chamber followed by pressurization time to reach target pressure (t'') (Table 3.1). Due to experimental difficulties, present study did not attempt to match

heating rates between TP (due to conduction heating) & PATP (due to compression heating). Only respective pre-process times were experimentally matched. It is worth noting that during PATP, T_2 is the sample temperature at which compression heating began and the sample temperature reached T_3, which is the maximum sample temperature at the end of pressure cycle. Beyond this point, the pressure remained constant, but temperature further increased slightly up to (T_3'). The time lag between T_3 and T_3' was about 30 seconds.

Differences in heat of compression characteristics between water, glycol, and carrot sample were empirically considered to achieve desired sample process temperature (T_3' -T_4) during various pressure-holding times (Table 3.1). The treatment also elevated glycol temperature within the pressure chamber sharply above process temperature (Figure 3.1), but equilibrated with the desired process temperature as a result of heat exchange with temperature-controlled bath as well as the test sample. The maximum glycol temperatures at 700 MPa for process temperatures 95, 105, 121^{o}C were 125, 135, and 149^{o}C, respectively. At 500 MPa, the maximum glycol temperatures under pressure at 95, 105, and 121^{o}C process temperatures were 119, 130, and 145^{o}C, respectively. Adverse effect of elevated glycol temperature on carrot sample was minimized through use of insulated syringe. This was further verified by monitoring the temperature of the water in the vicinity of carrot samples as well as in the gap between pouch and the syringe (sample holder) (Figure 3.1).

3.2.4. Thermal processing

The carrot cylindrical samples (10 mm dia x 10 mm height) were placed in custom-made aluminum tubes (12 mm ID x 42 mm height, 3 mm wall thickness, Luechapattanaporn et al., 2004; Rajan et al., 2006a). Each tube contained three carrot samples. The tubes were then submerged into a 28-l circulating oil bath (Model Neslab Ex 35, Fisher Scientific, Pittsburgh, PA), which was maintained at predetermined temperature. To match PATP and TP pre-process times, TP experiments employed two oil baths for heating the samples. The first oil bath was set at the temperature higher than the target process temperature. The temperature of the first oil bath for the thermal treatment at 95, 105 and 121°C was maintained at 101.5±1.0, 113±1.0 and 125±1.0°C, respectively. As soon as the temperature of the sample reached 5°C less than the target temperature, the sample were immediately transferred to the second oil bath maintained at target process temperatures. This procedure helped to minimize and control TP come-up time and match that with that of PATP.

The temperature was monitored using a K-type thermocouple (Omega Engineering, Stamford, CT) and recorded using a data logger (IOtech, Cleveland, OH). The thermocouple was located in the geometric center of the carrot samples. The samples were processed over a range of temperatures (95 to 121^{o}C) up to 60 min. At specified intervals, the samples were withdrawn and immediately cooled in ice-water mixture and analyzed within one hour after the treatment.

3.2.5. Analyses

3.2.5.1. Texture measurement

The texture profile analysis (2 cycles) was obtained using a Texture Analyzer (model 5542, Instron Texture Analyzer, Norwood, MA) equipped with a 500 N load cell. The cylindrical sample (10 mm dia x 10 mm height) was compressed up to 50% of initial height on a non-lubricated flat platform using a flat disc probe (dia 35 mm), with a constant crosshead speed of 1 mm/s (Vu et al., 2004). The peak force required to compress the samples were referred to as a measure of hardness (Bourne, 1978). The data were collected for five replicates and average values were reported.

3.2.5.2. Color measurement

Color values (L*, a*, b*) of the carrot samples were measured using a tristimulus colorimeter (CR-300, Minolta, Osaka, Japan). The apparatus was calibrated using a standard white tile (Y= 92.6, X= 0.3161, y = 0.3321). The samples were placed on the top of the light source (15 mm in opening) and L, a and b values were directly obtained from the chroma meter. Each measurement represented the average of 3 readings. The L* represents the lightness, + a* the red direction, - a* the green direction, + b* the yellow direction, and – b* the blue direction. The overall change in color (ΔE) was calculated by the following formula (Avila and Silva, 1999):

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad (3.2)$$

3.2.5.3. Microbial inactivation

For PATP, the minced carrot sample (2.0 g) was put in pouches (2.5 mm x 5mm) made with sterile stomacher bag (Fisher Scientific, Pittsburgh, PA). The pouches were heat sealed and placed into 10 ml polypropylene syringe. Water was used as pressure-transmitting fluid inside the syringe. A dummy sample was used to monitor the pressure

and temperature history during the treatment. Thermal inactivation was conducted by using custom-made aluminum tubes as described in thermal processing. After PATP and thermal processing, the samples were immediately cooled in ice-water mixture. Surviving natural flora was determined by plating them on trypticase soy agar (TSA) and incubating aerobically at 32^{o}C for 48 hours. Six process conditions were selected for various pressure-heat combinations, which were reported as potential conditions for significant log reduction in the microbial load (Rajan et al., 2006a). The conditions are as follows: 0.1 MPa, 121°C, 1 min; 500 MPa, 121°C, 1 min; 700 MPa, 121°C, 1 min; 0.1 MPa, 105°C, 30 min. 500 MPa, 105°C, 5 min, and 700 MPa, 105°C, 5 min. The process temperature was the temperature after pressurization during specified pressure-holding time (Table 3.1, T_3' -T_4) and treatment time was holding time at the target pressure.

3.2.5.4. Carotene analysis

In order to study the effect of PATP and TP on total carotene content, six process conditions similar to those used in microbial inactivation studies (described above) were selected. Carotene analysis was done using spectrophotometer method (Ranganna, 1986). First, the samples were ground and extracted using acetone (Sigma Aldrich Inc., St. Louis, MO). The pigment was transferred to petroleum ether (Sigma Aldrich Inc., St. Louis, MO) and washed five times with distilled water to remove extra acetone. The solution was then filtered through anhydrous sodium sulfate and made up to 100 ml. Absorbance was read on a spectrophotometer (Model number 4001/4, Spectronic, Garforth, Leeds, UK) at 452 nm. The experiments were conducted in triplicate and the average values were reported.

3.2.5.5. Scanning electron microscopy

The control, pressure treated, PATP and TP carrot samples (3.0 mm x 3.0 mm x 3.0 mm) were fixed in 2.5% glutaraldehyde in 0.1 M phosphate buffer at pH 7.4 and stored for a minimum of 72 h at 3 °C. The samples were again fixed in 1.0% Osmium tetroxide (OsO_4) for 90 min. The samples were then washed and dehydrated using graded ethanol series (50%, 70%, 80%, 95% and 100%) for twenty minutes each. The dehydrated samples were subjected to critical point drying (Pelco CPD-2, Ted Pella Inc, Redding, CA) and then sputter-coated with gold/palladium (Beck, 1996). The samples were scanned at 5 kV by Scanning Electron Microscope (Nova NanoSEM 400, FEI Company, Hillsboro, OR).

3.2.6. Data analysis

Data were analyzed with the SAS software (version 9.1.3, SAS Institute Inc., Cary, NC). The least significant difference procedures were used to compare means. Mean differences among PATP treatments and holding times were calculated with Fisher's least significant difference method, with significance at the 5% level ($P < 0.05$).

3.3. Results and discussion

3.3.1. Effect of thermal processing and PATP on color

The influence of TP and PATP on overall change in carrot color as a function of pressure and temperature is presented in Figure 3.2. Thermal treatment (0.1 MPa, Figure 3.2) degraded the color of carrot samples and the over all change in color was maximum at 121°C treatment. PATP (500 and 700 MPa, Figure 3.2) also caused changes in carrot color, but much lower than that of TP. The observations were consistent with earlier

PATP studies on color change for carrot (Matser et al., 2004) and meat containing tomato sauce (Rovere et al., 2000) samples. Samples treated at 500 MPa and 121^{o}C required elevated preprocess temperature (86.1^{o}C, immediately before pressurization) to reach 121 ^{o}C than those treated at 700 MPa (Table 3.1). This may resulted in higher overall color change for carrot samples treated at 500 MPa-121^{o}C than those processed at 700 MPa, 121^{o}C.

3.3.2. Effect of thermal processing and PATP on texture

Both TP and PATP treated samples exhibited initial tissue softening (steep negative slope during process come-up time) followed by a softening phase during subsequent holding time (Figure 3.3). As expected, TP treated samples lost more hardness than PATP samples for all the process temperatures studied. Thermally treated samples retained about 4.5% hardness value at 95^{o}C after 30 min processing, while samples treated at 121 °C retained only 1.5% hardness after 2 minutes of treatment time. The thermal softening of carrot was mainly due to loss of turgor pressure (Greve et al., 1994), increased cell separation due to solubilization of pectic substances of the cell wall (Van Buren, 1979).

Under PATP conditions, an increase in process temperature (95 to 121°C) decreased sample hardness ($P < 0.05$, Figure 3.3). Basak and Ramaswamy (1998) reported that carrot tissue softening increased with an increase in applied pressure. At temperatures up to 105°C, the loss of texture was more pronounced at 700 MPa. However, beyond 105°C, textural loss was more pronounced at 500 MPa. PATP treatment at 121°C and 500 MPa had higher texture loss (83.95%) than at 121°C and 700

MPa (37.91%). The differences in textural loss may be attributed to respective differences in sample pre-process temperature history (86.1 and 73.0^{o}C) just before pressurization (Table 3.1). Exposing the product to harsher pre-process temperature of 86.0°C might have caused β-elimination, which led to subsequent tissue softening. On the other hand, at process temperatures $\leq$105^{o}C, the carrot pre-process temperature just before pressurization was less than 67.5^{o}C.

Balogh et al. (2004) indicated that the rate of inactivation of pectin methylesterase (PME) in carrots increased with an increase in temperature above 66°C and the residual activity was found to be minimum at 74°C. The action of PME on pectin results in demethylated pectin, which may form the complex with Ca^{++} ion, contributing to enhancement of texture (Lee et al., 1979; Kato et al., 1997; Anthon et al., 2005).

With the interest of matching pre-process times, smaller size (10 mm diameter x 10 mm height) samples were used in the current study. Due to unique heat of compression (Rasanayagam et al., 2003), irrespective of the sample size, PATP is expected to provide relatively faster compressive heating during pressurization and expansion cooling upon depressurization. On the other hand, due to slower conduction heat transfer effects, it is likely take a much longer time for thermal equilibration in larger samples during TP. Further research is needed to compare the quality benefits of PATP and TP treatments as a function of sample size.

3.3.2. Effect of thermal processing and PATP on microbial inactivation

Results of reduction in natural flora under various pressure-thermal combinations were compared. All the PATP and TP conditions studied reduced the natural flora levels

to below detection limit (10 colony forming units (CFU) per g of the product). This indicated that the PATP was effective in controlling the natural flora in case of carrot. Krebbers et al. (2003) also reported the similar findings for PATP (90°C-700 MPa) treated tomato puree. Furthermore, Ahn et al. (2007) obtained up to 7 to 8 log reduction of several *Clostridium* and *Bacillus* surrogate spores including *B. amyloliquefaciens* after subjecting them to a combination treatment at 700 MPa and 121°C for less than 1 min. Similarly, Koutchma et al. (2005) determined a 6-log inactivation of *Geobacillus stearothermophilus* in egg patties at 105°C and 700 MPa for 5 min.

3.3.3. Effect of thermal processing and PATP on total carotene

Thermal treatment reduced carotene content of carrot samples by 25.2% (from 17.7 to 13.2 mg/100 g) and 12.1% (from 17.7 to 15.6 mg/100 g) at 105°C and 121°C, respectively (Figure 3.4a). The carotene loss increased with decreasing process temperature, probably due to prolonged exposure time at lower process temperature (105°C; ≈30 min) compared to elevated process temperatures (121°C; ≈ 1 min) (Figure 3.4a). Among the samples processed at 105°C over different pressures (0.1, 500 and 700 MPa), carotene retention was higher for PATP samples than TP samples. At 121°C, sample carotene retention was not significantly different among PATP and TP samples ($P > 0.05$) and maximum carotene retention was observed at 121°C-700 MPa (91.9%). Chen et al. (1995) and Kim et al. (2001) reported that carrot juice carotene was more stable under pressure treatment than that of thermal processing.

Examination of L*, a* and b* values of carrot samples (Figure 3.4b) under these conditions, indicated that there were no significant differences among the b* values of

control (raw) as well as TP as PATP samples ($P > 0.05$). Sample L* and a* values increased with an increase in process pressure (0.1 to 700 MPa). The trend was similar to that of change in carotene content during PATP and TP (Figure 3.4a).

3.3.4. Effect of thermal processing and PATP on microstructure

The microstructure of cross section of control (untreated, raw), pressure treated (700 MPa, 25°C, 5 min), PATP (700 MPa, 105°C, 5 min) and TP (105°C, 0.1 MPa, 30 min) carrot samples are presented in Figure 3.5. Raw carrot samples have almost isodiametrical and polyhedral cells with few intercellular spaces (Figure 3.5a). All the treatments studied damaged the cell structure of the raw sample, but extent of damage differed between treatments. Pressure treatment (700 MPa, 25°C, 5 min) had the least damage and affected the cell wall structure by changing cell architecture (Figure 3.5b). Rastogi and Niranjan (1998) indicated that high-pressure treatment of pineapple samples reduced intercellular material, increased permeability, and softened the tissue. Raw carrot samples had intact cell structure with clearly defined cell walls (Figure 3.5a). On the other hand, thermal processing (105°C, 0.1 MPa for 30 min) transformed the intact cell structure to separated and ruptured cells with non-distinct middle lamella possibly due to degradation of pectinacious material (Figure 3.5d). The extent of such thermal damage was limited in the case of PATP (700 MPa, 105°C, 5 min) (Figure 3.5c) and the texture was relatively better preserved (Figure 3.3) under these conditions.

The quality of products during PATP was influenced by the choice of preheating methods used. Due to experimental challenges, it was difficult to reproduce the rapid temperature increase due to heat of compression in PATP for TP samples.

These studies represented a comparison between a relatively abusive thermal process (TP) against a relatively mild pressure process (PATP). Futher studies are needed for a more through comparison.

3.4. Conclusions

Pressure-assisted thermal processing in general found to protect the quality attributes (such as color and total carotene content) of carrot samples than thermal processing. It may be due to the ability of PATP to provide rapid change in temperature of the treated samples due to compression heating during pressurization and expansion cooling during depressurization. The impact of PATP on texture was found to be influenced by PATP process and pre-process temperature histories. At 121°C, the potential benefits of PATP were diminished due to predominance of thermal effects. The application of PATP may open up the avenues to process fruits and vegetables associated with improved quality attributes.

References

Ahn J, Balasubramaniam, V.M., & Yousef, A.E. (2007). Inactivation kinetics of selected aerobic and anaerobic bacterial surrogate spores by pressure-assisted thermal processing. *International Journal of Food Microbiology*, 113(3), 321-329.

Anthon, G.E., Blot, L., & Barrett, D.M. (2005). Improved firmness in calcified diced tomatoes by temperature activation of pectin methylesterase. *Journal of Food Science*, 70(5), 342-7.

[AOAC] Association of Official Analytical Chemists. (1990). Official method of analysis Association of Official Analytical Chemists, 15th ed., Arlington, VA 930.04 p. 40,69.

Avila, I.M.L.B., & Silva, C.L.M. (1999). Modeling kinetics of thermal degradation of color in peach puree. *Journal of Food Engineering*, 39,161–6.

Balogh, T., Smout, C., Nguyen, B.L., Van Loey, A.M., & Hendrickx, M.E. (2004). Thermal and high-pressure inactivation kinetics of carrot pectinmethylesterase: From model system to real foods. *Innovative Food Science & Emerging Technology*, 5, 429-36.

Basak, S., & Ramaswamy, H.S. (1998). Effect of high pressure processing on the texture of selected fruits and vegetables. *Journal of Texture Studies*, 29, 587-61.

Beck, S.J. (1996). Electron microscopy: a handbook of techniques for the biologist Available from: www.sunynassau.edu/users/becks/Path3f/EM_manual.pdf. Accessed: Sep 15 2006.

Bourne, M.C. (1978). Texture profile analysis. *Food Technology*, 32 (7), 62–6.

Chen, B.H., Peng, H.Y., & Chen, H.E. (1995). Changes of carotenoids, colour and vitamin A contents during processing of carrot juice. *Journal of Agricultural and Food Chemistry*, 43, 1912-8.

Gola, S., Foman, C., Carpi, G., Maggi, A., Cassara, A., & Rovere, P. (1996). Inactivation of bacterial spores in phosphate buffer and in vegetable cream treated with high pressure. In High Pressure Bioscience and Biotechnology, Hayashi R, Balny C, (Eds). Amsterdam: Elsevier Science. pp 253-9.

Greve, L.C., Shackel, K.A., Ahmadi, H., McArdle, R.N., Gohlke, J.R., & Labavitch, J.M. (1994). Impact of heating on carrot firmness: Contribution of cellular turgor. *Journal of Agricultural and Food Chemistry*, 42(12), 2896-2889.

Heinz, V., & Knorr, D. (2001). Effect of high pressure on spores. In Ultrahigh pressure treatment of foods, Hendrickx MEC, & Knorr D, (Eds.). New York: Kluwer Academic/Plenum Publishers. p 77–116.

Hoogland, H., de Heij, W., van Schepdael, L. (2001). High pressure sterilization: novel technology, new products, new opportunities. *New Food*, 4(1), 21-6.

Juliano, P., Toldrág, M., Koutchma, T., Balasubramaniam, V.M., Clark, S., Mathews, J.W., Dunne, C.P., Sadlerand, G., & Barbosa-Cánovas, G.V. (2006). Texture and water retention improvement in high-pressure thermally treated scrambled egg patties. *Journal of Food Science*,71(2), E52-61.

Kato, N.H., Teramoto, A., & Fuchigami, M. (1997). Pectic substance degradation and texture of carrots as affected by pressurization. *Journal of Food Science*, 62(2), 359-62.

Kim, Y.S., Park, S.J., Cho, Y.H., Park, J. (2001). Effects of combined treatment of high hydrostatic pressure and mild heat on the quality of carrot juice. *Journal of Food Science*, 66(9), 1355-60.

Krebbers, B., Matser, A.M., Koets, M., & van den Berg, R.W. (2002). Quality and storage stability of high-pressure preserved green beans. *Journal of Food Engineering*, 54(1), 27-33.

Krebbers, B., Matser, A.M., Hoogerwerf, S.W., Moezelaar, R., Tomassen, M.M.M., & van den Berg, R.W. (2003). Combined high-pressure and thermal treatments for processing of tomato puree: evaluation of microbial inactivation and quality parameters. *Innovative Food Science & Emerging Technology*, 4(4), 377-85.

Lee, C.Y., Bourne, M.C., Buren, J.P. (1979). Effect of blanching treatment on the firmness of carrots. *Journal of Food Science*, 44, 615-6.

Luechapattanaporn, K., Wang, Y., Wang, J., Al-Holy, M., Kang, D.H., & Tang, J. (2004). Microbial safety in radio frequency processing of packaged foods. *Journal of Food Science*, 69(7), 201–6.

Margosch, D., Ehrmann, M.A., Gaenzle, M.G., & Vogel, R.F. (2004). Comparison of pressure and heat resistance of *Clostridium botulinum* and other endospores in mashed carrots. *Journal of Food Protection*, 67(11), 2530–7.

Matser, A.M., Krebbers, B., van den Berg, R.W., & Bartels, P.V. (2004). Advantages of high pressure sterilization on quality of food products. *Trends in Food Science and Technology*, 15(2), 79-85.

Rajan, S., Ahn, J., Balasubramaniam, V.M., & Yousef, A.E. (2006a). Combined pressure-thermal inactivation kinetics of *Bacillus amyloliquefaciens* spores in egg patty mince. *Journal of Food Protection*, 69(4), 853-60.

Rajan, S., Pandrangi, S., Balasubramaniam, V.M., & Yousef, A.E. (2006b). Inactivation of *Bacillus stearothermophilus* spores in egg patties by pressure-assisted thermal processing, *Lebensmittel-Wissenschaft* und-*Technologie*, 39(8), 844-51.

Ranganna, S. (1986). Handbook of analysis and quality control for fruit and vegetable products. 2nd ed. New Delhi: Tata McGraw Hill Publishing Co Ltd.

Rasanayagam, V., Balasubramaniam, V.M., Ting, E., Sizer, C.E., Bush, C., & Anderson C. (2003). Compression heating of selected fatty food materials during high-pressure processing. *Journal of Food Science*, 68(1), 254-59.

Rastogi, N.K., Niranjan, K. (1998). Enhanced mass transfer during osmotic dehydration of high pressure treated pineapples. *Journal of Food Science,* 63(3), 508-11.

Reddy, N.R., Solomon, H.M., Tetzloff, R.C., & Rhodehamel, E.J. (2003). Inactivation of *Clostridium botulinum* Type A spores by high-pressure processing at elevated temperature. *Journal of Food Protection*, 66 1402-1407.

Rovere, P., Gola, S., Maggi, A., Scaramuzza, N., & Miglioli, L. (1998). Studies on bacterial spores by combined pressure-heat treatments: Possibility to sterilize low-acid foods. In High pressure food science, bioscience and chemistry, Isaacs NS (Ed.). Cambridge, U.K.: The Royal Society of Chemistry. p 354–63.

Rovere, P., Squarcina, N., Gola, S., Sandei, L., Iametti, S., & Carpi, G. (2000). Effect of thermal treatment under high pressure on the quality of a meat sauce. *High Pressure Research*, 19, 99–107.

Ting, E., Balasubramaniam, V.M., Raghubeer, E. (2002). Determining thermal effects in high-pressure processing. *Food Technology*, 56(2), 31 –5.

Van Buren, J.P.S. (1979). The chemistry of texture in fruits and vegetables. *Journal of Texture Studies*, 10, 1-23.

Vu, T.S., Smout, C., Sila, D.N., Ly Nguyen, B., Van Loey, A.M.L., & Hendrickx, M.E.G. (2004). Effect of preheating on thermal degradation kinetics of carrot texture. *Innovative Food Science & Emerging Technology*, 5, 37-44.

Process Temperature (°C)	Pressure (MPa)	Sample temperature at different stages during processing (°C)				Time required at different stage of pre-processing (s)		
		Preheating (T_1)	Immediately before pressurization (T_2)	Immediately after pressurization (T_3)	Holding (T_3' - T_4)	Preheating (t')	Pressurization (t'')	Total[a] (t_1)
95	0.1	45.0 ± 1.0	-		95 ± 1.0	-	-	174
	500	38.5 ± 1.0	59.6 ± 0.7	82.8 ± 0.8	95 ± 1.0	142 ± 5.0	32 ± 3.0	174
	700	26.4 ± 1.0	50.9± 1.0	85.4 ± 0.6	95 ± 1.0	135 ± 7.0	39 ± 3.0	174
105	0.1	45.0 ± 1.0	-		105 ± 1.0	-	-	161
	500	43.1 ± 1.0	67.5 ± 0.8	94.1 ± 1.0	105 ± 1.0	129 ± 3.0	32 ± 2.0	161
	700	29.5 ± 1.0	57.9 ± 0.9	96.3 ± 0.7	105 ± 1.0	121 ± 5.0	40 ± 3.0	161
121	0.1	45.0 ± 1.0	-		121 ± 1.0	-	-	210
	500	59.4 ± 1.0	86.1 ± 0.7	113.5 ± 0.6	121 ± 1.0	178 ± 5.0	32 ± 2.0	210
	700	36.8 ± 1.0	73.0 ± 0.5	114.4 ± 0.5	121 ± 1.0	172 ± 4.0	38 ± 3.0	210

[a] t_1 is the sum of preheating (t') and pressurization time (t''). Depressurization time (< 4 s) is not shown.

Table 3.1. Pre-process temperature histories for thermal processing and pressure-assisted thermal processing carrot samples.

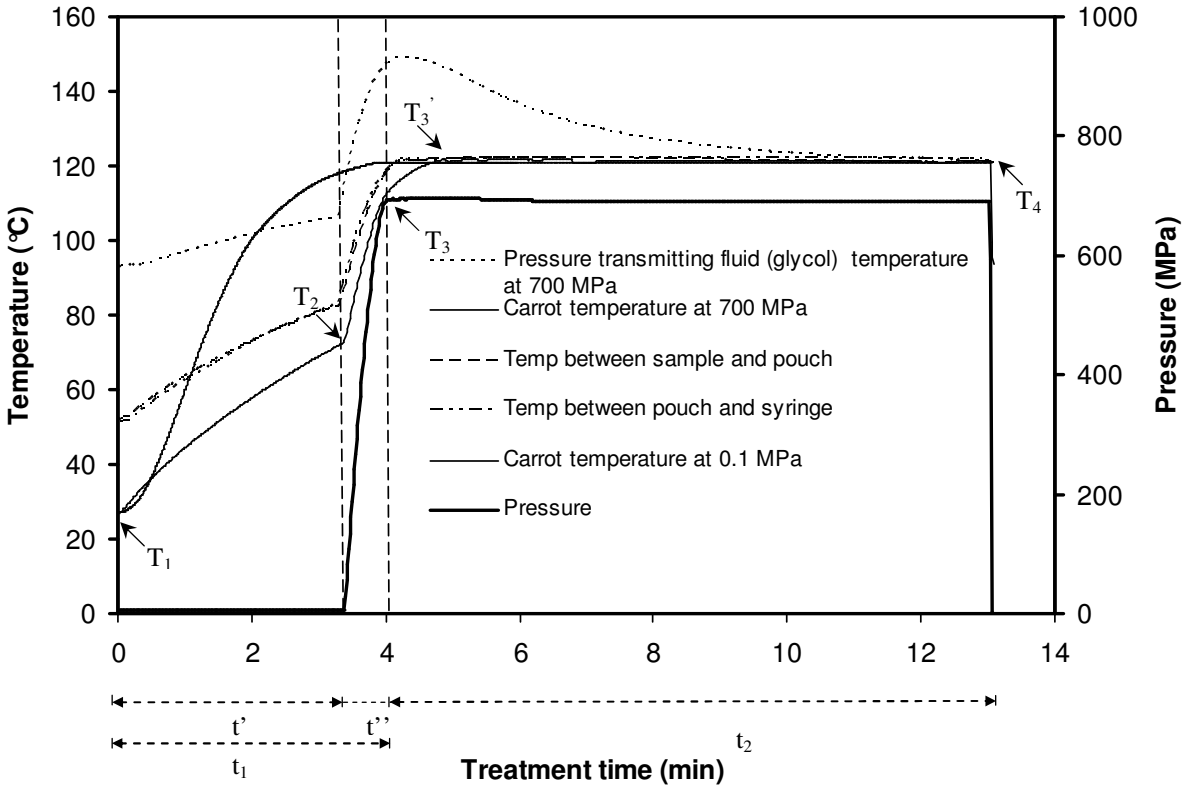
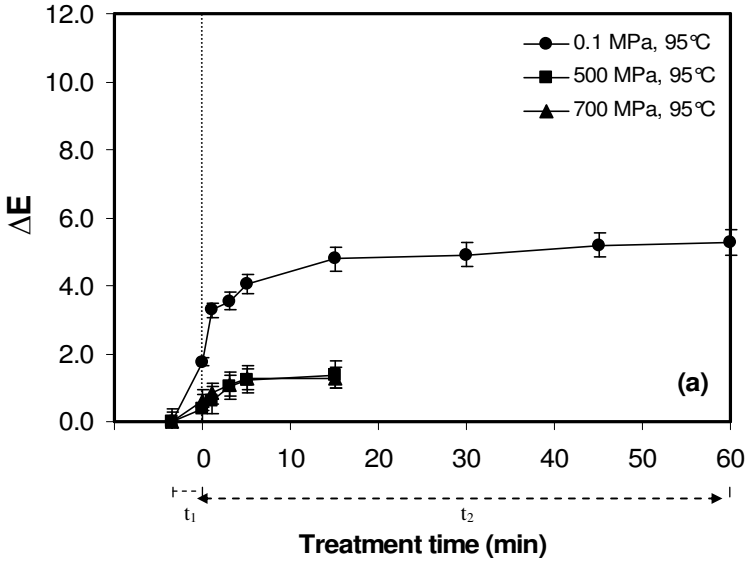
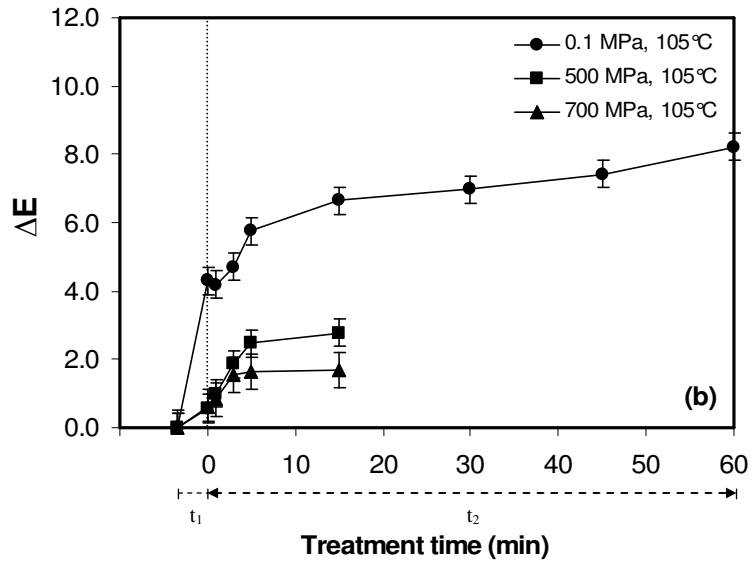


Figure 3.1. Pressure and temperature history of carrot sample, water and pressure- transmitting fluid (glycol) during preheating, compression and holding time for pressure-assisted thermal processing at 700 MPa, 121°C. Temperature history of carrot sample processed at 121°C was also shown for comparison. t', t'', t_1 and t_2 are the time of preheating, compression, come-up time and holding time, respectively.

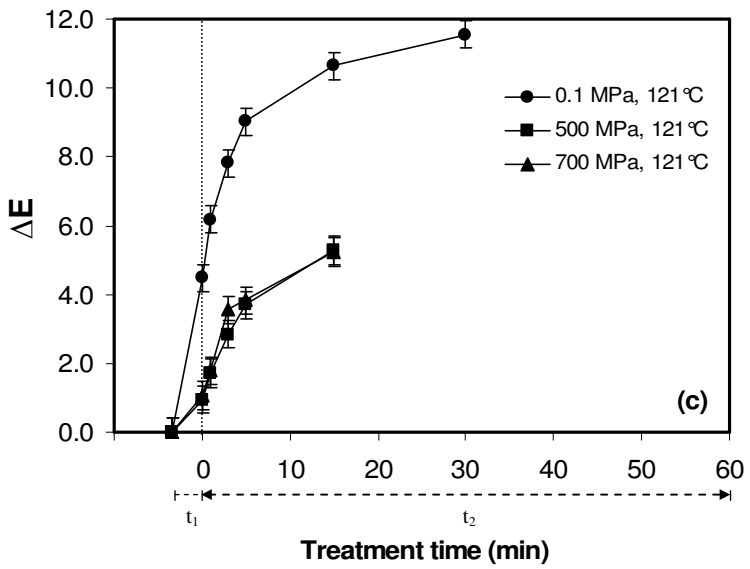


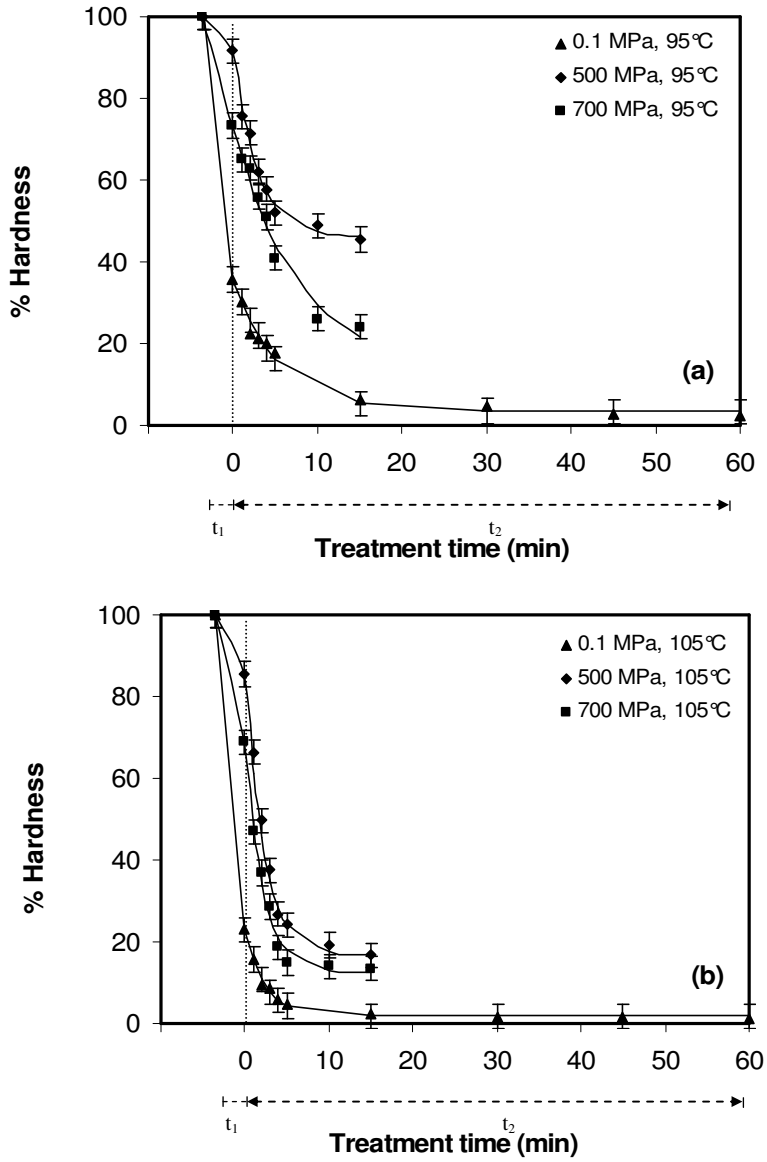


continued

Figure 3.2. Change in color of carrot during thermal processing, pressure-assisted thermal processing (a) 95°C; (b) 105°C; and (b) 121°C at different pressures. t_1 and t_2 are the come-up time and holding time, respectively.

Figure 3.2. continued

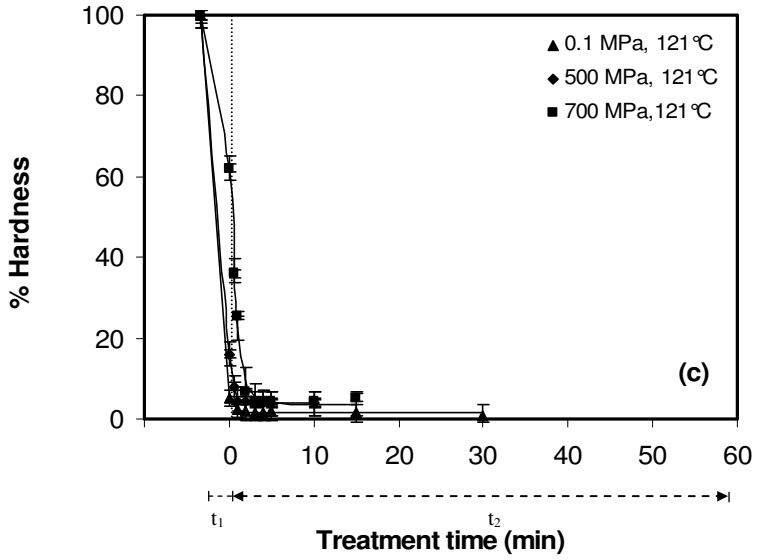




continued

Figure 3.3. Textural change of carrot during thermal processing, pressure-assisted thermal processing (a) 95°C; (b) 105°C; and (b) 121°C at different pressures. t_1 and t_2 are the come-up time and holding time, respectively.

Figure 3.3. continued



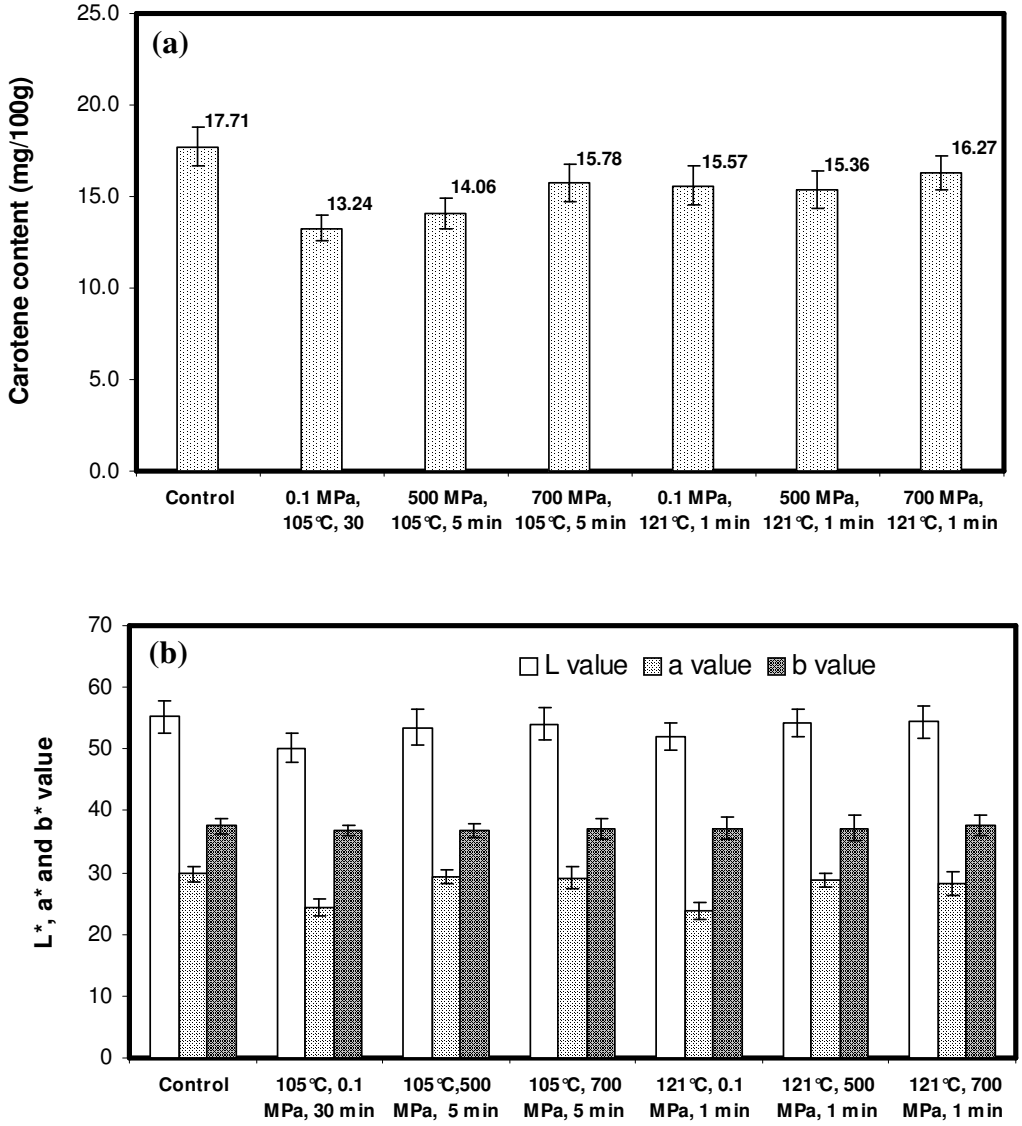


Figure 3.4. (a) Variation of carotene content and (b) corresponding L*, a* and b* values of carrot during thermal processing and PATP at different conditions.

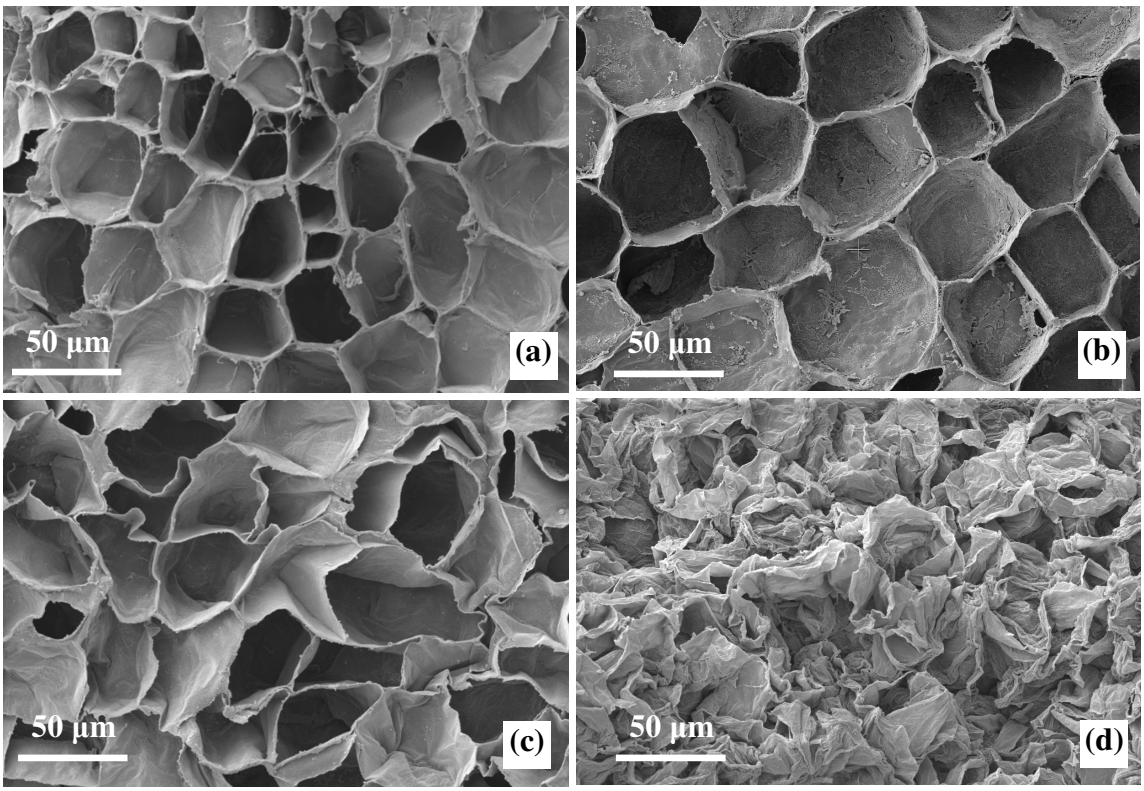


Figure 3.5. Microstructures of (a) control; (b) pressure treated (700 MPa, 25 °C, 5 min); (c) pressure-assisted thermal processed (700 MPa, 105 °C, 5 min); and (d) thermal processed (105 °C, 0.1 MPa, 30 min) carrot samples.

Chapter 4: Evaluating the Impact of Thermal and Pressure Treatment in Preserving Textural Quality of Selected Foods

Abstract

A study was conducted to evaluate the efficacy of various combinations of pressure and thermal treatments in preserving textural quality of selected foods. Carrot, zucchini, apricot, radish, and jicama were used as test samples. Pressure-assisted thermal processing (PATP; 600 MPa, 105^{o}C), high pressure processing (HPP; 600 MPa, 25^{o}C), and thermal processing (TP; 105^{o}C) experiments were conducted. Role of pressure (600 MPa) in preserving product quality while simultaneously (PATP) or sequentially (HPP-TP) exposed to elevated process temperature (105^{o}C) was also compared. Instrumental puncture, shear force, color and sensory analyses were utilized to compare the influence of the various process treatments. A crunchiness index (CI), relating product puncture force and stiffness, was able to characterize the severity of the process treatments on various products tested. Among the treatments, TP was the worst at retaining texture, but HPP-TP improved texture retention. In comparison to TP alone, PATP better retained texture and color. Jicama was least influenced by the treatments as compared to products tested. Process treatments investigated degraded the textural quality of zucchini and apricot. Instrumental CI results were also in agreement with the sensory data of carrot, red radish and jicama samples.

Keywords: pressure assisted thermal processing; high pressure processing; texture; color; quality.

4.1. Introduction

Thermal processing (TP) is the conventional method of food pasteurization and sterilization. While thermally processed products are safe, application of heat impairs food quality. Recent advances in alternative food processing have created new approaches for preserving food without compromising product quality. Among these methods, high pressure processing (HPP) is a promising food preservation method, wherein the food is exposed to high pressures for a short duration, with or without the addition of heat, to achieve microbial inactivation. Since pressure treatment does not break covalent bonds, it can retain food quality and fresh characteristics while extending microbiological shelf life. Depending upon the intensity of the pressure-heat treatment, both pasteurization and sterilization effects are possible.

High pressure pasteurization treatments use pressures about 600 MPa for several minutes at 20-45 ^{o}C (Lau & Turek, 2007). High pressure pasteurization treatments inactivate pathogenic and spoilage bacteria, yeasts, and molds. On the other hand, bacterial spores are resistant to pressure treatment at ambient temperature, even above 1000 MPa (Cheftel, 1995). Pressure-assisted thermal processing (PATP), also referred as pressure assisted thermal sterilization (PATS) or high pressure-high temperature sterilization (HPHT), involves a combined application of elevated pressures (500–900 MPa) and temperatures (90–120°C) for a short duration to a preheated food product

(Meyer et al., 2000; Ananta et al., 2001; Margosch et al., 2004; Rajan et al., 2006). Pathogenic spores such as *Clostridium botulinum* and varieties of *Bacillus* and *Clostridium* spoilage spores can potentially be inactivated through synergies of heat and pressure (Rovere et al., 1996; Margosch et al., 2004; Koutchma et al., 2005; Reddy et al., 2006; Ahn et al., 2007; Black et al., 2007; Zhu et al., 2008). In Feb. 2009, the Food and Drug Administration (FDA) has approved the filing of pressure-assisted thermal process for production of low acid foods (Food Processing, 2009). Industry is interested in this technology due to shorter thermal exposure times.

It is important to understand the role of simultaneous or sequential application of pressure-thermal treatment, on quality of various products. Pressure pretreatment (50-500 MPa) of vegetables before cooking (at 99.5^{o}C) was reported to improve texture of the processed product (Kasai et al., 1995). Pressure pretreatment might have helped improve the texture of the tissue by increasing tissue compactness and promoting biochemical changes associated with texture preservation (Basak & Ramaswamy, 1998; Oey et al., 2008). On the other hand, pressure, heat and their interactions can influence product quality during PATP. The instantaneous temperature changes induced by adiabatic heating during compression and adiabatic cooling upon decompression (Patazca et al., 2007) are often thought to reduce the product's thermal exposure during PATP. Moreover, researchers often conducted PATP experiments at moderate temperature (~105^{o}C process temperature and 600 MPa). These PATP conditions were reportedly provide better texture, color, and flavor and aroma retention compared with traditional retorted products (Hoogland et al., 2001; Krebbers et al., 2002; Krebbers et al., 2003;

Matser et al., 2004; Juliano et al., 2006; Zhu et al., 2008). Lau et al. (2007) reported that pressure sterilization (two pressure pulses at 700 MPa, 105^{o}C and 1 min pressure holding time for each pulse) provided a fresher, less processed flavor in chicken, salmon, eggs, potatoes, and green beans as a result of less total thermal exposure than traditional retorting. Juliano et al. (2006) observed that combined pressure-thermal treatment at 700 MPa at 105^{o}C is a promising technique for preservation of shelf-stable egg based product. Roeck et al. (2008) reported an improved retention of carrot texture processed at 80^{o}C under 600 MPa. Leadley et al. (2008) found that the firmness of PATP green beans subjected to preheating at an initial temperature of 86^{o}C, followed by two consecutive cycles of pressure treatment at 700 MPa for 2 min was generally twice as high as the samples processed at 121.1^{o}C in a traditional retort.

A study on food textural quality degradation under similar temperature history with and without pressure can improve our understanding on the role of pressure in protecting textural quality during combined pressure-thermal treatment. Further, it is of interest to develop approaches that will enable comparison of impact various pressure or heat treatments on textural quality. As pressure effects on product quality was also found to be a function of product matrix (Matser et al., 2004), documenting the impact of pressure-thermal treatment on several food products would be desired. Therefore, the objective of this research was to compare the impact of pressure, heat, and their combinations in preserving textural quality attributes of selected foods.

4.2. Materials and methods

4.2.1. Sample preparation

Baby carrots, zucchini, red radishes, jicamas, and apricots were sourced from a local grocery store. Sufficient quantities were purchased at the same time to minimize the variation in quality (and presumably age / source) of the raw material. The pH values of the carrot, zucchini, red radish, jicama and apricot samples were 5.2, 6.5, 5.9, 5.0 and 3.8, respectively, and the water activity (a_w) of the samples was about 0.99. Carrot (*Daucus carota* subsp. *sativus*) is a root vegetable with a crisp texture when fresh. Zucchini (*Cucurbita pepo*) is a small, fragile summer squash that cannot be stored for long periods. Radish (*Raphanus sativus*) is an edible root vegetable. The raw flesh has a crisp texture and a pungent, peppery flavor. Jicama (*Pachyrhizus erosus*), a warm season legume root crop also called "Yam Bean," is a brown-skinned turnip-shaped root with a crispy texture that is eaten raw or cooked (Gorny & Kader, 2008). The baby carrot (~8 tubers per 100 grams of carrot) and red radish (~ 4 tubers per 100 grams of red radish) samples were cleaned and unwanted roots and stems were removed. The zucchini samples were sliced into 2.5-cm thick disks. Jicamas were cut into sticks of 1.3 x 1.3 x 5.1 cm. Apricots were pitted and sliced into two halves. The samples (about 100 g) were vacuum packed in a 1 g/100 ml NaCl solution to prevent nutrient loss during processing. The ratio of sample to NaCl solution was 1:1 (w/v). Each sample was packaged by a vacuum packaging machine (Ultravac, UV 250, Koch Supplies Inc., MO, USA) in a clear Nylon/EVOH/Polyethylene retort pouch with high barrier properties (Win-Pak Ltd., Winnipeg MB, Canada).

4.2.2. High pressure processing

All of the high pressure processing (HPP; 600 MPa, 25^{o}C) and pressure-assisted thermal processing (PATP; 600 MPa, 105^{o}C) experiments were carried out using a 5-liter capacity, Iso-Lab High-Pressure Food Processor (Stansted Fluid Power Ltd, Essex, UK). A propylene glycol, water mix (1:2 w/v) was used as the pressure transmitting liquid. To reduce the temperature gradient between the samples, surrounding pressure medium and pressure chamber walls, propylene glycol was circulated through the external jacket of the pressure chamber. The following is the summary of various experiments (Figure 4.1) conducted to test the efficacy of combined pressure and thermal treatments in preserving quality attributes:

- HPP: Samples were pressure treated at 600 MPa and ~25^{o}C for 5 min pressure holding time. The equipment had 1.9 min compression (come-up) time, and 1.2 min decompression time. For this set of experiments, test samples in the basket were pre-chilled (~4^{o}C) before pressure treatment so that the in-process temperature achieved was a result of the adiabatic heating and heat exchange with surrounding pressure medium. The pressure vessel was maintained at ~25^{o}C. Two sets of samples were processed, one for evaluating pressure pasteurization effects, and the other to be subsequently thermally processed (HPP-TP) at 105^{o}C as described under the section on thermal processing. Processed samples were stored in a refrigerated environment until analyzed.
- PATP-R: Samples were subjected to pressure-assisted thermal processing (600 MPa at 105^{o}C) with 1.9 min compression (come-up) time, 5 min

holding time and 1.2 min decompression time. The treatment took advantage of the rapid compression and decompression capabilities of the high pressure equipment. Typical test runs involved preheating (PHT) prepackaged samples at 85 ± 1^{o}C in a water kettle for about 23 min before being loaded inside the pressure vessel. The pressure transmitting fluid was also preheated to desired initial temperature (~85^{o}C). Sample temperature during the preheating period was monitored with a K-type thermocouple (Omega Engineering, CT, USA) inserted into the geometric center of the sample. Preheated samples were then filled into a thermally insulated cylindrical sample basket (102 mm dia x 559 mm height) (Stansted Fluid Power Ltd, Essex, UK) and loaded into the high pressure equipment using a lift mechanism. To minimize heat loss from sample to surroundings during compression and holding time, the pressure chamber temperature was maintained at 95^{o}C. The temperature of the test samples during various pressure treatments was monitored at the top, center and bottom of the carrier basket using T-type thermocouples (Omega engineering, CT, USA) mounted in the sample pouch using a C-5.2 stuffing box (Ecklund-Harrison Technologies, FL, USA).

- PATP-SL: In this experiment, product thermal history during pressure assisted thermal processing (600 MPa, 105^{o}C, 5 min holding time) was adjusted to 'match' that of conventional retort processing (described under thermal processing (TP) experiments section). PATP-SL thermal history

included 23 min preheating (85 ± 1°C), 26.6 min step-wise compression, 5 min pressure holding time and 6.3 min decompression times. Accumulated thermal dosage of the sample at different processing conditions was calculated based on area under respective thermal history curve using trapezoidal rule. With similar thermal history for PATP-SL and TP samples, the role of pressure in preserving food quality attributes can be evaluated. The initial temperature of the pressure transmitting fluid was also adjusted. After processing, the samples were placed in an ice-water mix and kept under refrigerated conditions.

- PHT: Pressure-assisted thermal process (PATP) requires preheating (PHT) product to certain initial temperature. To document the influence of thermal exposure on product quality during preheating, a set of the samples preheated at 85 ± 1°C for 23 min were also analyzed. Packaged untreated samples served as the control (CTRL).

4.2.3. Thermal processing experiments

The TP experiments were conducted in a Surdry SL retort (APR95-l, Abadiano, Spain). Samples were processed using steam immersion. The temperature of processed samples during TP was monitored using data trace probes (Micropack III, Mesa Labs, Lakewood, CO, USA). Samples were processed at 105°C for a 5 min holding time. The thermal process come-up time was 47.5 min. In another set of experiments, samples that were previously pressure pasteurized (the same day) were subsequently thermally processed (HPP-TP). Immediately after processing, the pressure-pasteurized samples

were kept under chilled conditions (~4^{o}C) and thermally processed within 1 h. All processed samples were refrigerated at 4^{o}C until analysis.

4.2.4. Textural changes due to enzymatic activity

A separate set of experiments was conducted to evaluate the role of biochemical changes due to enzymatic activity, rather than the physical changes due to compression under pressure, in preserving product texture during treatment. Carrot samples were used as the model food. The carrots were pretreated by being soaked in a phosphate buffer pH 2.0 containing a 0.0035 mol/L sodium dodecylsulfate (SDS) solution to chemically inactivate the carrot pectinmethylesterase (PME) (Barrett, 2007). In order to estimate the enzyme activity, the soaked sample was incubated in a water bath at 50^{o}C for 1 h. PME activity was determined from methanol released from the sample during this time. Methanol was determined by the colorimetric reaction with alcohol oxidase and purpald (Anthon & Barrett, 2004). The absorbance was measured at 550 nm by spectrophotometer (Model number 4001/4, Spectronic, Garforth, Leeds, U.K.). Cooked sample (100 ^{o}C for 30 min) was used as the baseline for comparison. The enzyme activity of samples was monitored for up to a week during refrigerated storage. After establishing enzyme activity levels, soaked carrot samples without any apparent enzyme activity were then pressure sterilized (PATP-R) or thermally processed (TP) as described before.

4.2.5. Color measurement

A tristimulus colorimeter (CR-300, Minolta, Osaka, Japan) was used to determine L* (lightness), a* (redness or greenness), and b* (yellowness or blueness) color values of

various food products processed. The apparatus was calibrated using a standard white tile (Y = 92.6, X = 0.3161, y = 0.3321). The samples were placed on the top of the light source (15 mm in opening), and L*, a*, and b* values were directly obtained from the chroma meter. The color data were obtained from 6 replicates.

4.2.6. Texture measurement

Samples were cut into cylinders (10 mm dia x 10 mm height) for texture measurement. Puncture and Warner-Bratzler shear tests were conducted using a TA-XT2 Texture Analyser (Stable Micro Systems Ltd., Surrey, UK) with a load cell of 50 kg ± 1 g at crosshead speeds of 1 mm/s and 1.67 mm/s, respectively. Puncture tests utilized a 2 mm diameter puncture probe. Uniaxial compression tests using a 50 mm diameter cylindrical probe were also carried out at a crosshead speed of 1 mm/s to compare the role of different texture parameters in describing the sample textural transformation due to various treatments. All the textural measurements were performed approximately 10 times to minimize inherent sample-to-sample biological variations.

4.2.7. Textural parameter analysis

The force-deformation curve to rupture point obtained from the puncture test was fitted with a third order polynomial and the following texture parameters were extracted using Matlab (Version 7.1.0246, Matworks Inc., MA, USA) :

- $Grad_{\%}$: slope of force-deformation curve (N/mm) for the processed sample at different percentages (10-70%) of maximum puncture force. This value represents the sample stiffness (Mohsenin, 1970; Bourne, 2002; Gonzalez, 2009).

- F: max puncture force (N) of the processed samples (Mohsenin, 1970; Gonzalez, 2009). This represents the sample hardness.

From the knowledge of $Grad_{\%}$ and F, a crunchiness index (CI) was estimated for various samples as follows:

$$CI = \frac{F_{treatment}}{F_{ctrl}} + \frac{Grad_{\%treatment}}{Grad_{\%ctrl}} \quad (4.1)$$

where the subscripts 'treatment' and 'ctrl' refer to process treatment and control sample values, respectively.

4.2.8. Sensory evaluation

Sensory studies were conducted with 7 untrained industrial panelists (3 females and 4 males) with ages ranging from 25 to 55 years. A set of coded samples (CTRL, HPP, PATP-R, PATP-SL, TP, and HPP-TP) from carrot, red radish and jicama was presented to the panelists for comparison. The panelists were asked to rank the sample crunchiness, with 1 being the least crunchy and 7 being the crunchiest.

4.2.9. Data analysis

Data were analyzed with SAS software, version 9.1.3 (SAS Inst. Inc., Cary, N.C., USA). Least significant difference (LSD) procedures were used to compare means. Mean differences among treatments were calculated with Fisher's least-significant difference method, with significance at the 5% level ($P < 0.05$).

4.3. Results and discussions

In this study, our primary interest was to evaluate textural quality attributes of selected products exposed to similar temperature histories with and without pressure. It was not our intent to evaluate whether or not treated products reached commercial sterile

conditions. Thermal history (TP, PATP-SL) under the current study would not, by itself, render foods shelf-stable though it would be expected to do so when combined with high-pressure treatment at 600 MPa (PATP-R) and this is the topic of on-going research at various laboratories.

4.3.1 Sample temperature history

Figure 4.2 presents the thermal history of the PATP-R, PATP-SL, and TP samples. The initial temperature of TP samples was approximately 25^{o}C and subsequently reached the target 105^{o}C in the retort. PATP-R and PATP-SL samples were preheated (PHT) at 85^{o}C before pressurization. This enabled the product to reach the target process temperature at the target pressure due to compression. The maximum temperature of the pressure pasteurized samples (HPP) was approximately 25^{o}C. Among the sterilization treatments (TP, HPP-TP, PATP-R, PATP-SL), PATP-R samples had the lowest accumulated thermal dosage (2461 ^{o}C.min) while TP and TP-HPP samples had the highest accumulated thermal dosage (5263 ^{o}C. min). Due to equipment limitations, accumulated thermal dosage of PATP-SL (5160 ^{o}C.min) sample was slightly lower than that of TP.

PATP-SL samples attained lower process temperatures (98.8 ± 1 ^{o}C), possibly due to the heat loss experienced by the samples during the prolonged compression (26.6 min) time used to match process come-up time similar to that of TP. Due to rapid compression and decompression, maintaining process temperature (105 ± 1^{o}C) was not a hurdle for PATP-R samples. PATP-R samples had 6.7 ± 0.6^{o}C gradient between the top and bottom of the vessel while the PATP-SL samples demonstrated a 1.6 ± 0.2^{o}C

gradient. The longer compression time (26.6 min) used during PATP-SL might have helped equilibrate the temperature within the pressure chamber. The current study did not consider the impact of the temperature gradient on the product quality of PATP-R or PATP-SL samples.

4.3.2. Effect of various treatment on physical appearance of the samples

Visual examination of processed products provided some understanding on the severity of various treatments. Milder "nonthermal" pressure treatment (HPP) at ambient temperature did not significantly impact the sample appearance with the exception of zucchini. HPP significantly softened the zucchini and apricot. In the case of red radish, pressure treatment resulted in diffusion of red pigment into the internal tissue. Processes that had a thermal component (PATP, HPP-TP and TP) degraded quality attributes of the sample. Both TP and PATP disintegrated apricot tissue and sample lost shape. Similarly, zucchini samples were significantly softened and quality degradation was visibly noticed. Consequently, no additional instrumental or sensory quality data for the apricot or zucchini samples were collected. Possibly due to the prolonged soaking time (> 36 h) needed for enzyme inactivation in the SDS soaked carrot samples, these samples were significantly softened in comparison to the control. Subsequent TP or PATP treatments further disintegrated the cellular texture of SDS soaked samples. It was decided not to conduct further instrumental or sensory analysis on these SDS soaked samples.

4.3.3. Impact of process treatment on sample color

The influence of different treatments on the tissue color of carrot, red radish and jicama is given in Figure 4.3. For carrot, all treatments resulted in reduced L^* values as

compared to control samples (Figure 4.3a). The *a** value of TP and HPP-TP carrots were lower than that of PATP samples. Examination of *b* values of carrot samples (Figure 4.3a) under these conditions indicated that the treatments except HPP did not significantly ($P > 0.05$) influence b* values. Pressure treatment at low and moderate temperatures had limited effect on color pigments such as chlorophyll, carotenoids, and anthocyanin (Oey et al., 2008). Other researchers (Chen et al., 1995; Kim et al., 2001; Nguyen et al., 2007) also reported that carrot carotene was more stable under pressure treatment than under TP.

For the red radish samples, the skin and tissue had different response to different processing conditions. In comparison to untreated samples, various treatments (HPP, PATP-R, PATP-SL, HPP-TP, and TP) increased L* value, decreased a* and b* values of the radish skin (data not shown). The processing impact on red radish tissue color is shown in Figure 4.3b. Samples subjected to pressure treatment (HPP) and pressure treatment followed by thermal processing (HPP-TP) had lower L* value of the tissue than control and other treatments. In addition, for pressure treated (HPP, HPP-TP, PATP-R, PATP-SL) and TP samples, a* value of the tissue color increased significantly ($P < 0.05$), most probably due to diffusion of red color pigment following the disruption of the cellular structure (Figure 4.3b).

Among the products tested, jicama color was least influenced by the treatments (Figure 4.3c). Except preheat samples, pressure or heat treatments (HPP, HPP-TP, TP, PATP-R, PATP-SL) slightly decreased L*, b* values as compared to control samples but there was no significant difference among these treatments ($P > 0.05$).

4.3.4. Influence of different process conditions on textural quality

Figure 4.4 presents the typical force-deformation curve of the carrot, red radish and jicama samples after the different treatments. As the puncture probe penetrated into the untreated samples, a steep initial slope (i.e., stiffness) was observed. The puncture force reached a maximum value and then decreased to a lower value after tissue rupture. PATP, TP and, HPP treated carrot samples also showed similar force-deformation curves, but the magnitude of the slope and maximum rupture force differed from the control due to texture transformation. In addition, after the yield point (tissue fracture), different treatment-sample combinations resulted in different characteristic peaks. This may be due to the resistance of different vegetable cell layers (Gonzalez, 2009).

The texture parameters (F, $Grad_{20\%}$) extracted from the puncture tests are given in Figure 4.5. Depending on the processing methods, the texture of the vegetable samples are affected in different ways. The TP samples, as expected, had the most textural degradation: the maximum puncture force of the carrot, red radish and jicama samples were 0.5, 1.3, and 4.3 N, respectively (Figure 4.5a). The mechanical strength of vegetable cells is provided by the cell wall and the turgor pressure within the cell. Thermal treatments soften the tissue by decreasing turgor pressure (Greve et al., 1994), and by solubilizing cell wall pectic substances, which separate the vegetable cells (Van Buren, 1979).

Pressure treatment at room temperature (HPP) increased the puncture force value of the red radish samples, while decreased it slightly for the carrot samples (Figure 4.5a). Basak et al. (1998) suggested that the most probable reason for textural improvement

under high pressure processing is due to pectinmethylesterase (PME) activity and increased compactness of the cellular structure as a result of the elimination of air from the tissue.

Preheating at 85^{o}C decreased the puncture force of carrot and jicama ($P < 0.05$). PATP red radish and carrot samples had lower puncture values than those of the control and preheated samples, but had higher values than those of the TP and HPP-TP samples. For these PATP samples (carrot, red radish), there was no significant difference ($P > 0.05$) in hardness due to either the regular (PATP-R) or slow (PATP-SL) compression time. Roeck et al. (2008) suggested that the textural preservation of carrot samples processed at high pressure and high temperature may be due to the inhibition of the β-elimination reaction, i.e. split of glycosidic bonds of pectin at high temperature catalyzed by hydroxyl ion (Van Buren, 1979), either by high pressure/high temperature or by the lower degree of esterification of the pectin substance. In addition, the lowly-methylated pectin might form networks by binding with Ca^{++}, hence contributing to textural preservation. Araya et al. (2007) reported the degradation of pectin in cooked samples but not in pressurized samples. Studies of the microstructure of carrot samples showed that while tissue failure of the raw sample was mainly due to cell breakage, and failure of the thermally treated sample due to cell separation, PATP samples exhibited both mechanisms (Roeck et al., 2008).

Jicama samples seemed to have a sturdier texture than that of carrot and red radish samples and jicama samples were minimally impacted by various treatments. The PATP-SL treatments did not further decrease puncture force values as compared to control

sample. The HPP, HPP-TP and PATP-R samples had the same hardness. The jicama samples were also more resistant to TP (Figure 4.4c and 4.5). In comparison to the carrot samples, the stiffness of jicama and red radish samples was less influenced by the various treatments, most likely due to their sturdier cellular structure. On the other hand, a considerable loss of stiffness was observed with all the processed or preheated carrot samples. The HPP carrot samples became more rubbery (i.e., reduced $Grad_{20\%}$) but retained hardness (Figure 4.5). Finally, it is interesting to note that pressure pre-treatment followed by thermal processing (HPP-TP) better preserved the hardness of all the processed vegetables in comparison to the TP samples. High pressure pretreatment prior to thermal processing has been found to improve the texture of cooked vegetables (Kasai et al., 1995; Sila et al., 2004, 2007; Rastogi et al., 2008).

4.3.5. Crunchiness index

Puncture test results (Figure 4.5) do not provide comprehensive data for comparing the impact of various processes on product texture. Therefore efforts were made to identify additional instrumental textural parameters that can be used for this purpose. Earlier studies on high pressure processed foods used a variety of textural parameters to describe pressure-thermal effects with mixed results. Basak et al. (1998) used the slope of a linear section of the compression curve to describe hardness. Roeck et al. (2008) reported hardness as the force required to compress the sample to 70% thickness. Araya et al. (2007) used compression force to 30% strain and cutting force to 75% strain to compare the texture of high pressure treated samples. Sila et al. (2006) also described hardness as compression force to 30% strain. When the compressive force at

30% strain was used, Araya et al. (2007) reported an initial textural loss after high pressure treatment at ambient temperature as compared to the control sample. These findings were similar to those obtained by Basak et al. (1998), who used the slope of the linear section of the force-deformation curve. However, the cutting force of the HPP sample was higher than the control sample (Araya et al., 2007). The compression, shear or puncture forces are dependent on the strain level and the shape of the force deformation curves. Therefore, parameters obtained at different strain levels may give opposite conclusions. Furthermore, many studies have found that the pressure treated samples are transformed into a "rubbery" state (Araya et al., 2007).

Thus, the suggested texture represented by compression/puncture or shear force alone may not be a complete indication, especially since the textural transformations were observed in corresponding changes in both stiffness (slope of the linear section of the force deformation curve) and hardness (force required to deform sample) of the samples, but these two parameters do not always follow the same trend. Table 4.1 presents the textural parameters of carrots obtained from compression and shear tests. The compressive forces at different strain levels lead to different conclusions about the "hardness" of the HPP samples. At 30% strain, the compressive force showed a decrease, but at 50% and 75% strain, the compressive force increased at 0 min holding time and decreased at 5 min holding time. For the WB shear test, the max shear force did not have the same drastic difference between the control and HPP samples at 0 and 5 min holding time. The length of the force deformation curve can be used to estimate the extent of jaggedness or rupture intensity during the test (Norton et al., 1998). However, the

calculated lengths for various treatments did not provide any meaningful comparison (Table 4.2). These parameters either represented only a part of the textural transformation after high pressure processing (rupture force, slope) or were unable to give a strong discriminative index (length of the force-deformation curve).

The F_{max} and Grad obtained from the puncture tests partly indicated changes in the texture of processed samples. The combination of both parameters into a unified parameter (denoted as crunchiness index or CI) gave a better overall indication of the textural transformation during HPP and PATP (Table 4.2). During the puncture test, depending on the extent of the texture change, the slope of the force-deformation curve may experience an initial low slope due to the elastic compaction followed by a deflection when the slope increased up to the rupture point. The difference in slope may yield the various values of the crunchiness index. Therefore, the slope at different percentages of max puncture force was investigated to determine the range in which the crunchiness index most closely matched the sensory data. For the carrot samples, a crunchiness index based on the slope of the force deformation curve up to 70% of the max puncture force was able to discriminate among processed sample textural qualities in the same manner as the sensory test (Table 4.2). However, for the red radish samples, a crunchiness index calculated beyond 20% of the max puncture force was not able to provide meaningful information with respect to the texture transformation when compared against sensory data. In addition, at a low strain level, the change in force/deformation slope may also be due to other factors such as sample misalignment, in

which the sample slides before the probe really penetrates the samples. As a result, a slope at 20% of max puncture force was used to express the crunchiness index.

Figure 4.6 presents the crunchiness index of control, HPP, PATP, TP samples and their combined treatments. Unprocessed control samples had a maximum crunchiness index of 2.0. Possibly due to exposure to harsher thermal treatment for a prolonged time, TP carrot, red radish and jicama samples had the smallest crunchiness index values of 0.11, 0.36 and 1.18, respectively (Figure 4.6). Both PATP treatments had significantly higher crunchiness (0.92 to 1.74) values compared to TP for all the samples ($P < 0.05$). Pressure pretreatment followed by TP samples also had improved crunchiness values (0.49 to 1.61) compared to TP samples, but generally lower than PATP samples (Figure 4.6).

4.4. Conclusions

Pressure treatments better retained sample color than thermal treatments and it was product dependent. Among the treatments (TP, PATP, HPP, HPP-TP), HPP best preserved textural quality attributes of carrots, red radish and jicama. Both PATP-SL and PATP-R better preserved product quality than the TP samples. The beneficial effects may come from the densification of the tissue due to pressurization or biochemical changes of the pectic substances. Pressure treatment followed by thermal processing (HPP-TP) can improve textural quality of thermally processed samples. Among the products tested, jicama was least susceptible to textural damage. The crunchiness index can be used as an effective tool for comparing the instrumental textural quality of samples subjected to various process treatments.

References

Ahn, J., Balasubramaniam, V.M., & Yousef, A.E. (2007). Inactivation kinetics of selected aerobic and anaerobic bacterial spores by pressure-assisted thermal processing. *International Journal of Food Microbiology*, *113* (3), 321-329.

Ananta, E., Heinz, V., Schlüter, O., & Knorr, D. (2001). Kinetic studies on high-pressure inactivation of *Bacillus stearothermophilus* spores suspended in food matrices. *Innovative Food Science & Emerging Technologies*, *2*(4), 261–72.

Anthon, G.E., & Barrett, D.M. (2004). Comparison of three colorimetric reagents for the determination of methanol with alcohol oxidase. Application of the assay of pectin methylesterase. *Journal of Agricultural and Food Chemistry*, *52*, 3749-3753.

Araya, X.I.T., Hendrickx, M., Verlinden, B.E., Buggenhout, S.V., Smale, N.J., Stewart, C., & Mawson, A.J. (2007). Understanding texture changes of high pressure processed fresh carrots: A microstructural and biochemical approach. *Journal of Food Engineering, 80*, 873-884.

Barrett, D. (2007). Personal communication. University of California, Davis, CA.

Basak, S., & Ramaswamy, H.S. (1998). Effect of high pressure processing on the texture of selected fruits and vegetables. *Journal of Texture Studies*, *29*, 587–61.

Bourne, M. (2002). Food texture and viscosity: concept and measurement. Second edition. San Diego: Academic Press.

Black, E.P., Wei, J., Cortezzo, D.E., Koziol-Dube, K., Hoover, D.G., & Setlow, P. (2007) Analysis of factors influencing the rate of germination of spores of *Bacillus subtilis* by very high pressure. *Journal of Applied Microbiology*, *102*, 65–76

Cheftel, J.C. (1995). Review: High-pressure, microbial inactivation and food preservation. *Food Science and Technology International*, *1*(2/3), 75–90.

Chen, B.H., Peng, H.Y., & Chen, H.E. (1995). Changes of carotenoids, colour and vitamin A contents during processing of carrot juice. *Journal of Agricultural Food Chemistry*, *43*, 1912–8.

Food Processing. (2009). Pressure-assisted thermal sterilization accepted by FDA. http://www.foodprocessing.com/articles/2009/032.html (accessed July 9, 2009).

Gonzalez, M.E. (2009). Quantification of cell membrane integrity and its relevance to texture quality of onions: effects of high hydrostatic pressure and thermal processes. Ph.D. Thesis, University of California, Davis, CA, USA.

Gorny, T., & Kader, A. (2008). Post-harvest Technology Research & Information Center. UC Davis, Davis, CA. http://postharvest.ucdavis.edu/index.html last accessed May 24, 2008.

Greve, L.C., Shackel, K.A., Ahmadi, H., McArdle, R.N., Gohlke, J.R., & Labavitch, J. M. (1994). Impact of heating on carrot firmness: Contribution of cellular turgor. *Journal of Agricultural and Food Chemistry*, *42* (12), 2896-2889.

Hoogland, H., de Heij, W., & van Schepdael, L. (2001). High pressure sterilization: novel technology, new products, new opportunities. *New Food, 4*(1), 21-26.

Juiano, P., Toldra, M., Koutchma, T., Balasubramaniam, V.M., Clark, S., Mathews, J. W., Dunne, C.P., Sadler, G., Barbosa-Carnova, G.V. (2006). Texture and water retention improvement in high pressure thermally treated scrambled egg patties. *Journal of Food Science*. *71*(2), E52-E61.

Kasai, M., Hatae, K., Shimada, A., & Ibuchi, S. (1995). Pressure pre-treatment of vegetables for controlling the hardness before cooking. *Nippon Shokuhin Kagaku Kogaku Kaishi, 42*(8), 594–601.

Kim, Y.S., Park, S.J., Cho, Y.H., Park, J. (2001). Effects of combined treatment of high hydrostatic pressure and mild heat on the quality of carrot juice. *Journal of Food Science*, *66*(9), 1355–60.

Koutchma, T., Guo, B., Patazca, E., & Parisi, B. (2005). High pressure–high temperature sterilization: from kinetic analysis to process verification, *Journal of Food Process Engineering*, *28*(6), 610–629.

Krebbers, B., Matser, A.M., Koets, M., & Van Den Berg, R.W. (2002). Quality and storage stability of high-pressure preserved green beans. *Journal of Food Engineering*, *54*(1), 27–33.

Krebbers, B., Matser, A.M., Hoogerwerf, S.W., Moezelaar, R., Tomassen, M.M.M., & Van DenBerg, R.W. (2003). Combined high-pressure and thermal treatments for processing of tomato puree: evaluation of microbial inactivation and quality parameters. *Innovative Food Science & Emerging Technologies*, *4*(4), 377–85.

Lau, M.H., & Turek, E.J. (2007). Determination of quality difference in low-acid foods sterilized by high pressure versus retorting. In Doona, C.J., & Feeherry, F.E, High pressure processing of foods. (pp.195-217). Blackwell publishing & IFT press.

Leadley, C., Tucker, G., Fryer, P. (2008). A comparative study of high pressure sterilization and conventional thermal sterilization: Quality effects in green beans. *Innovative Food Science & Emerging Technologies*, *9*, 70-79.

Margosch, D., Ehrmann, M.A., Gänzle, M.G., & Vogel, R.F. (2004). Comparison of pressure and heat resistance of *Clostridium botulinum* and other endospores in mashed carrots. *Journal of Food Protection*, *67*(11), 2530-2537.

Matser, A.M., Krebbers, B., van den Berg R.W., & Bartels P.V. (2004). Advantages of high pressure sterilization on quality of food products. *Trends in Food Science and Technology, 15*(2), 79-85.

Meyer, R., Cooper, K.L., Knorr, D., & Lelieveld, H.L.M. (2000). High pressure sterilization of foods. *Food Technology, 54* (11), 67–72.

Mohsenin, N. (1970). Physical properties of plants and animal materials: structure, physical characteristics and mechanical properties. New York: Gordon and Breach, Science Publishers, Inc.

Nguyen, L.T., Rastogi, N.K., & Balasubramaniam, V.M. (2007). Evaluation of instrumental quality of pressure-assisted thermally processed carrots. *Journal of Food Science*, *72*, E264-E270.

Norton, C.R.T., Mitchell, J.R., & Blanshard, J.M.V. (1998). Fractal determination of crispy or crackly textures. *Journal of Texture Studies, 29*, 239-253

Oey, I., Lille, M., Van Loey, V., & Hendrickx, M. (2008). Effects of high pressure processing on colour, texture and flavor of fruit and vegetable-based food products: a review. *Trends in Food Science and Technology 19*, 320-328.

Patazca, E., Koutchma, T., & Balasubramaniam, V.M. (2007). Quasi-adiabatic temperature increase during high pressure processing of selected foods. *Journal of Food Engineering*, *80*(1), 199-205.

Rajan, S., Ahn, J., Balasubramaniam, V.M., & Yousef, A.E. (2006). Combined pressure-thermal inactivation kinetics of *Bacillus amyloliquefaciens* spores in egg patty mince. *Journal of Food Protection*, *69*(4), 853-860.

Rastogi, N.K., Nguyen, L.T., & Balasubramaniam, V.M. (2008). Effect of pretreatments on carrot texture after thermal and pressure-assisted thermal processing. *Journal of Food Engineering*, *88*, 541-547.

Reddy, N.R., Tetzloff, R.C., Solomon, H.M., & Larkin, J.W. (2006). Inactivation of *Clostridium botulinum* nonproteolytic type B spores by high pressure processing at moderate to elevated high temperatures. *Innovative Food Science and Emerging Technologies*, *7*, 169-175.

Roeck, A.D., Sila, D.N., Duvetter, T., Van Loey, A., & Hendrickx, M. (2008). Effect of high pressure/high temperature processing on cell wall pectic substances in relation to firmness of carrot tissue. *Food Chemistry*, *107*, 1225-1235.

Rovere, P., Maggi, A., Scaramuzza, N., Gola, S., Miglioli, L., Carpi, G., & Dall'Aglio, G. (1996). High-pressure heat treatments: Evaluation of the sterilizing effect and of thermal damage. *Industria Conserve*, *71*, 473-483.

Sila, D., Smout, C., Truong, V., & Hendrickx, M. (2004). Effects of high pressure pretreatment and calcium soaking on the texture degradation kinetics of carrots during thermal processing. *Journal of Food Science*, *69*, E205–E211.

Sila, D.N., Smout, C., Elliot, F., Van Loey, A., & Hendrickx, M. (2006). Non-enzymatic depolymerization of carrot pectin: Toward a better understanding of carrot texture during thermal processing. *Journal of Food Science*, *71*(1), E1–E9.

Sila, D., Yue, X., Van Buggenhout, S., Smout, C., Van Loey, A., & Hendrickx, M. (2007). The relation between (bio-)chemical, morphological, and mechanical properties of thermally processed carrots as influenced by high-pressure pretreatment condition. *European Food Research Technology*, *226*, 127-135.

Van Buren, J.P.S. (1979). The chemistry of texture in fruits and vegetables. *Journal of Texture Studies*, *10*, 1-23.

Zhu, S., Naim, F., Marcotte, M., Ramaswamy, H., & Shao, Y. (2008). High-pressure destruction kinetics of *Clostridium sporogenes* spores in ground beef at elevated temperatures. *International Journal of Food Microbiology*, *126*(1-2), 86-92.

Textural measurement	Control (Fresh sample)	HPP (600 MPa, 25°C 0 min)	HPP (600 MPa, 25°C, 5 min)
Uniaxial compression test			
Compressive force (N)			
At 30% strain	182.5 ± 14.8^{a}	123.4 ± 8.9^{b}	128.2 ± 11.9^{b}
At 50% strain	191.0 ± 8.6^{b}	216.8 ± 13.6^{a}	175.9 ± 17.6^{c}
At 75% strain	211.1 ± 6.4^{b}	221.8 ± 15.6^{a}	179.6 ± 5.8^{c}
WB shear test			
Max shear force (N)	102.4 ± 6.3^{c}	104.2 ± 10.8^{b}	108.2 ± 6.7^{a}

*Data with same letters in the row do not differ significantly from each other, whereas data with different superscripts differ significantly at the probability level $P < 0.05$. Data were estimated from 10 replicates. Time (0 and 5 min) refers to duration under pressure

Table 4.1. Comparison of different textural tests for high pressure processed (HPP) carrot samples.

		Crunchiness Index					
		Ctrl	**HPP**	**PATP-R**	**PATP-SL**	**HPP-TP**	**TP**
Carrot	***% of max puncture force***						
	10%	2.00[a] (± 0.22)	1.20[b] (±0.19)	0.94[c](±0.10)	1.03[c](±0.10)	0.60[d](±0.16)	0.12[e](±0.06)
	20%	2.00 [a] (± 0.22)	1.17[b](±0.19)	0.92[c](±0.10)	0.93[c](±0.10)	0.49[d](±0.16)	0.11[e](±0.06)
	30%	2.00 [a] (± 0.23)	1.22[b] (±0.17)	0.96[c](±0.10)	1.04[c](±0.11)	0.64[d](±0.18)	0.11[e](±0.05)
	40%	2.00 [a] (± 0.19)	1.27[b] (±0.18)	0.99[c](±0.11)	1.08[c](±0.12)	0.67[d](±0.16)	0.10[e](±0.03)
	50%	2.00 [a] (± 0.18)	1.33[b](±0.14)	1.04[c](±0.13)	1.13[c](±0.13)	0.70[d](±0.14)	0.23[e](±0.03)
	60%	2.00 [a] (± 0.18)	1.42[b](±0.21)	1.11[c](±0.14)	1.21[c](±0.13)	0.74[d](±0.15)	0.09[e](±0.03)
	70%	2.00 [a] (± 0.17)	1.55[b](±0.18)	1.21[c](±0.14)	1.32[c](±0.16)	0.80[d](±0.13)	0.17[e](±0.03)
	Length of F-D curve	39.41 (± 4.15)	37.28(±3.49)	31.69(±1.78)	32.10(±2.72)	26.99(±1.82)	24.32(±0.52)
Perceived crunchiness by the sensory panelists		**Control**	**> HPP**	**>PATP-R**	**~PATP-SL**	**>HPP-TP**	**>TP**

*Data with same letters in the row do not differ significantly from each other, whereas data with different superscripts differ significantly at the probability level $P < 0.05$. Data were estimated from 10 replicates

The notation "X > Y" indicated that sample processed by treatment "X" has a greater crunchiness (as perceived by the panelists) than the sample processed by the treatment Y. Similarly, "X~Y" indicated both treatments X and Y resulted in samples with very similar crunchiness (as perceived by panelists)

continued

Table 4.2. Comparison of crunchiness index values against sensory crunchiness ranking as influenced by various pressure-thermal treatment.

Table 4.2. continued

Red Radish	***% of max puncture force***						
	10%	2.00 [a] (± 0.24)	1.64[b](±0.23)	1.25[c](±0.28)	1.36[c](±0.26)	0.61[d](±0.14)	0.37[e](±0.11)
	20%	2.00 [a] (± 0.21)	1.69[b](±0.17)	1.33[c](±0.13)	1.34[c](±0.14)	0.61[d](±0.13)	0.36[e](±0.11)
	30%	2.00 [a] (± 0.19)	1.98[a](±0.22)	1.48[b](±0.32)	1.61[b](±0.29)	0.65[c](±0.14)	0.41[d](±0.11)
	40%	2.00 [a] (± 0.22)	2.05[a](±0.27)	1.58[b](±0.33)	1.72[b](±0.30)	0.67[c](±0.14)	0.42[d](±0.12)
	50%	2.00 [a] (± 0.22)	2.13[a](±0.24)	1.68[b](±0.35)	1.82[a](±0.31)	0.69[c](±0.15)	0.43[d](±0.12)
	60%	2.00 [b] (± 0.21)	2.20[a](±0.23)	1.79[c](±0.36)	1.93[b](±0.33)	0.71[d](±0.15)	0.44[e](±0.12)
	70%	2.00 [b] (± 0.22)	2.28[a(]±0.23)	1.90[b](±0.38)	2.04[b](±0.35)	0.72[c](±0.16)	0.45[d](±0.12)
	Length of F-D curve	29.51 (± 1.83)	31.74(±2.64)	30.46(±2.79)	31.02(±1.51)	24.85(±0.78)	24.35(±0.50)
Perceived crunchiness by the sensory panelists		**Control**	**> HPP**	**>PATP-R**	**~PATP-SL**	**>HPP-TP**	**>TP**
Jicama	***% of max puncture force***						
	10%	2.00 [a] (± 0.17)	1.49[b](±0.16)	1.48[b](±0.17)	1.57[b](±0.24)	1.44[b](±0.19)	1.00[c](±0.24)
	20%	2.00 [a] (± 0.28)	1.66[b] (±0.16)	1.59[b](±0.16)	1.74[b](±0.23)	1.61[b](±0.19)	1.18[c](±0.26)
	30%	2.00 [a] (± 0.19)	1.65[b] (±0.16)	1.70[b](±0.17)	1.75[b](±0.22)	1.58[b](±0.19)	1.10[c](±0.26)
	40%	2.00 [a] (± 0.25)	1.70[b](±0.17)	1.78[b](±0.17)	1.81[b](±0.22)	1.63[b](±0.19)	1.13[c](±0.26)
	50%	2.00 [a] (± 0.22)	1.76[b](±0.17)	1.85[b](±0.18)	1.87[b](±0.22)	1.68[b](±0.20)	1.15[c](±0.25)
	60%	2.00 [a] (± 0.21)	1.82[a](±0.17)	1.93[a](±0.18)	1.94[a](±0.22)	1.73[a](±0.22)	1.17[b](±0.26)
	70%	2.00 [a] (± 0.18)	1.88[a](±0.18)	2.01[a](±0.19)	2.00[a](±0.23)	1.79[a](±0.29)	1.20[b](±0.26)
	Length of F-D curve	50.59 (±7.15)	42.47(±2.93)	46.33(±3.928)	47.08(±3.57)	39.58(±3.26)	29.41(±3.61)
Perceived crunchiness by the sensory panelists		**Control**	**> HPP**	**~PATP-R**	**~PATP-SL**	**~ HPP-TP**	**>TP**

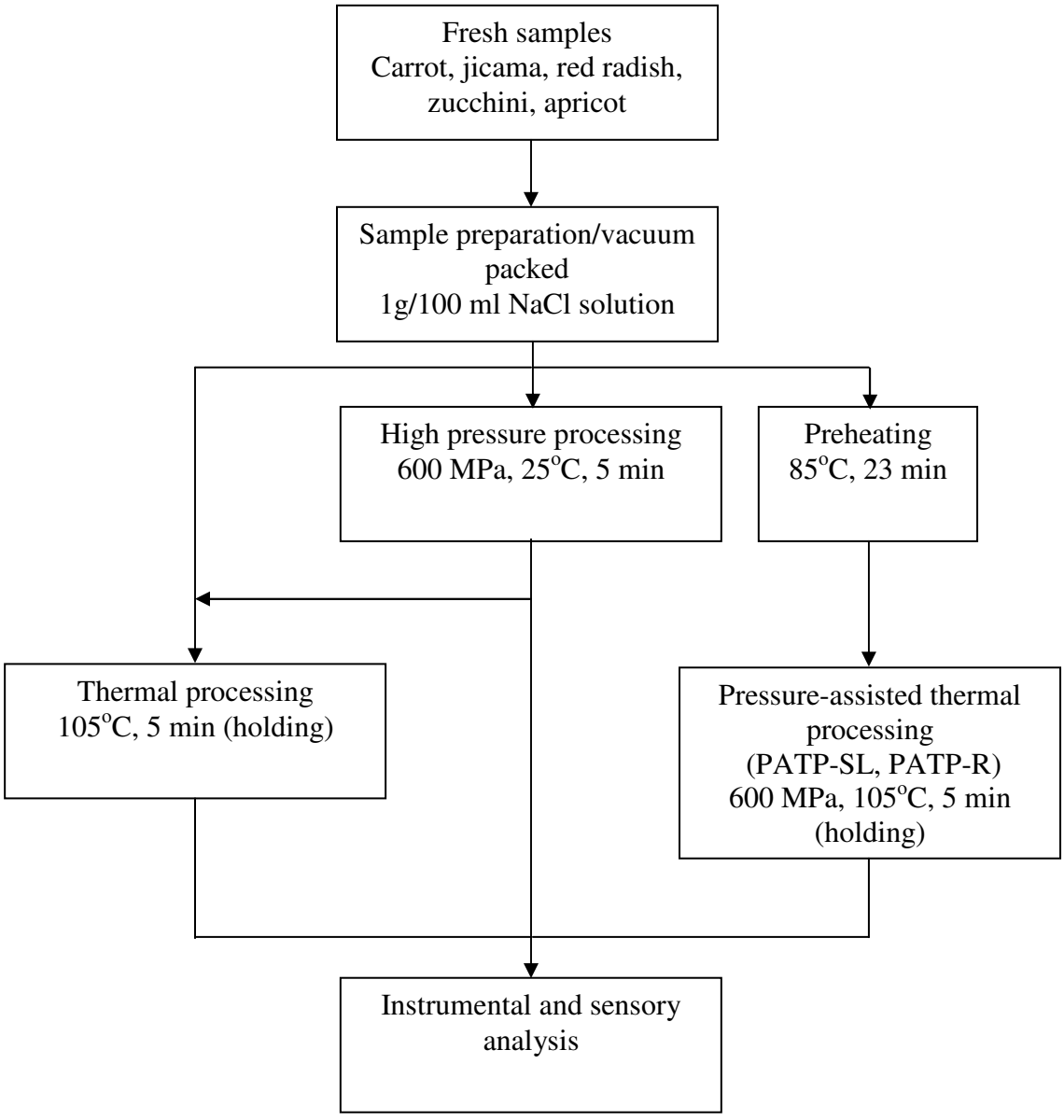


Figure 4.1. Schematic diagram outlining various experimental conditions. R and SL designate different compression time of pressure-assisted thermal processing (PATP).

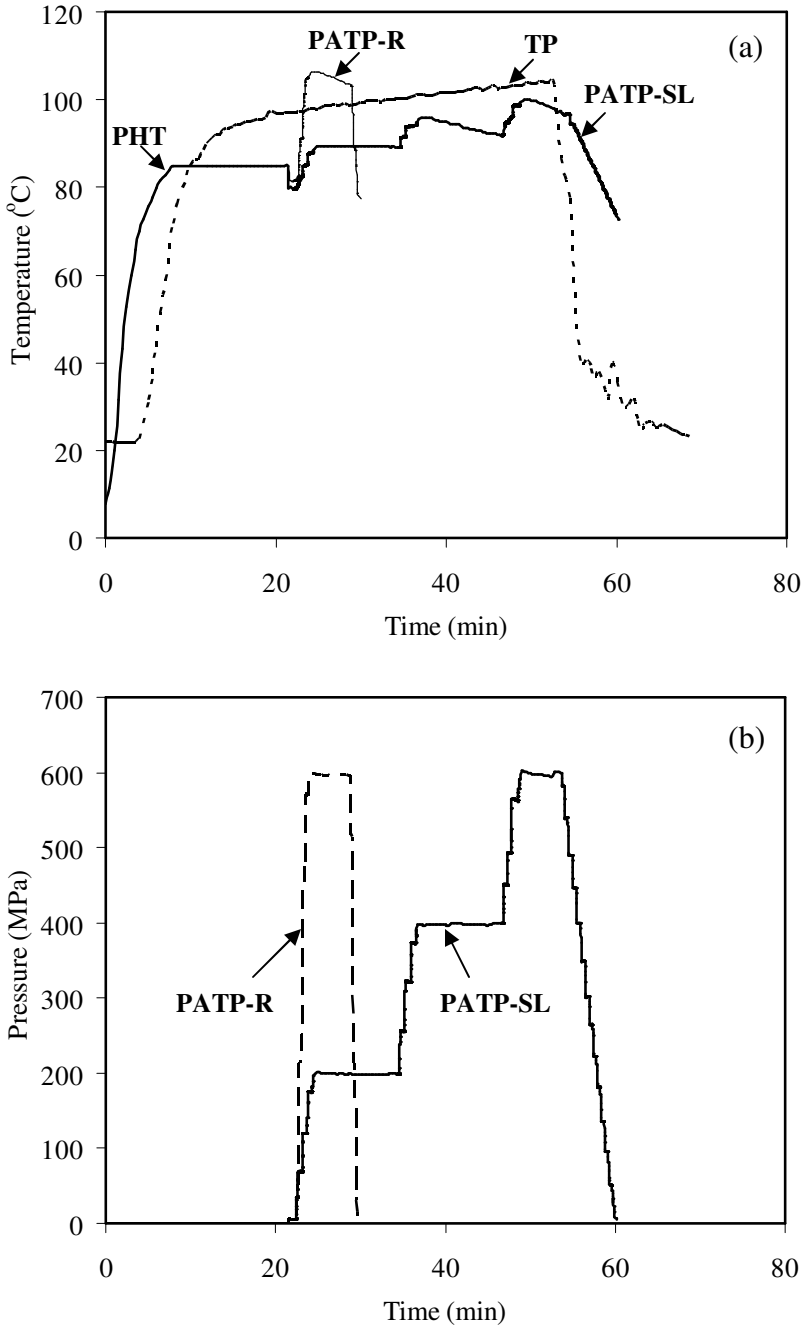
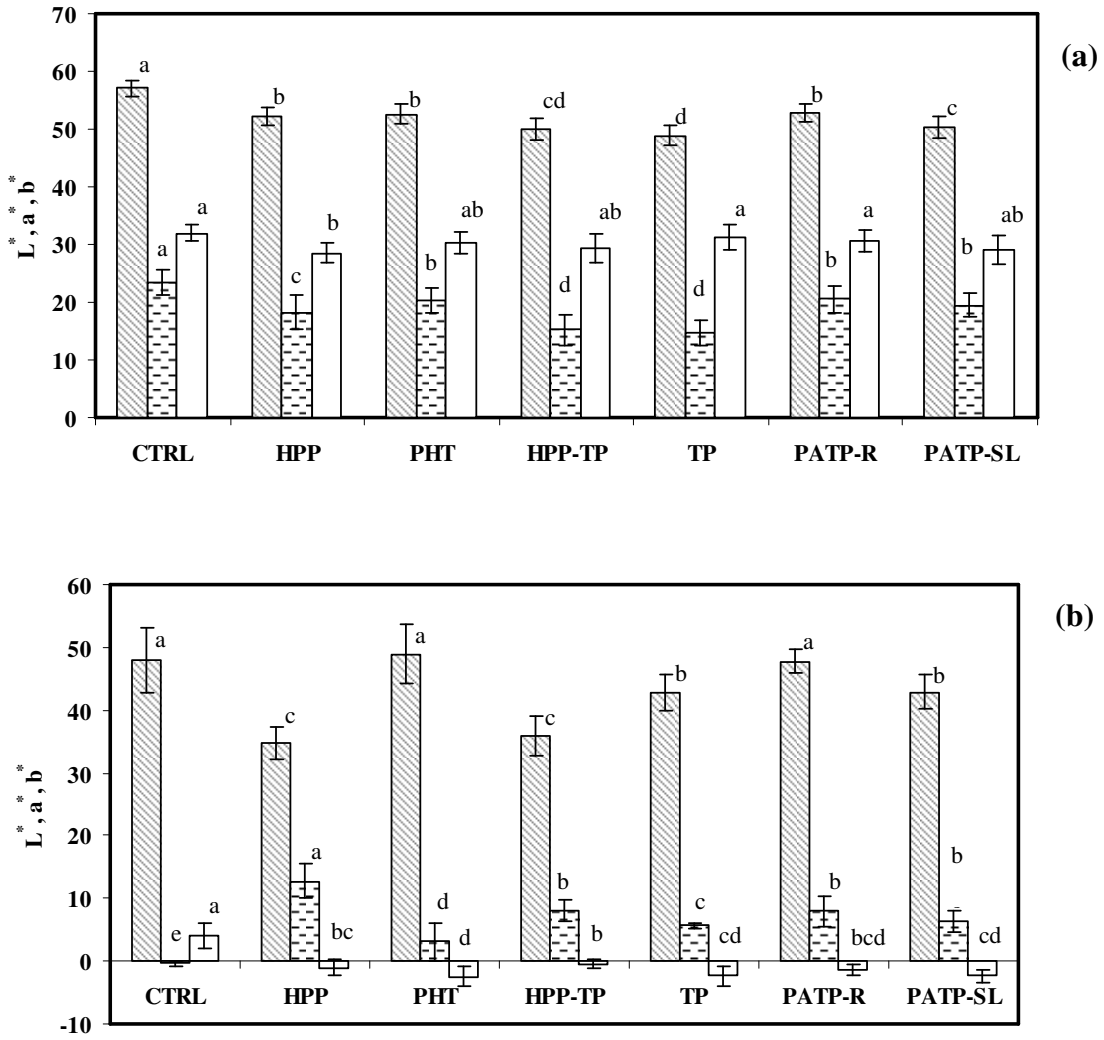


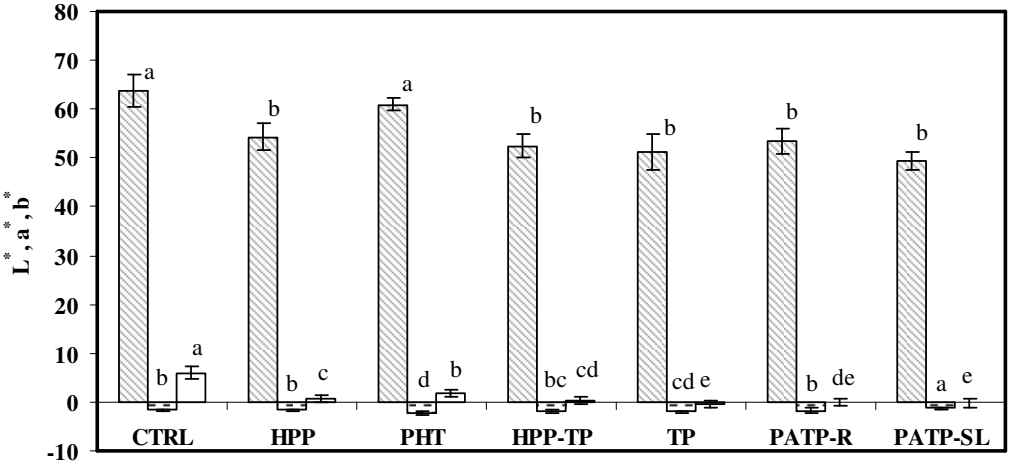
Figure 4.2. The temperature (a) and pressure (b) history of pressure-assisted thermal processing (PATP-R: 600 MPa, 105°C, 5 min; PATP-SL: 600 MPa, 105°C, 5 min) samples. R and SL designate different compression time of PATP treatments. Additionally, thermal histories of the samples collected during thermal processing (TP: 105°C, 5 min) and preheating before PATP (PHT; 85°C, 23 min) are also provided in Figure a.



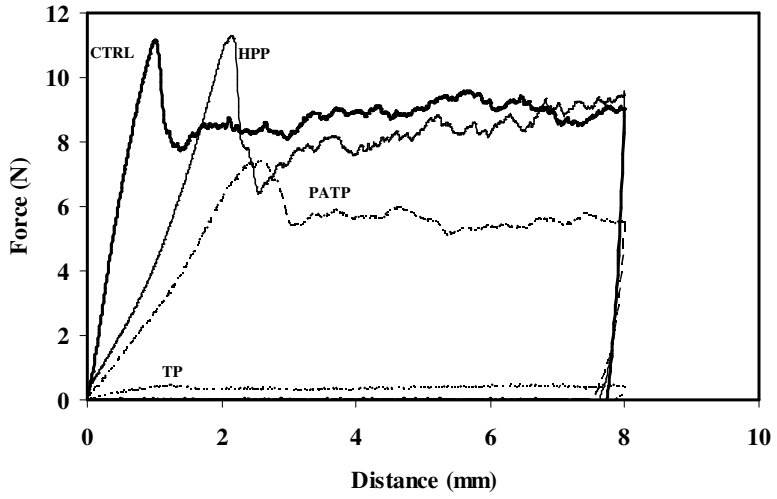
continued

Figure 4.3. Color of (a) carrot; (b) red radish and (c) jicama tissues under different processing conditions: CTRL (raw sample); HPP (600 MPa, 25 ^{o}C, 5 min); PHT (85^{o}C, 23 min); HPP-TP (HPP: 600 MPa, 25^{o}C, 5 min, followed by TP: 105^{o}C, 5 min); TP (105^{o}C, 5 min); PATP-R (600 MPa, 105^{o}C, 5 min); PATP-SL: 600 MPa, 105^{o}C, 5 min). R and SL designate different compression time of PATP treatments. Data were estimated from 6 replicates. Within the same color parameter, values with different letter are significantly different ($P < 0.05$). ▨ L*; ⊡ a*; □ b*.

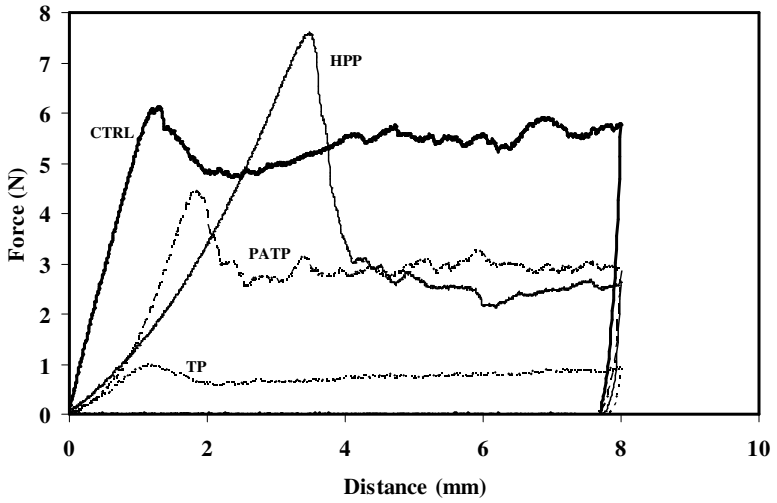
Figure 4.3 continued



(c)



(a)

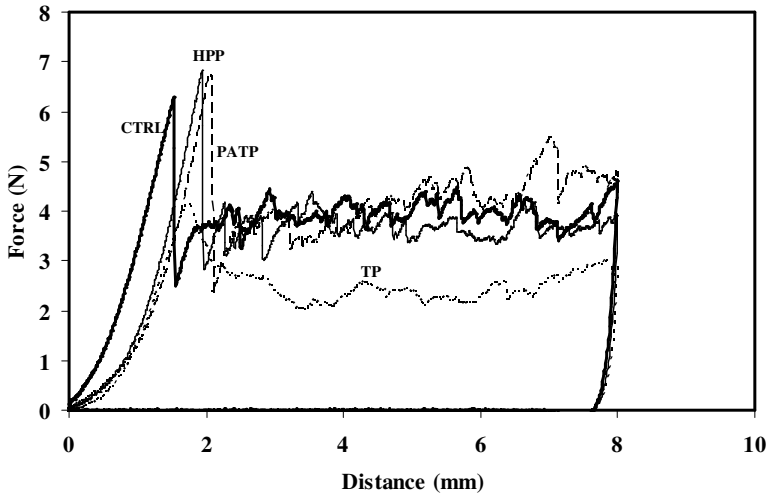


(b)

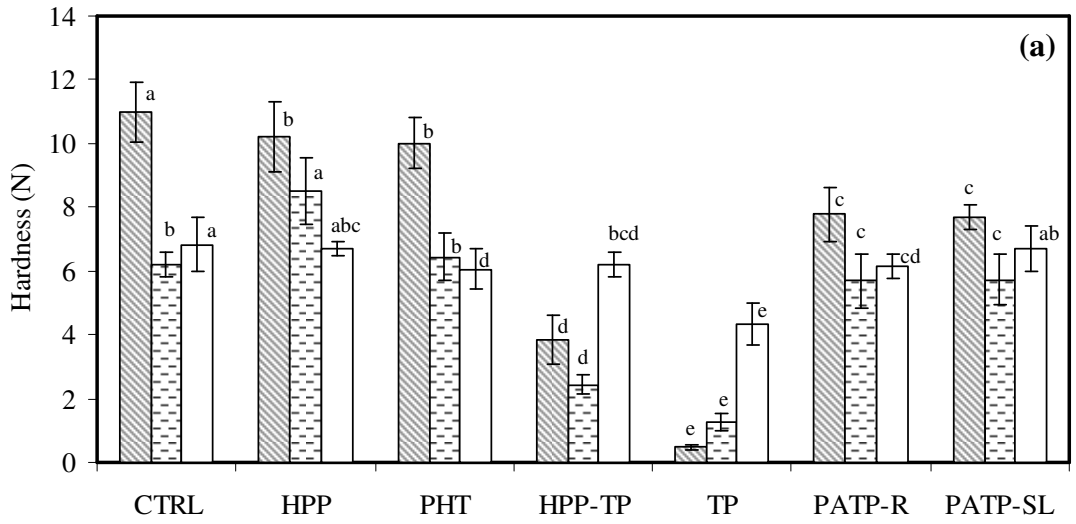
continued

Figure 4.4. Sample force-deformation curves for (a) carrot, (b) red radish and (c) jicama samples treated by various process conditions: CTRL (raw sample); HPP (600 MPa, 25^{o}C, 5 min); TP (105^{o}C, 5 min); PATP (600 MPa, 105^{o}C, 5 min).

Figure 4.4. continued



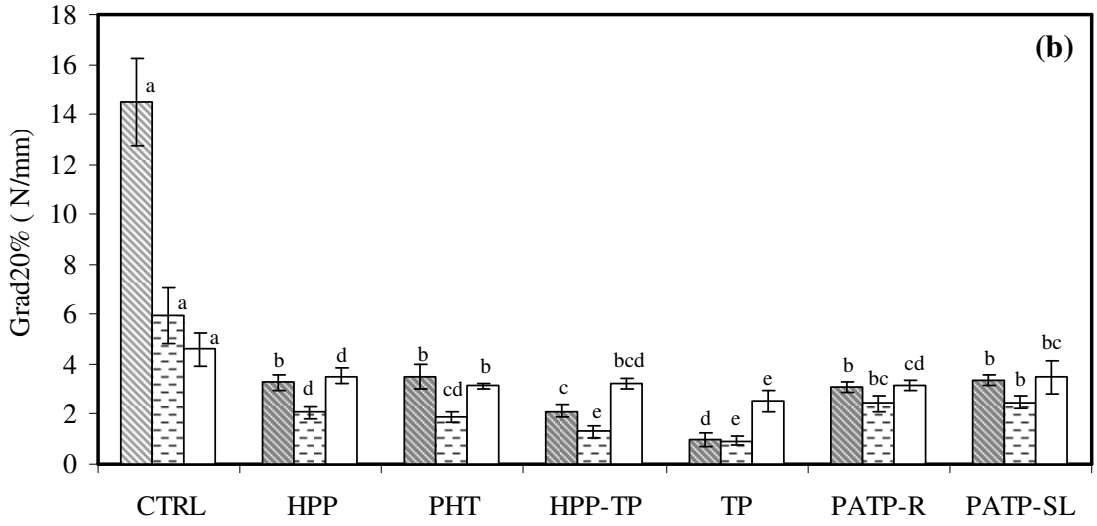
(c)

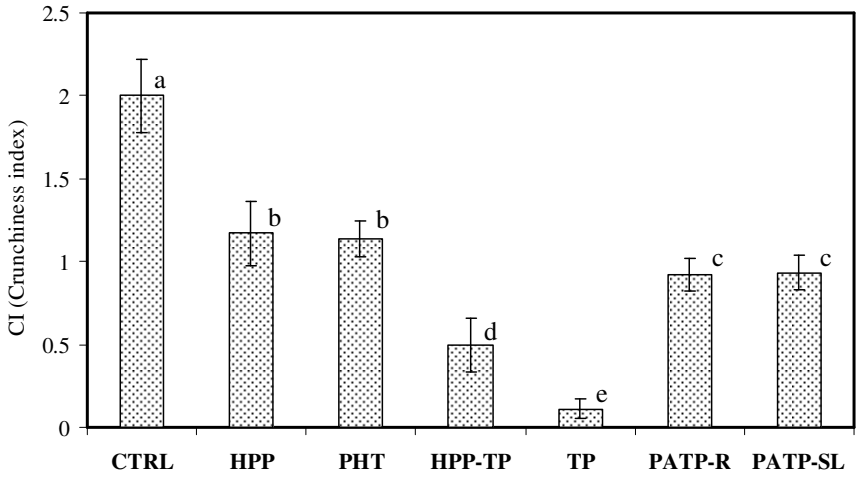


continued

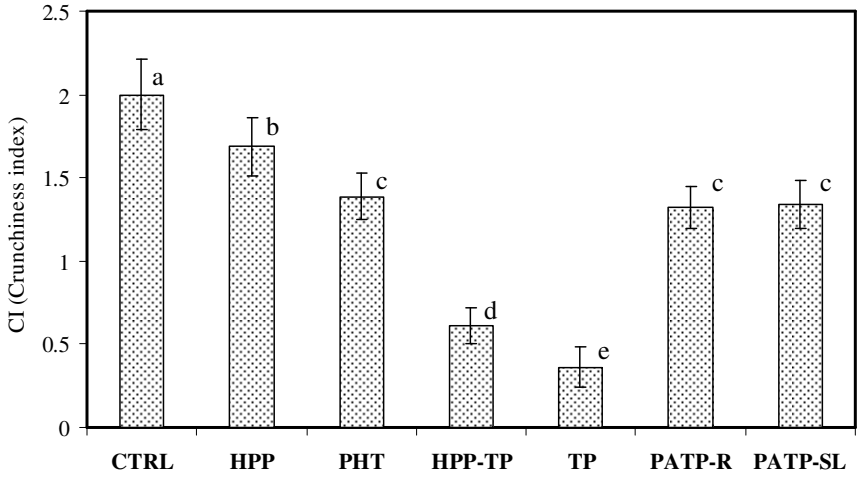
Figure 4.5. Effects of different processing conditions on the texture of carrot, red radish and jicama measured by puncture test (a) max puncture force; and (b) slope of force-deformation curve at 20% max puncture force. CTRL (raw sample); HPP (600 MPa, 25^{o}C, 5 min); PHT (85^{o}C, 23 min); HPP-TP (HPP: 600 MPa, 25^{o}C, 5 min, followed by TP: 105^{o}C, 5 min); TP (105^{o}C, 5 min); PATP-R (600 MPa, 105^{o}C, 5 min); PATP-SL: 600 MPa, 105^{o}C, 5 min). R and SL designate different compression time of PATP treatments. Data were estimated from 10 replicates. Within the same sample, values with different letter are significantly different ($P < 0.05$). ▨ carrot; ▤ red radish; □ jicama.

Figure 4.5. continued





(a)

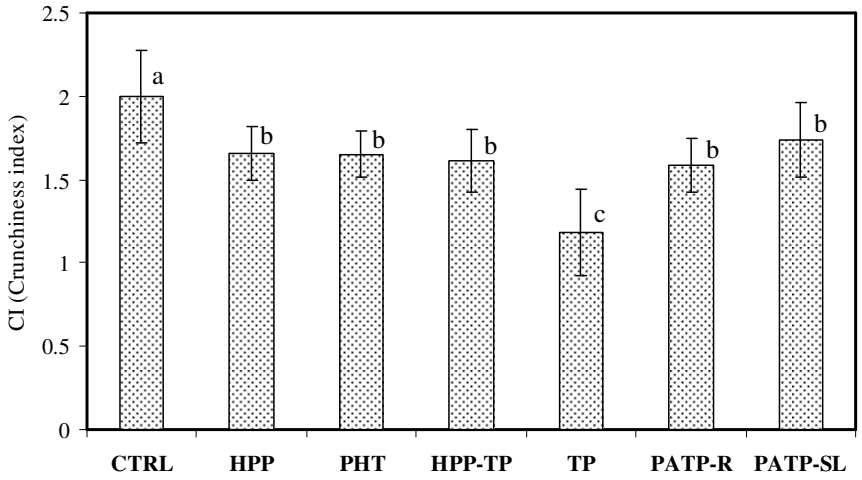


(b)

continued

Figure 4.6. Crunchiness index for (a) carrot; (b) red radish and (c) jicama samples processed by pressure treatment (HPP: 600 MPa, 20°C, 5 min), preheat (PHT: 85°C, 23 min), thermal process (TP: 105 °C, 5 min), and pressure-assisted thermal process (PATP-R: 600 MPa, 105°C, 5 min; PATP-SL: 600 MPa, 105°C, 5 min). R and SL designate different compression time of PATP treatments. Data were estimated from 10 replicates. Values with different letter are significantly different ($P < 0.05$).

Figure 4.6. continued



(c)

Chapter 5: Determination of In-situ Thermal Conductivity, Thermal Diffusivity, Volumetric Specific Heat and Isobaric Specific Heat of Selected Foods under Pressure

Abstract

The knowledge of in-situ thermal properties of food materials under pressure is useful in evaluating process uniformity, equipment design and process optimization. The objective of this research was to determine thermal conductivity (k), thermal diffusivity (α), volumetric specific heat (ρC_p) and isobaric specific heat (C_p) of selected foods under pressure. The line heat source method was adapted to fabricate a dual needle probe that withstood elevated pressures. The probe was calibrated using published NIST data for distilled water and probe-specific calibration factors were estimated. In-situ thermal properties were determined from 0.1 to 600 MPa at 25^{o}C for tomato puree, soy protein isolate (10% W:V), soybean oil, guacamole, honey, cream cheese and sucrose solution (10% W:V). Within the range of our experimental conditions, all thermal properties changed with the application of pressure. Application of pressure increased k linearly and among the tested food materials, the maximum increase in k values under pressure was observed for soybean oil (0.173 -0.256 W/m^{o}C), while k of honey showed the least change (0.324 – 0.396 W/m ^{o}C). Thermal diffusivity of the test materials increased with increasing pressure and the data can be expressed as a 2nd order polynomial function of pressure. Isobaric specific heat of food materials decreased with increase in pressure.

The maximum combined uncertainty in the measurement of k, α, ρC_p and C_p were 3.1, 6.8, 6.6 and 6.9%, respectively.

Key words: high pressure processing, thermal properties, specific heat, thermal conductivity, thermal diffusivity

5.1. Introduction

High pressure processing (HPP) has been used to inactivate pathogenic bacteria and produce novel food products of high quality. Value added, pressure pasteurized foods have been commercially available and the pressure-assisted thermal sterilization (PATS) process has been approved by Food and Drug Administration (FDA) for production of low acid foods. Application of high pressure processing in the food industry has generated interest in estimating in-situ thermal properties of foods under pressure. Thermal properties such as thermal conductivity, diffusivity and specific heat are important in optimization of the high pressure processes and prediction of food quality degradation or microbial safety of pressure treated foods via mathematical modeling (Otero & Sanz, 2003).

In the engineering literature, a number of methods have been developed for the measurement of properties of materials under pressure. These include the pioneering studies by Bridgman on heat capacity (Bridgman, 1912) and thermal conductivity of water (Bridgman, 1923). Thermal conductivity data for water were also reported by Lawson (1959) and Kestin (1984). Abdugalatov and Magomedov (1994) investigated thermal conductivity of sodium and potassium chloride solutions up to 100 MPa.

Only recently, food researchers began investigating techniques for estimating in-situ food properties under pressure. These included thermal conductivity (Safarov et al., 1999; Denys & Hendrickx, 1999; Niassar et al., 2000; Ramaswamy et al., 2007; Zhu et al., 2007, 2008; Werner et al., 2007, 2008), thermal diffusivity, volumetric specific heat (Zhu et al., 2007) and specific heat (Safarov et al., 1999; Barbosa, 2003).

Barbosa (2003) measured in-situ sound velocity under pressure and then estimated thermophysical properties of food models such as specific heat, density, compressibility etc. from thermodynamic equations. However, the technique may not be applicable in multiphase or heterogeneous materials due to scattering of sound waves (Povey, 1998; Min, 2008) within many food materials. The dual needle probe based on the line heat source principle was used by Zhu et al. (2007) to measure thermal conductivity, diffusivity and volumetric specific heat of potato and cheddar cheese at 5 and 25^{o}C up to 350 MPa. The objective of this study was to measure thermal conductivity, thermal diffusivity, volumetric specific heat and isobaric specific heat values of selected foods under pressure up to 600 MPa at 25^{o}C.

5.2. Materials and methods

5.2.1. Pressure generating unit

The experiment was conducted using a custom made high pressure system (26190, Harwood Engineering Inc., MA). The system was rated up to 1000 MPa with approximately 25 MPa/second pressurization rate. Depressurization was manually controlled and could be completed in less than 4 seconds. The pressure transmitting medium contained 50% propylene glycol (w/v) (Safe-T-Therm, Houghton Int. Inc, PA) in demineralized water (Chemical store, Ohio State University). The cylindrical pressure chamber had interior dimensions of 25 mm dia x 152 mm depth. The pressure chamber had an external jacket for temperature control which circulated fluid from to a temperature controlled propylene glycol bath.

5.2.2. Dual needle probe design

The dual needle probe (Figure 5.1) was fabricated by following the design principles of the well-known line heat source technique (Nix et al., 1969; Bristow et al., 1994, Zhu et al., 2007) and adapted to work under elevated pressure conditions for this study. The probe essentially consisted of two parallel stainless steel needles. The first central needle was made from a stainless steel hypodermic tube (VITA gauge 20, Needham, MA) with outer diameter: 0.71 mm and thickness: 0.15 mm, and was used for measuring thermal conductivity. The length/diameter ratio of the needle was kept at 60 to minimize axial heat flow error (Sweat, 1986; Murakami et al., 1996). A loop of insulated constantan heating wires (TFCC-003; Omega Engineering, Stamford, CT; diameter 0.076 mm) was inserted along with type K thermocouple wires (TFCY-003; TFAL-003; Omega Engineering, Stamford, CT; diameter 0.076 mm). Type K thermocouples were used because their *emf* is not affected by elevated pressures (Bundy, 1961). The thermocouple junction was positioned at the middle length of the probe. The tip of the central needle in contact with tested food materials was sealed with epoxy resin (Devcon 2 Ton epoxy, Riviera beach, FL) to avoid inflow of sample into the needle. The other end was kept open, so the pressure medium could act as filling material and prevent deformation of the probe (Denys et al., 1999; Zhu et al., 2007).

The second needle utilized a K-type thermocouple probe (KMQSS-040U-7, Omega Engineering, Stamford, CT) mounted at a distance r ~ 2.0 mm from the central needle. The distance r was selected to ensure the condition $0.16 < \beta < 3.1$ (Eq. 5.1) recommended by Nix et al. (1967) was satisfied:

$$\beta = \frac{r}{2\sqrt{\alpha t}} \quad (5.1)$$

where β is a dimensionless number, α is thermal diffusivity (m^2/s); r is distance between two needles (m) and t is time (s). The heating wire in the central probe was heated using a DC voltage supplied by a power source (BK precision, Mouser Electronics Inc., TX; 615-1621A). The voltage, temperature values were recorded using a data acquisition system (CR 23X Micrologger, Campbell Scientific, Inc., Logan, UT). The power input was calculated knowing the resistance of the heating wire and the applied voltage. To prevent electric short-circuits which may interfere with the thermocouple readings, the junctions of the electrical power supply were insulated with epoxy (Devcon 2 Ton epoxy, Riviera beach, FL).

5.2.3. Sample holder

The dual needle probe was housed inside a cylindrical sample holder made from polycarbonate (19 mm x 90 mm; US plastics, Lima, OH) and connected to the pressure chamber top closure (Figure 5.1). A movable piston coupled with an O-ring was used to contain the sample and transmit the applied pressure to the contents of the sample holder. To reduce the friction between the O-ring and sample holder, a thin layer of silicon-based lubricant (Dow Corning, Midland, MI) was applied to the O-ring before experiment.

5.2.4. Probe calibration

The probes were calibrated with distilled water at 100 MPa intervals up to 600 MPa at 25^{o}C. We used water as the calibration material by following the procedures of Ramaswamy et al. (2007). The calibration factor for thermal conductivity and diffusivity

of the probe were calculated from published NIST data for water under pressure (Harvey et al., 1996).

$$f_k = \frac{k_{NIST}}{k} \tag{5.2}$$

$$f_\alpha = \frac{\alpha_{NIST}}{\alpha} \tag{5.3}$$

Subscript NIST denotes data taken from published NIST source (Harvey et al., 1996) and f_k, f_α, are calibration factors for thermal conductivity and diffusivity, respectively. Additional cross-validation experiments using these calibration factors were subsequently conducted using glycerol (Acros Organics, Fairlawn, NJ), whose thermophysical properties values are readily available in the literature (Nilsson et al., 1986).

5.2.5. Food materials

Thermal conductivity, thermal diffusivity and specific heat of selected food materials (sucrose solution, tomato puree, soy protein isolate, soybean oil, guacamole, honey and cream cheese) were determined at 25 ^{o}C over the pressure range up to 600 MPa. Isolated soy protein (PROFAM 891, ADM, Decatur, IL) 10% and sucrose (JT Baker, Phillipsburg, NJ) solution 10% was prepared in demineralized water (Chemical store, Ohio State University) as described by Min et al., (2009). Soybean oil, honey (Pure clover Grade A), cream cheese (Philadelphia, Kraft Foods) and tomato were purchased from a local grocery store (Columbus, OH). Tomato puree was prepared by chopping the tomatoes and pureeing in a blender, and removing seeds using a sieve. Guacamole (Trader Joe's, Needham Heights, MA) was purchased from a local store. Tomato puree

and guacamole samples were further de-aerated to remove occluded air by applying vacuum before subjecting them to pressure treatment.

5.2.6. Test procedure

For each run, about 25 g of sample was loaded into the sample holder and closed using the movable piston (Figure 5.1). The sample holder was visually examined for entrapped air bubbles, which were removed through a weeping-hole in the center of the movable piston. A screw was used to seal the weeping-hole after air removal. The sample holder, together with top enclosure was inserted into the pressure chamber and the system sealed by tightening the retaining screw (Figure 5.1).

After the sample reached thermal equilibrium with the external conditioning jacket, a pre-determined level of DC power (1.8 W/m) was applied. Preliminary experiments verified that convection effects were kept to a minimum at this power level. Thermal conductivity experiments utilized sample temperature recorded at 0.2 s intervals up to 60 s. Thermal diffusivity experiments were conducted up to 200 s. The reported thermal conductivity, specific heat, and thermal diffusivity values each were averages of 6 replicates. From the temperature histories of the test samples, the thermal conductivity, thermal diffusivity, and specific heat values of the test samples were calculated by solving the unsteady state Fourier equation. The solution was implemented in Matlab (version 7.1.0246, Mathworks Inc, Natick, MA) as described in the following section. To verify the impact of pressure treatment on measured property values, an additional set of experiments were carried out before and after pressure treatment at atmospheric pressure conditions.

5.2.7. Theoretical consideration

The cylindrical solution of Fourier's equation for unsteady-state radial heat conduction in an infinite medium (Carslaw and Jaeger, 1959; Ingersoll et. al., 1954) is given by:

$$\Delta T = \frac{Q}{2\pi k}\int_{\beta}^{\infty}\frac{e^{-x^2}}{x}dx \qquad (5.4)$$

where ΔT is the temperature rise (^oC), Q denotes the supplied power per unit length (W/m); k is thermal conductivity (W/m^oC); and x is a dummy variable. Eq. 5.4 can be expressed using an infinite power series as below (Nix et al., 1969):

$$\Delta T = \frac{Q}{2\pi k}\left[\frac{-Ce}{2} - \ln\beta + \frac{\beta^2}{2.1!} - \frac{\beta^4}{4.2!} + \cdots\right] \qquad (5.5)$$

For thermal conductivity, if $\beta < 0.16$, temperature rise can be approximated by Eq. 5.6 with less than 1% error (Nix et al., 1969):

$$\Delta T = \frac{Q}{2\pi k}\ln\sqrt{\frac{t_2}{t_1}} \qquad (5.6)$$

where ΔT is the temperature increase (^oC) between the time intervals t_1, t_2 (s). From Eq. 5.6, thermal conductivity can be estimated from the slope of the natural logarithm of temperature versus time by linear regression.

Using the temperature history measured by the second thermocouple sensor, thermal diffusivity values were estimated by a Newton-Raphson iterative solution for Eq. 5.5. An initial value of $\beta = 10^{-10}$ was used. While solving Eq. 5.5, to ensure convergence, the first 50 terms in the power series were used. Beyond 50 terms, the estimated truncation error was not significant ($< 10^{-18}$).

Knowing thermal diffusivity and thermal conductivity values, volumetric specific heat values were calculated by using the relationship:

$$\rho C_p = \frac{\alpha}{k} \tag{5.7}$$

To evaluate the specific heat of the food materials, density data of the respective foods under pressure reported by Min et al. (2009) was used.

$$C_p = \frac{\rho C_p}{\rho} \tag{5.8}$$

5.2.8. Prediction of thermal properties of tested foods under pressure

Pressure dependency of thermal properties was empirically modeled by relating the thermal property values (X) with pressure (P). The data were fitted to a general polynomial equation of the form:

$$X = a_0 + a_1 P + a_2 P^2 + a_3 P^3 \tag{5.9}$$

Coefficients of Eq. 5.9, a_0, a_1, a_2, a_3 were estimated by regression analysis (Matlab, Version 7.1.0246, Matworks Inc., MA)

5.2.9. Statistical analyses

Means were compared using least-significant difference (LSD) procedures by SAS software, version 9.1.3 (SAS Inst. Inc., Cary, N.C., USA). Mean differences among treatments were calculated with Fisher's least-significant difference method, with significance at the 5% level ($P < 0.05$).

5.2.10. Uncertainty analyses

In measuring thermal conductivity, diffusivity and specific heat by the dual needle probe, the main sources of experimental error are those associated with the measurements

of temperature, pressure, time and power. Uncertainties related to the pressure, power and the time measurements were in turn based on the operating characteristics of the data acquisition instruments (Ramaswamy et al., 2007). Errors may also arise from the deviation of the probe design from theory (finite probe length, radius, thermal mass, change in distance between the probes, and difference in thermophysical properties of the probe and food materials). The deviation of measured values from the true ones was caused by measurement errors which included components arising from random or systematic effects. The uncertainty associated with error in estimating thermal properties were analyzed by following NIST guidelines (Taylor & Kuyatt, 1994). These uncertainties can be classified, into two main categories: type A and type B (Kirup & Frenkel, 2006). Type A standard uncertainty was evaluated:

$$u(x_i) = \left(\frac{1}{n(n-1)} \sum_{k=1}^{n} (X_{i,k} - \overline{X_i})^2 \right)^{1/2} \tag{5.10}$$

where $u(x_i)$ denotes type A uncertainty and $\overline{X_i}$ is the mean of n independent observations $X_{i,k}$. Type B standard uncertainty was evaluated based on our scientific judgment of the available information of factors likely to affect the measurands. Assuming the measurements were uncorrelated, the combined uncertainty was estimated based on the law of propagation of uncertainty as below:

$$u_c^2(G) = \sum_{i=1}^{N} \left(\frac{\partial G}{\partial x_i} \right)^2 u^2(x_i) \tag{5.11}$$

where $u_c(G)$ is the combined uncertainty in measuring thermophysical property G; $u(x_i)$ was standard uncertainty component (type A or B) of the input x_i.

5.3. Results and discussions

Figure 5.2 shows a typical temperature history recorded by central and outer thermocouple sensors during high pressure processing experiments. After reaching thermal equilibrium (~25^{o}C), the temperature of the test sample increased during pressurization due to heat of compression and was subsequently allowed to equilibrate back to 25^{o}C. Representative thermal histories during thermal conductivity and thermal diffusivity measurements were presented in Figure 5.2 a & b.

5.3.1. Probe calibration

The probe specific calibration factors for thermal conductivity and thermal diffusivity were estimated by comparing experimental data of the distilled water against those published from NIST (Figure 5.3). The calibration factors ranged between 1.032-1.079 for thermal conductivity and 1.101-1.245 for thermal diffusivity. Deviation of probe design parameters from theory (e.g., finite radius, thermal mass, finite length, contact resistance between the probe and sample) might have contributed to the variation in the calibration factors. It is interesting to note that pressure had limited or no effect on the calibration factors. Figure 5.4 compares the experimental thermal conductivity and diffusivity data of glycerol as a function of pressure against that of the published literature (Nilsson et al., 1986). There was reasonable agreement between measured and reported data. Measured thermal properties at atmospheric pressure were also compared against published data in the literature (Table 5.1).

5.3.2. Influence of pressure on thermal conductivity

The influence of pressure on thermal conductivity of foods at 25^{o}C is shown in Figure 5.5. Within the range of our experimental conditions, thermal conductivity of foods increased linearly as a function of pressure. For example, when the pressure increased from 0.1 to 600 MPa, thermal conductivity of 10% sucrose solution increased from 0.557 W/m^{o}C to 0.752 W/m^{o}C. Similarly thermal conductivity of cream cheese increased from 0.347 W/m^{o}C (at 0.1 MPa) to 0.477 W/m^{o}C (at 600 MPa). Upon depressurization, thermal conductivity values of the material reverted to values close to those measured at atmospheric pressure before pressure treatment (data not shown).

Increase in thermal conductivity values of foods with increasing pressure was also reported by earlier researchers (Denys & Hendrickx, 1999; Ramaswamy et al., 2007, Zhu et al., 2007, 2008; Werner et al., 2009). Pressure dependency of thermal conductivity is a function of compressibility of materials (Bridgman, 1923). Under pressure, the intermolecular distance is decreased hence reducing the mean free path of the molecules, and results in an increase in thermal conductivity.

It appears that for aqueous solutions, change in thermal conductivity under pressure is mainly a function of water fraction. Thermal conductivity of 10% (w/v) sucrose solution and tomato puree (5.04% solid content) closely followed the thermal conductivity values of water. Similar observations were also made by Werner et al. (2009) who reported that thermal conductivity of sugar solutions was primarily a function of applied pressure and mass fraction. In the case of honey, the main components were glucose (35.7%), fructose (41.0%), galactose (3.0%) and water (17.1%) (USDA National Nutrient Data base). Thus, the k values of honey were less influenced by pressure (Figure

5.5). Min et al. (2009) reported that honey had lower compressibility values than that of water and 10% sucrose solutions, and that compressibility decreased with increasing sugar content (2.5-50%).

Among the substances tested, soybean oil had the lowest thermal conductivity values (0.173 W/m^{o}C to 0.256 W/m^{o}C) (Figure 5.5). Min et al. (2009) observed that soybean oil had higher compressibility than that of water up to 100 MPa, similar compressibility between 100 MPa to 300 MPa and less compressibility between 300 to 700 MPa. However, thermal conductivity of soybean oil in general did not exhibit a nonlinear pressure dependency relationship.

Werner et al. (2008) reported a nearly linear relationship between $(1/k)(\partial k/\partial P)_T$ and isothermal compressibility of plants oils. Relative change in thermal conductivity of liquid under pressure was characterized by:

$$\lambda\ (T, P) = \delta(T, P)^{g} \tag{5.12}$$

Where,

$$\lambda = \frac{k_p}{k_o} \tag{5.13}$$

$$\delta = \frac{\rho_p}{\rho_o} \tag{5.14}$$

and

$$g = \frac{\rho}{\nu}\left(\frac{\partial \nu}{\partial \rho}\right)_T + \frac{1}{3} \tag{5.15}$$

Subscripts “p” “o” denotes values of k and ρ at an arbitrary pressure “p” and atmospheric pressure. g derived from the relationship between mean molecular frequency

(ν) and density (ρ) (Werner et al., 2008). From equation X, it is evident that relative thermal conductivity change under pressure is influenced by both the relative density change of the material under pressure as well as the intrinsic properties of the material represented by constant g.

In the absence of experimental ν values, g can be empirically determined by a simple linear regression between pressure dependent thermal conductivity and density. Using k values estimated in the current study and ρ values reported by Min et al. (2009), the estimated g values of 10% sucrose solution, soy protein isolate, soybean oil, honey and guacamole were 2.01, 1.54, 2.42, 2.23 and 2.33, respectively.

Among the liquid materials (soybean oil, honey and 10% sucrose solution), g was highest for soybean oil and lowest for honey. In addition, over the range pressure studied, relative density change of honey was lowest (Min et al., 2009), which may help explain the least relative increase in thermal conductivity of honey in the current study. Soybean had approximately the same relative density as that of 10% sucrose solution at 600 MPa, but higher g values. This may explain higher pressure dependency of thermal conductivity of soybean oil than sucrose solution.

Depending on the composition of protein, denaturation may take place at different pressure levels. Some protein fractions like β-lactoglobulin are denatured at pressure above 100 MPa but other show resistance to pressure treatment at higher pressure levels (Pfister et al., 2001). Thermal conductivity of 10% soy protein solution and cream cheese (~6% protein) before and after pressure treatment were similar indicating that

within the experimental conditions of the study pressure denaturation did not have significant effects on the measured properties.

5.3.3. Influence of pressure on thermal diffusivity

Pressure dependence of thermal diffusivity is presented in Figure 5.6. The results generally indicate a slight increase in thermal diffusivity with pressure. Among the tested food materials, soybean oil (from 0.075 x 10^{-6} to 0.118 x 10^{-6} m^2/s) and honey (from 0.091 x 10^{-6} to 0.122 x 10^{-6} m^2/s) had the lowest thermal diffusivity values. No significant change in thermal diffusivity was observed before and after pressure treatment at 600 MPa and 25^oC (data not shown). Cream cheese and guacamole had higher thermal diffusivity values, but lower than that of water and high moisture content foods (10% sucrose, tomato puree, 10% soy protein). Thermal diffusivity values estimated for cream cheese in this study (0.114-.145 x 10^{-6} m^2/s; from 0.1 MPa to 400 MPa at 25^oC) were similar to the values (~0.12-0.13 x 10^{-6} m^2/s, from 0.1 MPa to 350 MPa at 25^oC) reported for cheddar cheese by Zhu et al. (2007). The authors also reported a positive pressure dependency of thermal diffusivity following a second order polynomial.

5.3.4. Influence of pressure on volumetric specific heat

Volumetric specific heat showed only a slight pressure dependency (Figure 5.7). As both thermal conductivity and diffusivity increased with pressure (see Figure 5.5 & 5.6), the ratio between them (Eq. 5.7) become relatively pressure independent (Zhu et al., 2007). Contrary to the trend exhibited by the food substances, volumetric specific heat of glycerol was reportedly increased with pressure (Nilsson et al., 1986).

5.3.5. Influence of pressure on isobaric specific heat

Specific heat of the selected foods under pressure at 25 ^{o}C is given in Figure 5.8. Most of the food materials' specific heats decreased with increase in pressure. For example, specific heat of the 10% sucrose solution decreased from 4.08 KJ/kg ^{o}C to 3.31 KJ/kg ^{o}C when pressure increased from 0.1 to 600 MPa. The results were in agreement with Barbosa (2003) who also reported decrease in specific heat values for 10% sucrose solution from 3.95 KJ/kg ^{o}C to 3.64 KJ/kg ^{o}C over 600 MPa pressure increase. It is worth noting that guacamole samples showed an initial increase in C_p values up to 100 MPa and subsequently decreased with increasing pressure beyond 100 MPa (Figure 5.8), which may be attributed to entrapped air bubbles present in the sample during loading. Efforts were made to de-aerate the guacamole sample by applying vacuum, but it might not have removed all the entrapped air in the void spaces.

Bridgman (1913) evaluated the specific heat of 12 organic liquids under pressure and found an complex pressure and temperature dependence of specific heat. The specific heat at constant pressure (C_p) decreased in the relatively low pressure range and increased when pressure surpassed above a certain threshold limit. Bridgman attributed pressure dependency of specific heat to change of potential of attractive force between molecules, the association of molecules and partition of different components of internal energy with changing pressure (Bridgman, 1912).

Specific heat of food materials at 25^{o}C decreased with increase in pressure. This is contrary to temperature dependency of specific heat, which in general is reported to increase with increase in temperature (Kumar et al., 2008). More studies are needed to investigate the combined pressure-thermal effects on specific heat.

5.3.6. Prediction of thermal properties under pressure

Various regression coefficients of Eq. 5.9 relating the thermal properties as a function of pressure at 25^{o}C are tabulated in Table 5.2. It is interesting to note that while thermal conductivity of the food materials can be described by a linear equation, thermal diffusivity and isobaric specific heat followed 2nd or 3rd order polynomial relations. Care must be exercised not to extrapolate these empirical relationships outside the experimental range of this study (0.1 to 600 MPa at 25^{o}C).

5.3.7. Uncertainty analysis

Within the range of experimental conditions studied, thermal conductivity measurement had an uncertainty between 0.9-3.1%. Similarly the uncertainty associated with thermal diffusivity, volumetric specific heat, and specific heat were 2.6-6.8%, 3.4-6.6%, and 3.4-6.9%, respectively.

5.4. Conclusions

A dual needle probe was used successfully to measure in-situ pressure dependent thermal conductivity, thermal diffusivity, and specific heat values of selected food materials up to 600 MPa at 25^{o}C. Thermal conductivity of tested material increased linearly with increase in pressure. Thermal diffusivity in general increased with pressure and can be described by a second order polynomial equation. Specific heat of tested foods decreased as pressure increased up to 600 MPa.

The in-situ changes in the measured property values under pressure were temporary, and the values after depressurization returned to values close to initial values before pressurization. The data generated will be useful for the design of high pressure equipment and process optimization.

References

Abdulagatov, I. M., & Magomedov, U. B. (1994). Thermal conductivity of aqueous solutions of NaCl and KCI at high pressures. *International Journal of Thermophysics*, 15, 401– 413.

Barbosa, R.D. (2003). High pressure and temperature dependence of thermodynamic properties of model food solutions obtained from in-situ ultrasonic measurement. Dissertation. University of Florida.

Bridgman, W.P. (1912). Thermodynamic properties of liquid water to 80^{o} and 12,000 kgm. *Proceedings of American Academy of Arts and Sciences*, 48, 309-362.

Bridgman, W.P. (1913). Thermodynamic properties of twelve liquid between 20^{o} to $80\ ^{o}$ and up to 12,000 kgm. per sq. cm. *Proceedings of American Academy of Arts and Sciences*, 49, 3-114.

Bridgman, W.P. (1923). Thermal conductivity of liquids under pressure. *Proceedings of American Academy of Arts and Sciences*, 59, 141-169.

Bristow, K.L., Kluitenberg, G.J., & Horton, R. (1994). Measurement of soil thermal properties with a dual-probe heat-pulse technique. *Journal of American Society of Soil Science*, 58(5), 1288-1294.

Bubník, Z., Kadlec, P., Urban, D., Bruhns, M. (1995). Sugar Technologists Manual, Bartens, Berlin. p155.

Bundy, F.P. (1961). Effect of pressure on emf of thermocouples. *Journal of Applied Physics*, 32(3), 483-488.

Carslaw, H. S., & Jaeger, J. C. (1959). Conduction of heat in solids. S*econd ed*. New York: Oxford University Press, pp. 302, 340–341.

Choi, Y., & Okos, M.R. (1983). The thermal properties of tomato juice concentrates. *Transactions of the American Society of Agricultural Engineers*, 26(1), 305-311.

Choi, Y. (1985). Food property prediction as effected by temperature and composition. Dissertation. Purdue University.

Choi, Y., & Okos, M.R. (1986). Thermal properties of liquid foods-Review. In Physical and chemical properties of food, Okos, M.R. (Ed). American Society of Agricultural Engineers, Michigan, USA. pp35-77

Clark, P.E., Waldeland, C.R., & Cross, R.P. (1946). Specific heat of vegetable oils from 0^{o} to 280 ^{o}C. *Industrial and Engineering Chemistry*, 38, 350-353.

Dadarlat, D., Gibkes, J., Bicanic, D., & Pasca, A. (1996). Photopyroelectric (PPE) measurement of thermal parameters in foods products. *Journal of Food Engineering*, 30, 155-162.

Denys, S., & Hendrickx, M. (1999). Measurement of the thermal conductivity of foods at high pressure. *Journal of Food Science*, 64 (4), 709-713.

Harvey, A.H., Peskin, A.P., & Klein, S.A. (1996). NIST/ASME Standard Reference Database 10. Version 2.2, Boulder, Colo.: National Institute of Standards and Technology.

Kestin, J., Sengers, J. V., Kamgar-Parsi, B., & Levelt Sengers, J. M. H. (1984). Thermophysical properties of fluid H_2O. *Journal of chemical reference data*, 13, 175–183.

Kirup, L., & Frenkel, R.B. (2006). An introduction to uncertainty in measurement using the GUM (Guide to the expression of uncertainty in measurement), (pp. 35-161). Cambridge: Cambridge University Press.

Kumar, P., Coronel, P., Simunovic, J., Sandeep, K.P. 2008). Thermophysical and dielectric properties of salsa con queso and its vegetable ingredients at sterilization temperatures. *International Journal of Food Properties*, 11(1), 112-126

Lawson, A.W., Lowell, R., & Jian, A.L. (1959). Thermal conductivity of water at high pressures. *Journal of Chemical Physics*, 53, 643-647.

Lopez, J.A.B., Mandelis, A. (2003). Self-consistent photothermal techniques: Application for measuring thermal diffusivity in vegetable oils. *Review of Scientific Instruments*, 75(1), 700-702.

Incropera, F.P, & DeWitt, D.P. (1990). In Fundamentals of heat and mass transfer. John Wiley and Sons, Inc., NY.

Ingersoll, L.R., Zobell, O.J., & Ingersoll, A.C. (1954). Heat conduction with engineering and geological applications. McGrawHill:NewYork. pp 143-147.

Min, S.K. (2008). Properties of food and buffer solutions during high pressure processing: In-situ measurement of density, compressibility, electrical conductivity and reaction volume. Dissertation. The Ohio State University.

Min, S., Sastry, S.K, Balasubramaniam, V.M. (2009). Compressibility and density of select liquid and solid foods under pressures up to 700 MPa. *Journal of Food Engineering*, 96(4), 568-574.

Murakami, E.G., Sweat, V.E., Sastry, S.K., & Kolbe, E., Hayakawa, K., & Datta, A. (1996). Recommended design parameters for thermal conductivity probes for non-frozen food materials. *Journal of Food engineering*, 1, 93-113.

Narayama, K.B., & Murthy, M.V.K. (1981). Heat and mass transfer characteristics and the evaluation of thermal properties of moist food materials. *Transactions of the American Society of Agricultural Engineers*, 24(3), 789-793.

Niassar, M.S., Hozawa, M., & Tsukada, T. (2000). Development of probe for thermal conductivity measurement of food materials under heated and pressurized conditions. *Journal of Food Engineering*, 43, 133-139.

Nilsson, O., Sandberg, O., & Bäckström. (1986). dc-ac hot-wire procedure for determining thermophysical properties under pressure. *Review of Scientific Instrument*, 57(9), 2303-2309.

Nix, G.H., Lowery, G.W., Vachen, R.I., & Tanger, G.E.. (1967). Direct determination of thermal diffusivity and conductivity with a refined line-source technique. In: Progress in astronautics and aeronautics, Heller, G.G. (Ed). Academic Press, New York, pp. 113–116.

Nix, G.H., Vachon, R.I., Lowery, G.M., & McCurry, A.T. (1969). The line-source method: procedure and iteration scheme for combined determination of conductivity and diffusivity. *Proceedings of 18th Conference on Thermal Conductivity*, 999-1008

Otero, L., & Sanz, P.D. (2003). Modeling heat transfer in high pressure food processing: a review. *Innovative Food Science and Emerging Technologies*, 4, 121-134.

Pfister, M.K.H., Butz, P., Heinz, V., Dehne, L.I., Knorr, D., & Tauscher, B. (2001). Influence of high pressure treatment on chemical alterations in foods. A literature review. Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin, Tabellen, Berlin.

Povey, M.J.W. (1998). Ultrasonics of food. *Contemporary Physics*, 39(6), 467-478.

Ramaswamy, R., Balasubramaniam, V.M., Sastry, S.K (2007). Thermal conductivity of selected liquid foods at elevated pressures up to 700 MPa. *Journal of Food Engnieering*, 83(3), 444-451.

Riedel, L. (1949). Thermal conductivity measurement on sugar solutions, fruit juices and milk. Chemie-Ingenieur-Technik, 21(17), 340-341.

Safarov, M. M., Usupov, S. T., & Tagoev, S. A. (1999). Thermophysical properties of vegetable oils in a wide range of temperatures and pressures. *High Temperature High Pressure*, 31, 43-48.

Short, B.E., & Bartlett, L.H. (1944). The specific heat of foodstuffs. The University of Texas, Publication No. 4432. Engineering Research Series No. 40.

Sopade, P.A., Halley, P.J., & D'Arcy, B.R. (2006). Specific heat capacity of Australian honeys from 35 to 165^{o}C as a function of composition under differential scanning calorimetry. *Journal of Food Processing and Preservation*, 30, 99-109.

Sweat, E.V., & Parmelee, C.E. (1978). Measurement of thermal conductivity of dairy products and margarines. *Journal of Food Process Engineering*, 2, 187–197.

Sweat, V.E. (1986). Thermal properties of foods. In Rao, M.A., & Rizvi, S.S.H. (Eds), Engineering properties of foods. Marcel Dekker, NewYork, 49-87.

Taylor, B. & Kuyatt, C. (1994). Guidelines for evaluating and expressing uncertainty of NIST measurement results. NIST Technical Note, 1297.

Touloukian, Y.S., Liley, P.E., & Saxena, S.C. (1970). Thermophysical properties of matter, Vol. 3: Thermal conductivity, nonmetallic liquids and gases. IFI/Plenum, New York.

Werner, M., Baars, A., Werner, F., Eder, C., Delgado, A. (2007). Thermal conductivity of aqueous solutions under high pressure. *International Journal of Thermophysics*, *28*, 1161-1180.

Werner, M., Baars, A., Eder, C., Delgado, A. (2008). Thermal conductivity and density of plant oils under high pressure. *Journal of Chemical Engineering Data*, 53, 1444-1452.

Zhu, S., Ramaswamy, H.S., Marcotte, M., Chen., Shao, Y., & Le Bail, A. (2007). Evaluation of thermal properties of food materials at high pressures using a dual-needle line heat source method. Journal of Food Science, 72(2), E49-E56.

Zhu, S., Marcotte, M., Ramaswamy, H., Shao, Y., & Le-Bail, A. (2008). Evaluation and comparison of thermal conductivity of food materials at high pressure. *Food and Bioproduct Processing*, 86, 147-153.

Food materials	Experimental values			Published values		
	k (W/m ^{o}C)	α (10^{6} m^{2}/s)	C_p* (kJ/kg ^{o}C)	k (W/m ^{o}C)	α (10^{6} m^{2}/s)	C_p (kJ/kg ^{o}C)
10% Sucrose	0.557	0.131	4.081	0.607 [ref1e], 0.566 [ref2b]	0.133 [ref3h]	3.952 [ref4e], 3.936 [ref5a]
10% Soy protein	0.515	0.130	3.791	n/a	n/a	n/a
Soybean oil	0.173	0.075	2.531	0.165-0.178 [ref6b], 0.174 [ref7c], 0.23 [ref8d]	0.140 [ref8d], 0.089-0.090 [ref9f]	1.918 [ref10b], 1.930 [ref11c]
Honey	0.324	0.091	2.424	0.380-0.40 [ref12e]	n/a	1.88-2.34 [ref13i]
Tomato puree	0.544	0.136	3.910	0.596 [ref14h]	0.144 [ref14h]	4.052 [ref14h]
Guacamole	0.414	0.126	3.154	n/a	n/a	n/a
Cream cheese	0.347	0.115	2.996	0.380 [ref15b]	n/a	n/a
Glycerol	0.296	0.094	2.497	0.283 [ref16d], 0.288 [ref17d], 0.286 [ref18g]	0.092 [ref16d], 0.935 [ref18g]	2.439 [ref16]*, 2.427 [ref18g]

[ref1]: Bubnik et al., 1995; [ref2]: Riedel, 1949; [ref3]: Narayana et al., 1981; [ref4]: Barbosa, 2003; [ref5]: Short et al., 1944; [ref6]: Werner et al., 2008; [ref7]: Choi, 1985; [ref8]: Dadarlat et al., 1996; [ref9]: Lopez et al., 2003; [ref10]: Clark et al., 1946; [ref11]: Safarov et al., 1999; [ref12]: Ramaswamy et al., 2007; [ref13]: Sopade et al., 2006; [ref14]: Choi et al., 1983; [ref15]: Sweat et al., 1978; [ref16]: Nilsson et al., 1986; [ref17]: Toloukian et al., 1970; [ref18]: Incropera et al., 1990

[a]: 0-26 ^{o}C; [b]: 20 ^{o}C; [c]: 21^{o}C; [d]: room temperature; [e]: 25 ^{o}C; [f]: 26 ^{o}C; [g]: 27 ^{o}C; [h]: 30 ^{o}C; [i]: 35 ^{o}C

*: calculated from k, α and density values at atmospheric pressure

n/a: not available in literature

Table 5.1. Measured and published values of thermal conductivity, diffusivity and specific heat of selected food material at atmospheric pressure and 25^{o}C.

Food materials	a_0	a_1	a_2	a_3	R^2
Thermal conductivity					
10% sucrose	0.560	0.0003	-	-	0.98
Tomato puree	0.531	0.0003	-	-	0.96
10% soy protein isolate	0.515	0.0002	-	-	0.99
Guacamole	0.421	0.0002	-	-	0.97
Cream cheese	0.363	0.0002	-	-	0.95
Honey	0.329	0.0001	-	-	0.95
Soy bean oil	0.177	0.0001	-	-	0.99
Thermal diffusivity					
10% sucrose	0.129	0.0002	-0.0000001	-	0.99
Tomato puree	0.130	0.0001	-0.00000006	-	0.85
10% soy protein isolate	0.128	0.0001	-0.00000006	-	0.83
Guacamole	0.122	0.00007	-0.00000002	-	0.83
Cream cheese	0.111	0.00006	0.00000002	-	0.92
Honey	0.093	0.000001	0.00000008	-	0.95
Soy bean oil	0.077	0.00002	0.00000008	-	0.94
Specific heat					
10% sucrose	4.116	-0.0034	0.000004	-	0.94
10% soy protein isolate	3.844	-0.0023	0.000002	-	0.78
Guacamole	3.190	0.0025	-0.00001	0.00000001	0.75
Honey	2.432	0.00007	-0.000001	-	0.96
Soy bean oil	2.493	-0.000008	-0.000001	-	0.83

Table 5.2. Coefficients of regression equation (Eq. 5.9) for thermal conductivity, thermal conductivity, diffusivity and isobaric specific heat of selected food materials under pressure at 25°C.

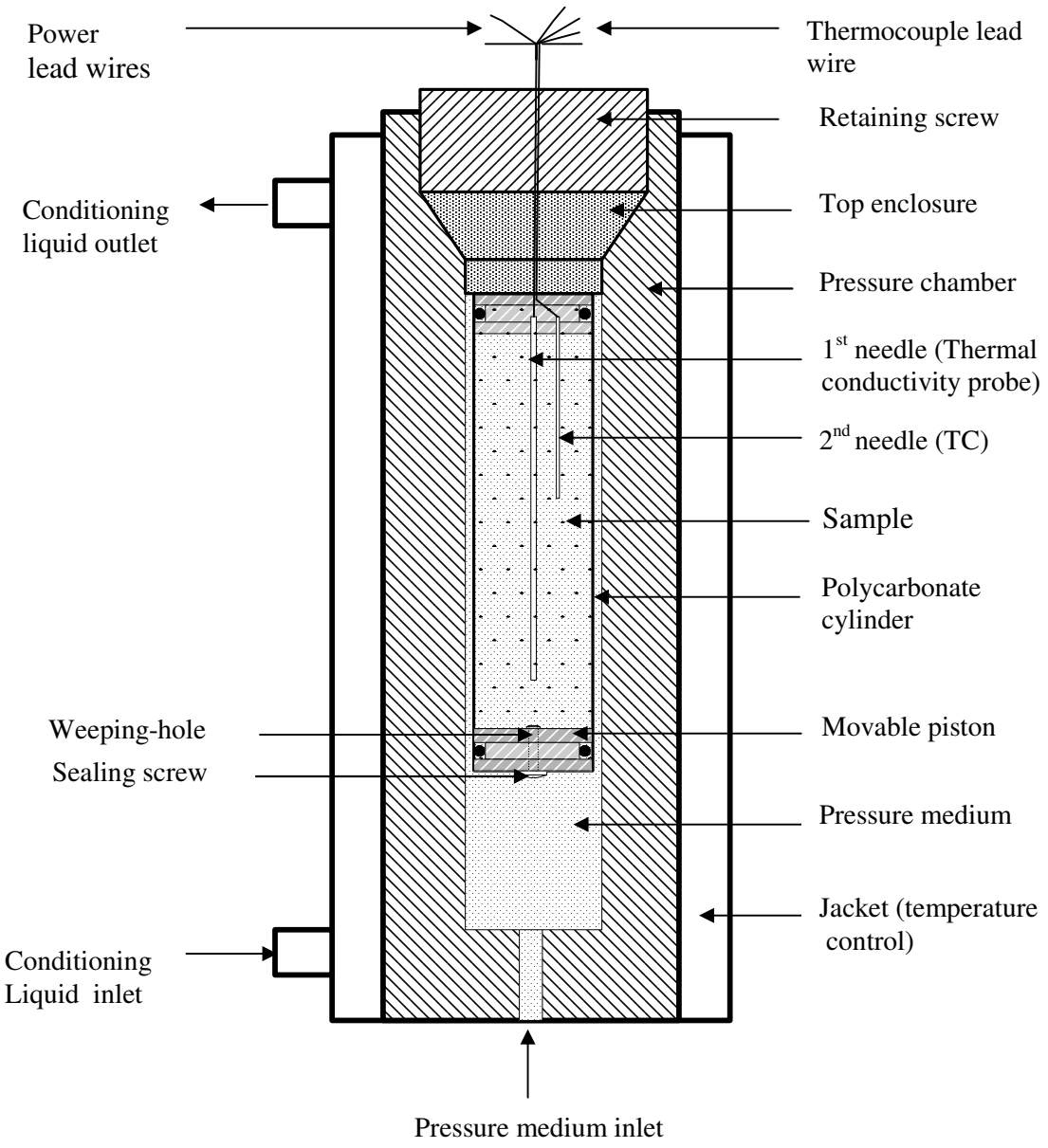


Figure 5.1. Schematic diagram of the experimental setup showing the pressure chamber, sample holder and dual needle probe used for the determination of thermal conductivity, diffusivity and specific heat.

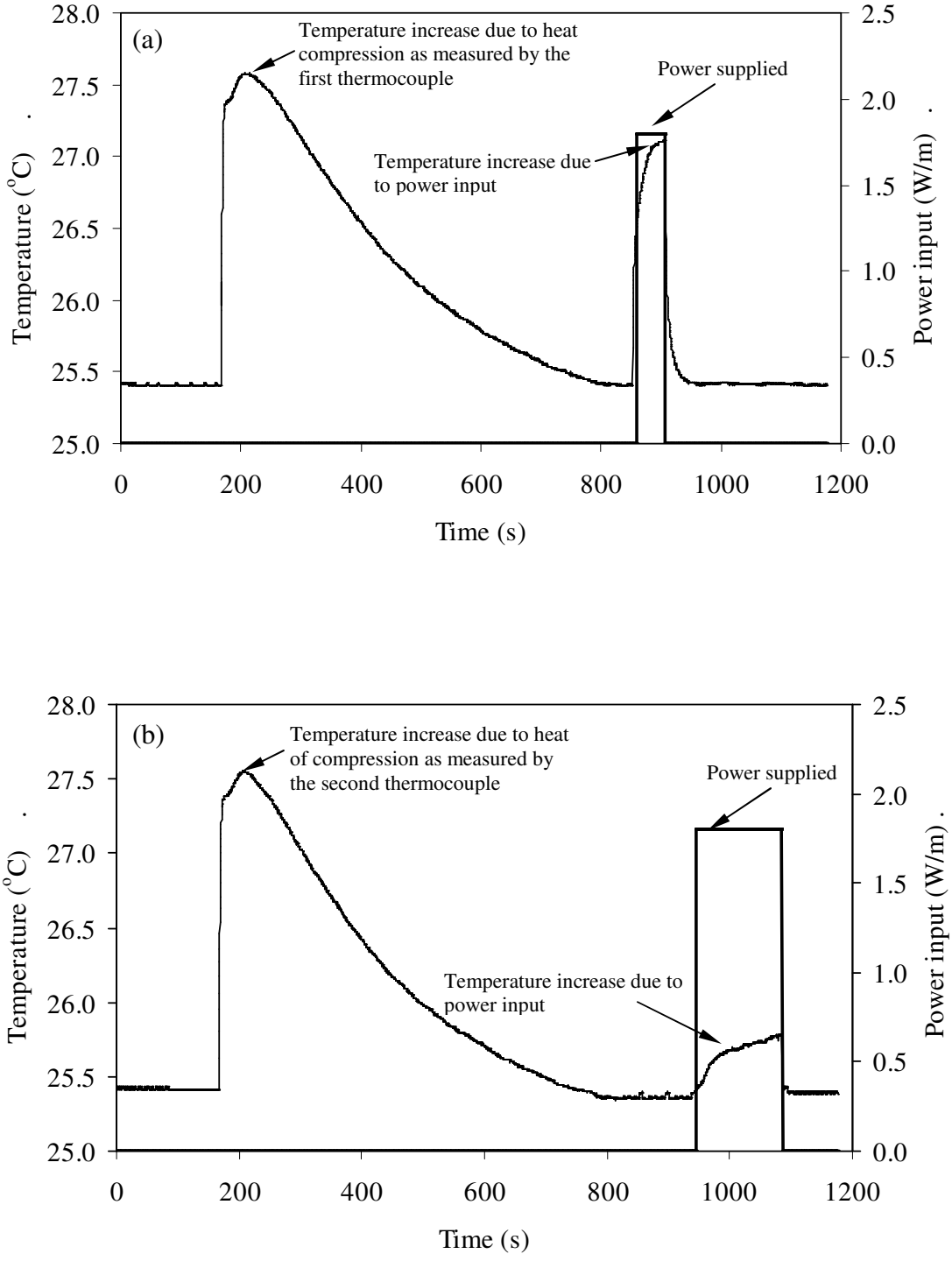


Figure 5.2. Typical time-temperature history of the test samples during the estimation of thermal conductivity (a) and diffusivity (b) under pressure.

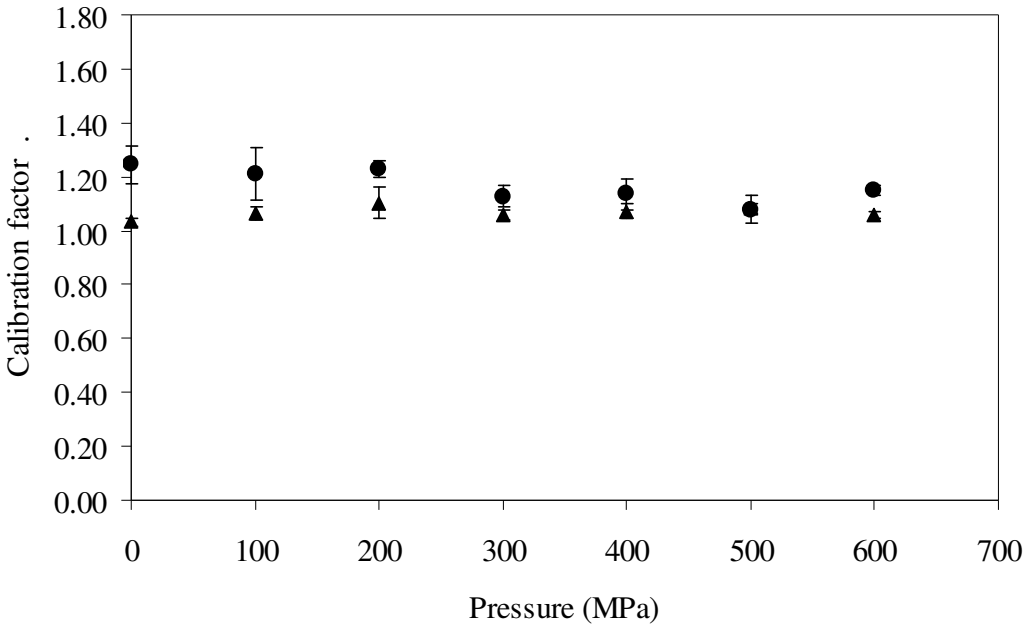


Figure 5.3. Probe specific calibration factors for thermal conductivity and diffusivity up to 600 MPa at 25°C. Water was used as the calibration fluid and the experimental data were compared against published NIST data (Harvey et al., 1996). (▲) Thermal conductivity; (●) Thermal diffusivity.

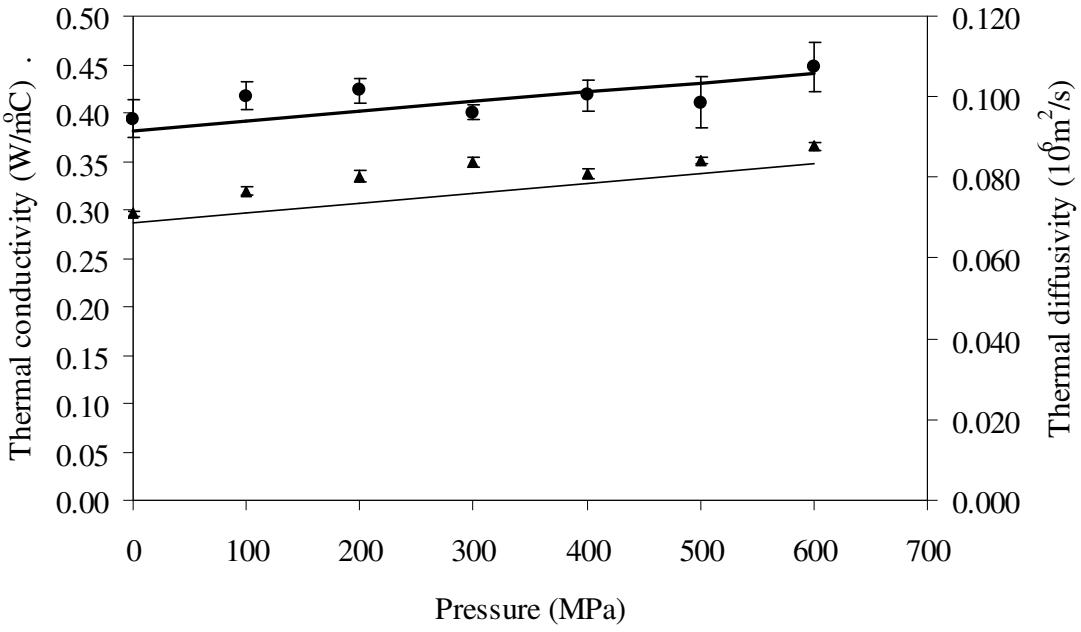


Figure 5.4. Comparison of experimentally measured thermal conductivity and diffusivity values of glycerol against those reported by Nilsson et al. (1986). (——) Reported thermal conductivity; (▲) Measured thermal conductivity; (——) Reported thermal diffusivity; (●) Measured thermal diffusivity.

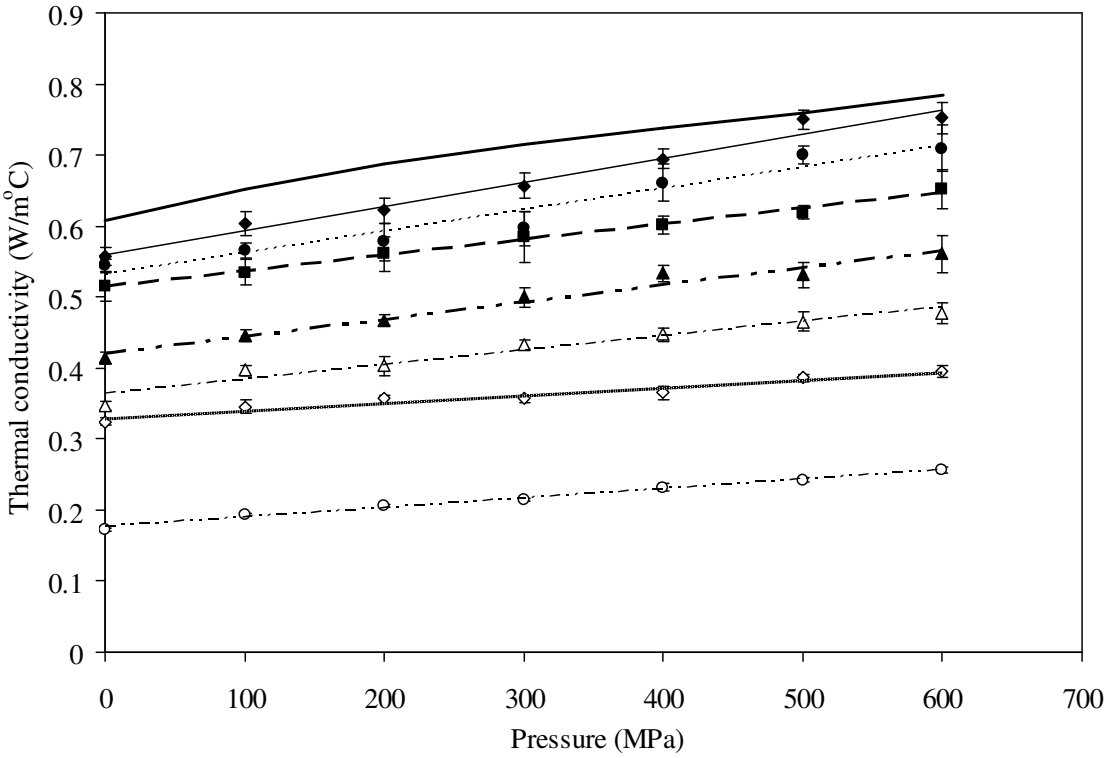


Figure 5.5. Thermal conductivity of selected foods under pressure at 25°C. Error bar indicated mean ± standard deviation. (———) Water (NIST); (◆) 10% Sucrose; (●) Tomato puree; (■) 10% soy protein isolate; (▲) Guacamole; (△) Cream cheese; (◇) Honey; (○) Soybean oil; (——) Fitted line (10% sucrose); (- - - -) Fitted line (Tomato puree); (— —) Fitted line (10% soy protein isolate); (— · ·) Fitted line (Guacamole); (— · — ·) Fitted line (Cream cheese); (▪▪▪▪▪▪▪▪) Fitted line (Honey); (— · · —) Fitted line (Soybean oil).

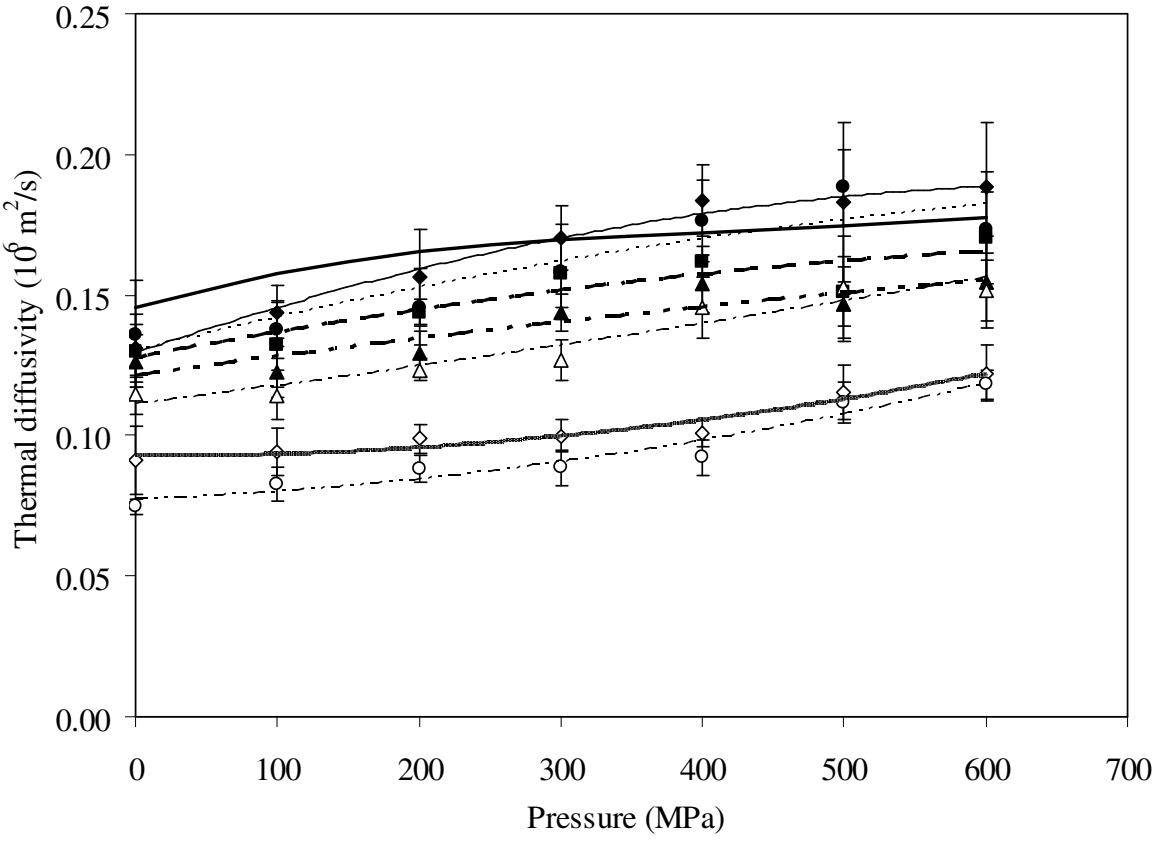


Figure 5.6. Thermal diffusivity of selected foods under pressure at 25°C. Error bar indicated mean ± standard deviation. (———) Water (NIST); (◆) 10% Sucrose; (●) Tomato puree; (■) 10% soy protein isolate; (▲) Guacamole; (△) Cream cheese; (◇) Honey; (○) Soybean oil; (———) Fitted line (10% sucrose); (- - - -) Fitted line (Tomato puree); (— —) Fitted line (10% soy protein isolate); (— · ·) Fitted line (Guacamole); (— · — ·) Fitted line (Cream cheese); (▪▪▪▪▪▪▪▪▪) Fitted line (Honey); (— · · —) Fitted line (Soybean oil).

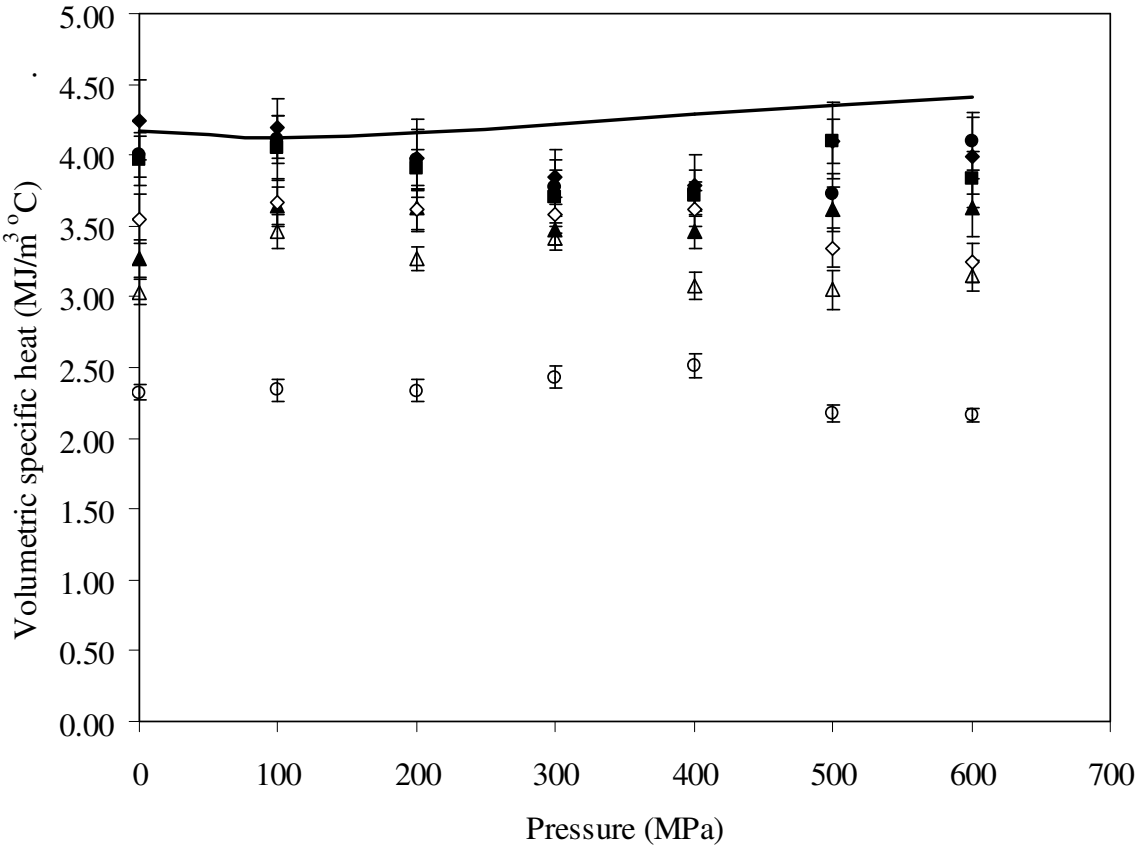


Figure 5.7. Volumetric specific heat of selected foods under pressure at 25°C. Error bar indicated mean ± combined standard uncertainty. (——) Water (NIST); (◆) 10% sucrose; (●) Tomato puree; (■) 10% soy protein isolate; (▲) Guacamole; (△) Cream cheese; (◇) Honey; (○) Soybean oil.

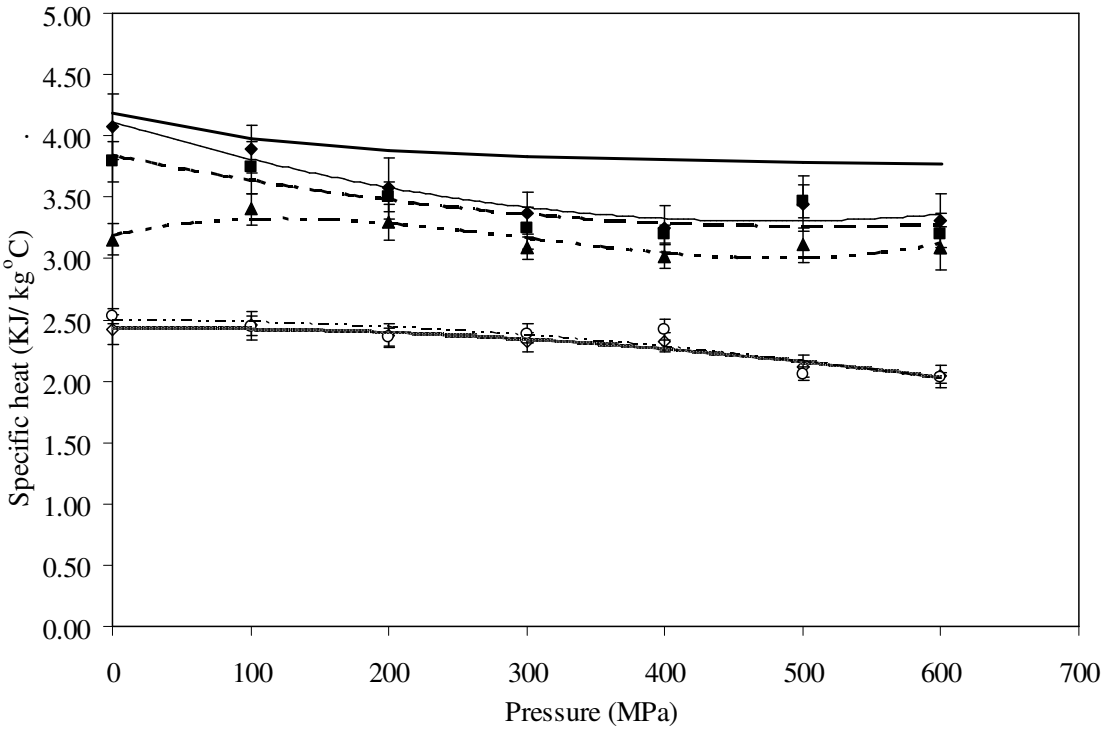


Figure 5.8. Specific heat of selected foods under pressure at 25°C. Error bar indicated mean ± combined standard uncertainty. (———) Water (NIST); (◆) 10% sucrose; (■) 10% soy protein isolate; (▲) Guacamole; (◇) Honey; (○) Soybean oil; (———) Fitted curve (10% sucrose); (— —) Fitted curve (10% soy protein isolate); (— · ·) Fitted curve (Guacamole) ; (▪▪▪▪▪▪▪▪▪) Fitted curve (Honey); (— · · —) Fitted curve (Soybean oil).

Chapter 6: Estimation of Accumulated Lethality under Pressure-Assisted Thermal Processing

Abstract

Pressure-assisted thermal processing (PATP) involves combined application of pressure and heat where both pressure and temperature contribute to spore lethality. A study was conducted to develop an integrated process lethality model taking into consideration the lethal contribution of both pressure and heat on spore inactivation. Assuming the momentary inactivation rate was dependent on survival ratio and momentary pressure-thermal history, a differential equation was formulated and numerically solved using Rung-Kutta method. Published data on combined pressure-heat inactivation of *Bacillus amyloliquefaciens* spores were used to obtain model kinetics parameters that considered both pressure and thermal effects. The model was experimentally validated under several process scenarios using a pilot scale high pressure food processor. Using first order kinetics in the model resulted in overestimation of log reduction compared to experimental values. When the n^{th} order kinetics was used, computed accumulated lethality and the log reduction values were found to be in reasonable agreement with experimental data. Within the experimental conditions

studied, spatial variation in process temperature resulted up to 3.5 log variation in survivors between top and bottom of the carrier basket. Predicted log reduction of *B. amyloliquefaciens* spores in deinoized water and carrot paste had satisfactory accuracy (1.074-1.117) and regression coefficients (0.92-0.83). Under comparable process condition, log reduction was approximately similar for single- and double-pulse pressure treatment. The developed model can be a useful tool to examine the effect of combined pressure-thermal treatment on bacterial spore lethality and assess PATP microbial safety.

Key words: Pressure assisted thermal processing, accumulated lethality, process non-uniformity, bacterial spores, F-value.

6.1. Introduction

Pressure treatment at ambient temperature has been proven to be a viable alternative pasteurization method for the inactivation of vegetative bacteria, viruses, and yeasts (Farkas and Hoover, 2000; Smelt, 1998). However, the bacterial spores cannot be inactivated by pressure alone at ambient temperature even up to 1500 MPa (Sale et al., 1970; Maggi et al., 1996). Pressure in combination with heat is needed for bacterial spore inactivation. Pressure-assisted thermal processing (PATP), also known as pressure-assisted thermal sterilization (PATS), involves combined pressure (500-900 MPa) and heat (90-120°C) treatment for the inactivation of bacterial spores (Gola et al., 1996; Rovere et al., 1998; Heinz et al., 2001; Ananta et al., 2001; Reddy et al., 2003; Koutchma et al., 2005; Rajan et al., 2006a,b; Patazca et al., 2006; Black et al., 2007; Bull et al., 2009; Akhtar et al., 2009). In Feb. 2009, Food and Drug Administration (FDA) has approved the filing of pressure-assisted thermal sterilization (PATS) processes for production of low acid foods (http://www.foodprocessing.com/vendornews/2009/019.html).

Sterilization process equivalent time (F-value) has been traditionally used to establish thermal processes (Pflug, 1995). It represents the equivalent time at a specified temperature delivered to a container or unit of product for the purpose of sterilization. The target F-value depends on both the required level of safety and the heat resistance of the target spore.

Thermal process calculations normally assume that bacterial destruction follows first order kinetics (Eq. 6.1).

$$\log S(t) = \log\left(\frac{N}{N_0}\right) = \frac{-t}{D} \qquad (6.1)$$

Where S(t) is the momentary survival ratio; N represents the number of spore survivors after treatment time t (min), while N_0 is the initial spore population. D is decimal reduction time (min). D value can also serve as the indicator of the thermal sensitivity of the studied microorganism.

Bigelow's general method (Bigelow et al., 1921) has been used for calculating lethal rate (LR) during thermal process (Eq. 6.2)

$$LR = 10^{\frac{(T-T_0)}{z}} \tag{6.2}$$

where T_0 = reference temperature, ^oC (normally 121.1^oC); z = thermal resistance constant, ^oC; T = process temperature, ^oC at any time during thermal process. Integrating lethal rate over process time can be used to determine sterilization process equivalent time (accumulated process lethality), F_T.

$$F_T = \int 10^{-\frac{T-Tref}{z}} dt \tag{6.3}$$

The sterilization process equivalent time calculated at 121.1°C is termed as F_0 (Pflug, 1995). Corradini et al. (2006) pointed out that thermal death time calculated by Eq. 6.3 and relevant relations were only valid when both isothermal survival curve and temperature dependence of D is log linear.

During PATP, both pressure and temperature can contribute to spore lethality. The decimal reduction time (D) and process resistance constant (z) become a function of both pressure and temperature. Various researchers (Ananta et al., 2001; Rajan et al., 2006a; Margosch et al., 2004a; Margosch et al., 2006, Ahn et al., 2007) further observed that during PATP, bacterial spores do not always follow the first order kinetics. In

addition, F-value had to include pressure come-up time when transient pressure and temperature was observed. Researchers (Margosh et al., 2004b; Ahn et al., 2007) reported measurable fraction of spores was inactivated during pressure come-up time.

Various researchers attempted to use F-value concept to compare the benefits of PATP in preserving quality of foods against thermal processing (Leadley et al., 2008) or process efficacy of different PATP conditions (Koutchma et al., 2005, Bull et al., 2009). In the absence of kinetics data of the target spore as a function of pressure and temperature, F-value was often calculated utilizing only thermal history and ignoring the lethal effect of pressure (Leadley et al., 2008; Bull et al., 2009). Development of a model taking both pressure and temperature lethal contribution into account will facilitate exploring process microbial safety under different processing scenarios. The objective of this study was to develop a model for determining accumulated lethality during PATP, considering the combined effects of pressure and temperature on spore inactivation.

6.2. Materials and methods

6.2.1. Model development

Figure 6.1 summarized various stages in the development of an accumulated PATP process lethality model. The model was developed with the following assumptions:

1. Momentary inactivation rate $\frac{d(\log S(t))}{dt}$ depended only on the momentary surviving ratio $\log S(t)$, process temperature and pressure.
2. Inactivation curves followed respective linear or non-linear kinetics within the range of temperature and/or pressure considered.

3. There was no injury, repair or growth of bacterial spores during PATP.
4. Only the pressure and temperature contributed to process lethality. Process lethality occurred above a minimum threshold pressure (>500 MPa) and temperature (> 90°C) for the inactivation of *B. amyloliquefaciens* spores. This threshold level may be different for different bacterial spores. The potential contribution of transient pH shift to lethality under pressure was not considered.

where $S(t)= N/N_0$; N_0 and N are the initial number of spore population and the spore survivors at any given process time t, respectively. The model considered both linear (Eq. 6.1) and non-linear (Eq. 6.4) inactivation kinetics for calculating accumulated process lethality.

For non-linear kinetics, a general n^{th} order kinetic model (Margosch et al., 2006) was chosen and can be described by:

$$\frac{dN}{dt} = -k\, N^{n} \tag{6.4}$$

Analytical solution of Eq. 6.4 can be presented as:

$$\log \frac{N}{N_0} = \log \left(1 + k\ t\ N_0^{n-1}(n-1)\right)^{\frac{1}{1-n}} \tag{6.5}$$

where k is the rate constant and n is the reaction order. Kinetics parameter $k_{T,P}$ can be expressed as a function of process temperature and pressure based on thermodynamic equations (Hawley, 1971):

$$\begin{aligned} \ln k_{T,P} &= a_0 \frac{1}{T} + a_1 \frac{(P-P_0)^2}{T} + a_2 \frac{(P-P_0)(T-T_0)}{T} \\ &+ a_3 \frac{1}{T}\left[T\left(\ln \frac{T}{T_0} - 1 \right) + T_0 \right] + a_4 \frac{P-P_0}{T} + a_5 \frac{T-T_0}{T} \end{aligned} \tag{6.6}$$

Similarly, the reaction order, $n_{T,P}$, can be related to pressure and temperature:

$$n_{T,P} = a_0 + a_1 P + a_2 T + a_3 P^2 + a_4 T^2 + a_5 PT \qquad (6.7)$$

For linear kinetics, Eq. 6.1 was selected. The decimal reduction time ($D_{T,P}$) in Eq. 6.1 was related to pressure and temperature by an empirical equation:

$$D_{T,P} = 10^{(a_0 + a_1 P + a_2 T + a_3 P^2 + a_4 T^2 + a_5 PT)} \qquad (6.8)$$

6.2.2. Computation of accumulated process lethality

Limited authors have reported combined pressure-thermal inactivation kinetics data under iso-thermal and iso-baric process conditions (Patazca et al., 2006; Rajan et al., 2006a, Ahn et al., 2007; Margosh et al., 2006). For any unknown arbitrary PATP process with dynamic or static pressure and temperature conditions, the corresponding accumulated lethality and inactivation curve can be constructed from several discrete iso-thermal and iso-baric processes. A similar approach has been used during thermal processing by earlier researchers (Campanella et al., 2001; Corradini et al., 2006).

The momentary inactivation rate $\frac{d(\log S(t))}{dt}$ at a specified instant during any arbitrary pressure-temperature history was assumed to be equal to that of an isothermal-isobaric process having the same pressure and temperature values:

$$\frac{d \log S(t)}{dt} = \left[\frac{d \log S(t^*)}{dt^*}\right]_{T,P} = -\frac{k\, N_0^{(n-1)}}{2.303\,(1 + k\, t^*\, N_0^{n-1}(n-1)} \qquad (6.9)$$

where t* is the treatment time of a isothermal-isobaric process at which the momentary surviving ratio S is equal to that of the arbitrary process. Momentary surviving ratio for the arbitrary process and the isothermal-isobaric process can be related as:

$$\log S(t) = \log S(t^*) = \log \left(1 + k_{T,P}\, t^* N_0^{(n_{T,P}-1)} (n_{T,P}-1)\right)^{\left(\frac{1}{1-n_{T,P}}\right)} \qquad (6.10)$$

From Eq. 6.10, the treatment time t* of isothermal-isobaric process was extracted and substituted in Eq. 6.9. Then, the momentary inactivation rate $\frac{d(\log S(t))}{dt}$ can be described as a function of the time (t) of the arbitrary process considered

$$\frac{d \log S(t)}{dt} = -\frac{k_{T,P}\, N_0^{(n_{T,P}-1)}\, 10^{(n_{T,P}-1)\log S(t)}}{2.303} \qquad (6.11)$$

Similarly, the differential equation for linear kinetics (Eq 6.1) was expressed as below:

$$\frac{d \log S(t)}{dt} = -\frac{1}{D_{T,P}} \qquad (6.12)$$

For any arbitrary process, knowing the pressure-temperature history, the corresponding inactivation curve was constructed by solving the differential equation (Eq. 6.11) using Rung-Kutta method (Matlab, Version 7.1.0246, Matworks Inc, MA). Once the inactivation curve was constructed, the accumulated lethality can be calculated from a known surviving ratio:

$$F_0 = \log S(t) D_{121.1C,\,0.1MPa} \qquad (6.13)$$

6.2.3. Experimental validation of the model

6.2.3.1. Iso-thermal and Iso-baric kinetics data

B. amyloliquefaciens spores are among the most pressure-temperature resistant spores than some of the traditional surrogates such as *Geobacillus stearothermophilus* and *Clostridium sporogenes* (Black et al., 2007; Ahn et al., 2007; Margosch et al., 2006).

Accordingly, experimental data on PATP inactivation of *B. amyloliquefaciens* spores suspended in egg patty as a function of pressure and temperature (Rajan et al., 2006a) was used for the estimation n^{th} order kinetics parameters ($k_{T,P}$, $n_{T,P}$) and linear kinetics parameter $D_{T,P}$ by non-linear regression (Matlab, Version 7.1.0246, Matworks Inc, MA). The values of regression coefficients of Eq. 6.6, 6.7 and 6.8 were given in Table 6.1.

In addition, using the model, the accumulated lethality and the corresponding log reduction under various process conditions presented by Rajan et al. (2006a) were also determined.

6.2.3.2. Inoculated sample preparation

Spores of *B. amyloliquefaciens* TMW 2.479 Fad 82 were used for validation experiment. The spore suspension was prepared by adapting the procedures described elsewhere (Rajan et al., 2006a). Decimal reduction time values, $D_{105C,\ 0.1\ MPa,}$ $D_{105C,\ 600\ MPa}$ of the prepared spore crop in deionized water (DIW) were about 28.1 and 0.84 min, respectively. This spore crop had slightly higher resistance than those reported by Rajan et al. (2006a). Rajan et al. (2006a) reported $D_{105C,\ 0.1\ MPa,}$ $D_{105C,\ 600\ MPa}$ values as 24 min and 0.72 min, respectively. Differences in preparation of spore media, and food matrices might have influenced these values.

Spore samples were inoculated into DIW and carrot paste (CP). For spore inoculated in DIW sample, 0.2 ml of *B. amyloliquefaciens* spore suspensions (~10^9 spores/ml) was added to 1.8 ml DIW and the aliquot was aseptically transferred into a pouch (polyethylene bags, 5.0 x 2.5 cm, no. 01-002-57, Fisher Scientific). The final spore

concentration was about 1.4 x 10^8 spores per ml. The sample pouches were then sealed using an Impulse heat sealer (American International Electric, Whittier, CA, USA). The sealed pouches were kept in ice-water bath until experiment was conducted.

For inoculated CP samples were prepared as follows. Shelf-stable carrot paste (pH = 5.2, a_w= 0.935) (Gerber products Co, Fremont, MI) was purchased from local grocery store. Sample of CP (1.8 g) and 0.2 ml of spore suspension were placed inside a pouch (polyethylene bags, 50 x 25 mm, no. 01-002-57, Fisher Scientific) and heat sealed (Impulse Food Sealer, American International Electric, Whittier, CA). The final spore concentration was about 1.1 x 10^8 spores per g of CP. The content was then mixed thoroughly and samples were kept in ice-water batch before experiment.

6.2.3.3. Pressure-assisted thermal processing experiments for model validation

Experiments were carried out using a pilot scale (Iso-lab high pressure food processor S-IL-110-610-08-W, Stansted Fluid Power Ltd, Essex, UK). The cylindrical pressure chamber had an internal diameter of 110 mm and 610 mm height. Propylene glycol (Brenntag Mid-South Inc., St. Louis, MO) was utilized as the pressure transmitting medium. The system had ability to adjust the compression and decompression rates. Pressurization and depressurization rates at ~6.5 MPa/s and ~8.3 MPa/s, repectively were used. To maintain iso-thermal process conditions during the treatment, the external jacket of the pressure chamber was kept at 105^{o}C and the test samples were preheated to certain initial temperature (~75^{o}C). Subsequently, using adiabatic heat of compression, the samples reached the desired process temperature.

Inside the pressure chamber, samples were loaded into a cylindrical stainless steel carrier basket (95 mm dia, 590 mm length) (FPG 11650.110, Stansted Fluid Power Ltd, Essex, UK). The equipment had provisions for monitoring the temperature at three different spatial locations of the carrier basket using T-type thermocouple. Additional details of the experimental setup are reported previously (Nguyen et al., 2009).

The inoculated pouch sample as well as a dummy sample pouch for temperature monitoring were placed together inside a larger pouch (70 mm x 140 mm) filled with DIW. Temperature inside the dummy pouch during experiments was monitored using calibrated a T-type thermocouple (Omega engineering, CT, USA). Thermocouple wire junctions were welded together using TC welder (Hotspot, DCC Corporation, Pennsauken, NJ). The thermocouple was fed through the pouch using a C-5.2 stuffing box (Ecklund-Harrison Technologies, Fort Myers, FL) (Figure 6.2). The pressure-temperature data was collected every second using data acquisition system (Scan1000 v4.4.67, Hexatec Solutions Ltd., Northumberland, UK). The large pouch containing inoculated sample and dummy sample pouch for temperature measurement were mounted within the carrier basket using a custom made sample rack. The larger pouch along with the carrier basket containing the pressure transmitting fluid was preheated to certain initial temperature (~75^{o}C) before loading into the high pressure vessel (Nguyen et al., 2009).

The following PATP experiments were conducted to evaluate the model performance for predicting accumulated lethality:

1. *Predicting the effects of sample spatial variation during PATP treatment*

Samples were mounted within the carrier basket at the geometric center in three different (top, middle and bottom) positions, 286 mm apart, to evaluate the spatial variation effects. Samples were processed at 600 MPa for 5 min at a target process temperature of 105^{o}C. Food matrix effects were evaluated with DIW and CP samples. Each of the PATP experiments was independently repeated three times.

2. *Predicting the effects of pressure pulsing*

   Additional experiments were carried out to compare the model performance in predicting the efficacy of single and double pulse treatment. Single pulse experiments were performed at 600 MPa, 105^{o}C for 5 min. Double pulse experiments utilized the same process conditions (600 MPa, 105^{o}C), but the holding time for each pulse was kept at 2.5 min. The pulse interval between two pulses was about 10 s. To minimize the number of experiments, middle loading position was used for loading samples for double pulse experiments. Three independent runs were conducted for each process condition.

6.2.3.4. Enumeration of surviving spores from the treated samples

Treated spore samples were immediately cooled in ice-water mix and enumerated within 3 hours after processing. For CP samples, the 2 ml-treated sample was mixed with 18 ml of 0.1 % peptone water and homogenized for 2.5 min in a stomacher at 230 rpm (Seward Lab Stomacher, Norfolk, UK. The 1 ml of sample contents (DIW sample) or aliquot (CP sample) were serially diluted in 9 ml of 0.1% peptone water and then pour plated on Trypticase soy agar (TSA). After incubated at 32 ^{o}C for 48 h, the viable count

of the surviving spores were enumerated. Colonies were counted with a dark-field Quebec colony counter (Leica Microsystems, Richmond Hill, Ontario, Canada). The detection limit for the enumeration procedure was 10 colony forming units (CFU) per g or ml of food matrix.

6.2.3.5. Evaluating the model performance

The developed model was used to predict log reduction, using specified pressure-temperature history of the experimental conditions. Subsequently, knowing corresponding experimentally observed log reduction values, the model performance was evaluated base on mean square of error (MSE), R^2 and accuracy factor (A_f) (Chen and Hoover, 2003; Rajan et al., 2006a).

$$MSE = \frac{\sum (\text{predicted} - \text{observed})^2}{n} \tag{6.14}$$

$$A_f = 10^{\frac{\sum |\log(\text{predicted/observed})|}{n}} \tag{6.15}$$

In which the model capable of yielding good prediction should have small MSE, A_f, and high R^2 values.

6.3. Results and discussions

Preliminary tests were conducted to evaluate the accuracy of the developed model in predicting PATP lethality using published literature. Figure 6.3A presents predicted vs published data (from Rajan et al. 2006) of the log reduction for various PATP conditions. The model predictions utilized both linear and n^{th} order inactivation kinetics. As evident from these figures, n^{th} order kinetics better predicted the log reduction during PATP treatment, while linear kinetics overestimated PATP log reductions especially with

increasing pressure holding times. Similarly, predicted log reduction by n^{th} order model was more close to experimental values for non-isothermal condition (Figure 6.3B). Therefore, the accumulated lethality presented in subsequent sections was only based on n^{th} order inactivation kinetics.

6.3.1. Sample pressure-temperature history during PATP treatment

Figure 6.4 presented the sample pressure-temperature history collected in deionized water sample (top loading position) during single- (Figure 6.4.a) and double-pulse (Figure 6.4.b) process and the corresponding accumulated process lethality.

Table 6.2 and 6.3 summarized the samples temperature at various stages during PATP treatments. After preheating the test samples (data not shown), the samples were loaded inside the pressure vessel at temperature T_0 (Table 6.2 & 6.3). After closing the vessel, pressurization (t_1-t_2) started at T_1 and reached T_2. The process temperature (T_2-T_3) was the average temperature of the test samples during pressure holding time. The samples were held for specified holding time (t_2-t_3) and depressurized (t_3-t_4).

In this study, our primary aim was to compute the accumulated lethality values for specific process conditions rather than evaluating and minimizing the process non-uniformity within the pressure chamber. The studies utilized low ratio of product to glycol volume and thus thermal variation in the glycol greatly influenced the sample temperature history. In addition, variation in initial product and glycol temperatures within the carrier basket as well as the glycol temperature within the pressure chamber, sample loading time (which can influence heat loss during pressure holding) also influenced sample temperature at various stages of processing (Table 6.2 and 6.3). For a

given process run, samples placed in the top location experienced higher temperature than those placed in the bottom (Table 6.2). This highlighted the need for understanding process non-uniformity within a pressure vessel for sterilization studies. Factors such as equipment design, insulating properties of the pressure vessel and packaging material, sample-pressure transmitting fluid ratio, properties of the pressure transmitting fluid, influence the process non-uniformity within a pressure vessel and this is a topic of current researches in various laboratories (Hartmann et al., 2004).

6.3.2. Accumulated lethality during PATP

The accumulated lethality for both single and double-pulse treatment in general increased with increase in pressure holding time (Figure 6.4). As expected, calculated accumulated lethality during pre-heating and come-up time was negligible. Similarly, negligible lethality was also found during the time elapse between two pulses ($t_{1\text{-}4} - t_{2\text{-}1}$; Figure 6.4.b) as the temperature and pressure dropped below lethal values (i.e, < 90^{o}C and < 500 MPa). The total accumulated process lethality during single pulse treatment at 600 MPa, 105^{o}C and 5 min pressure holding time was about 0.99 min while it was about 0.94 min during double-pulse process (Figure 6.4). This lethality calculation ($F_{P,T}$) included the lethal effects of both pressure and temperature. When only thermal lethality was considered (F_T) under the same process conditions, the accumulated lethality for single pulse treatment was 0.03 min, while that of double-pulse treatment was 0.02 min.

6.3.3. Effects of sample spatial variation on accumulated lethality during PATP

For the spatial variation effects of samples, the developed accumulated lethality (calculated based on combined pressure-thermal effects) model reasonably predicted the

log-reductions in various test samples placed at different geometric locations (Table 6.4). However, ignoring pressure lethality from calculation of accumulated lethality during PATP treatment underestimated log reductions of the processed samples. Calculated combined pressure-thermal accumulated lethality for DIW and CP samples ranged from 0.74 – 1.90 and 0.70 – 1.13 min, respectively. The corresponding predicted log reductions under these conditions were 3.0-7.6 and 2.8-4.5 (Table 6.4). The model closely predicted the experimental values for DIW (A_f = 1.07, R^2 = 0.92) and CP (A_f = 1.12, R^2 = 0.83). Within the range of conditions of the study, the experimentally determined log reductions were slightly higher than predicted values (Table 6.4). The deviation between experimental and predicted log reduction could be due to differences in spore crop resistance, process equipment, and food matrix compositional differences.

As discussed in previous section, samples held at top positions experienced higher process temperature during pressure holding (Table 6.2) than those held at the bottom position. This also influenced the corresponding log-reductions. For example, between the top and bottom positions, 600 MPa-105^{o}C and 5 min holding time resulted in a maximum temperature gradient of 18.1 and 7.1 ^{o}C in DIW and CP samples. The corresponding maximum difference in log reductions in DIW and CP samples placed between top and bottom positions were 3.5 and 3.1, respectively.

Similarly, Juliano et al. (2009) observed a spatial temperature variation up to 7^{o}C between top and bottom position. This resulted in 3 log difference in inactivation predicted by linear inactivation kinetics model. Various approaches can be used to minimize temperature gradient within the pressure vessel. This included using insulation

material, optimizing product-pressure transmitting load, controlling the initial temperature of the product and pressure transmiting fluid and the pressure vessel (Hartmann and Delgado, 2003; 2005).

6.3.4. Influence of pulsed pressure treatment on accumulated lethality

For dynamic pressure treatments, the model performance in pilot scale high pressure processor was reasonabley satisfactory with MSE and accuracy factor from 0.24-0.26 and 1.129-1.077, respectively (Table 6.5). The double-pulse treatment resulted in similar log-reduction as that of a single-pulse treatment at equivalent holding time and pressure-temperature combinations (Table 6.3, 6.5). When the pressure lethality was ignored, double-pulse treatments also had very low accumulated lethality ranging from 0.02 to 0.05 min

It is worth noting that the spatial temperature distribution and log-reduction within a pressure vessel for the same target process pressure-temperature holding time were likely influenced by various pressure equipment design parameters. This included chamber diameter to length ratio, chamber volume and its insulation characteristics, pressurization and depressurization rate, type of pressure transmitting fluid used, ratio of sample to pressure transmitting fluid, etc (Hartmann et al., 2003; Hartmann et al., 2004). This can be illustrated by comparing the double-pulse treatment pressure-temperature history obtained during this current study (using a pilot scale high pressure processor) against those published by Ratphitagsanti et al. (2009) using a laboratory scale high pressure processor. Both studies processed *B. amyloliqufaciens* spores suspended in DIW at 600 MPa, 105^{o}C for similar holding times and utilized glycol as the pressure

transmitting fluids. In pilot scale high pressure machine, the first and second pulse had almost similar process temperatures ($T_{1\text{-}2}$- $T_{1\text{-}3}$, $T_{2\text{-}2}$-$T_{2\text{-}3}$; Table 6.3). The two pulses had a maximum temperature difference about 0.9 ^{o}C. On the other hand, Ratphitagsanti et al. (2009) reported that process temperature during the second pulse increased to 112^{o}C (~7 ^{o}C temperature increase from the first pulse) and enhanced lethality (2.4 to 4.0 logs) during double-pulse treatment as compared to single pulse treatment.

The apparent contradictions between the studies could be attributed to thermal time constant of the respective equipment. Lab scale unit had pressure chamber with relatively small volume (53.2 ml) and diameter (22.9 mm). The pilot scale unit had much higher volume capacity (5224 ml) and larger diameter (110 mm). Assuming the heat capacity (C_p), density (ρ) and heat transfer coefficient (h) of the pressure transmitting fluid in two machines is the same and the system can be simplified by a lumped capacity analysis. Thermal time constant ($\rho VC_p/hA$; where h and A are convective heat transfer coefficient and surface area, respectively) of the large equipment was about 5 time higher than that of laboratory scale high pressure equipment. This indicated that sample processed in a small equipment might have gained more heat during the elapse time between two-pulses. More researches are required to understand the effects of equipment design parameters and relevant factors such as choice of pressure transmitting fluids and insulating packaging properties on the PATP process uniformity and microbial efficacy.

The developed lethality model was based on published inactivation kinetics parameters of *B. amyloliquifaciens* spores. In the future, when inactivation kinetics parameters for other bacterial sproes, especially *Clostridium botulinum*, become

available, the concept can be extended to establish process efficacy based on accumulated lethality calculation. Similarly, very limited data are available on enzymatic or quality degradation kinetics during combined pressure-thermal treatment (Hernández and Cano, 1998; Ly Nguyen et al., 2003). Once such data become available under PATP conditions, the present model could be further used for process optimization studies involving microbial safety and quality degradation.

6.4. Conclusions

An accumulated lethality model was developed to predict the effect of various pressure-heat treatment combinations on spore inactivation. Accumulated model using n^{th} order kinetic parameters satisfactorily predicted the inactivation trend of *B. amyloliquifaciens* spores processed using a pilot scale high-pressure processing equipment under static and dynamic treatment conditions. For a given process temperature and desired level of lethality, combined pressure-heat lethal treatment reduced the process time than thermal process at atmospheric pressure. However, at elevated temperatures, thermal effects dominated over pressure effect. The developed approach will be useful for the food processors to evaluate microbial efficacy of various pressure-heat treatments.

References

Ahn, J., Balasubramaniam, V.M., & Yousef, A.E. (2007). Inactivation kinetics of selected aerobic and anaerobic bacterial surrogate spores by pressure-assisted thermal processing. *International Journal of Food Microbiology*, 113(3), 321-329.

Akhtar, S., Paredes-Sabja, D., Torres, J.A., & Sarker, M.R. (2009). Strategy to inactivate *Clostridium perfringens* spores in meat products. *Food Microbiology*, 26, 272–277.

Ananta, E., Heinz, V., Schluter, O., & Knorr, D. (2001). Kinetic studies on high-pressure inactivation of *Bacillus stearothermophilus* spores suspended in food matrices. *Innovative Food Science & Emerging Technologies*, (2), 261-272.

Bigelow, W.D. (1921). The logarithmic nature of thermal death time curves. *Journal of Infectious Diseases*, 29, 528–536.

Black, E.P., Setlow, P., Hocking, A.D., Stewart, C.M., Kelly, A.L., & Hoover, D.E. (2007). Response of spores to high-pressure processing. *Comprehensive Food Science and Food Safety*, 6, 103-119.

Bull, M.K., Olivier, S.A., van Diepenbeek, R.J., Kormelink, F., & Chapman, B. (2009). Synergistic Inactivation of spores of proteolytic *Clostridium botulinum* strains by high pressure and heat is strain and product dependent. *Applied and Environmental Microbiology*, 75(2), 434–445.

Campanella, O.H., & Peleg, M. (2001). Theoretical comparison of a new and the traditional method to calculate *Clostridium botulinum* survival during thermal inactivation. *Journal of Science of Food and Agriculture*, 81, 1069-1076.

Chen, H., & Hoover, D. G. (2003). Modeling the combined effect of high hydrostatic pressure and mild heat on the inactivation kinetics of *Listeria monocytogenes* Scott A in whole milk. *Innovative Food Science and Emerging Technologies*, 4 25–34.

Corradini, M.G., Normand, M.D., & Peleg, M. (2005). Calculating efficacy of heat sterilization processes. *Journal of Food Engineering*, 67, 59-69.

Corradini, M.G., Normand, M.D., & Peleg, M. (2006). Expressing the equivalence of non-isothermal and isothermal heat sterilization processes. *Journal of Science of Food and Agriculture*, 86, 785-792.

Farkas, D., & Hoover, D. (2000). High pressure processing. In Special supplement: Kinetics of microbial inactivation for alternative food processing technologies. *Journal of Food Science Special Supplement*, 47-64.

Gola, S., Foman, C., Carpi, G., Maggi, A., Cassarà, A., & Rovere., P. (1996). Inactivation of bacterial spores in phosphate buffer and in vegetable cream treated with high pressures. In *High pressure bioscience and biotechnology*, Hayashi, R., Balny, C., (Eds). Amsterdam: Elsevier Science. p 253–9.

Hartmann, C., & Delgado, A. (2003). The influence of transport phenomena during high-pressure processing of packed food on the uniformity of enzyme inactivation. *Biotechnolgy and Bioengineering*, 82(6), 725-35.

Hartmann, C., & Delgado, A. (2005). Numerical simulation of thermal and fluiddynamical transport effects on a high pressure induced inactivation. *Simulation Modeling Practice and theory,* 13, 109-18.

Hartmann, C., Delgado, A., & Szymczyk, Z. (2003). Convective and diffusive transport effects in a high pressure induced inactivation process of packed foods. *Journal of Food Engineering*, 59, 33-44.

Hartmann, C., Schuhholz, J.P., Kitsubun, P., Chapleau, N., Le Bail, A., & Degado, A. (2004). Experimental and numerical analysis of the thermo fluid dynamics in a high-pressure autoclave. *Innovative Food Science and Emerging Technologies*, 5, 399-411.

Hawley, S.A. (1971). Reversible pressure-temperature denaturation of chymotrypsinogen. *Biochemistry*, 10(13), 2436-2442.

Heinz, V., & Knorr, D. (2001). Effect of high pressure on spores. In Ultrahigh pressure treatment of foods, Hendrickx, M.E.C., Knorr, D. (Eds). New York: Kluwer Academic/Plenum Publishers. p 77–116.

Hernández, A., & Cano, M.P. (1998). High-pressure and temperature effects on enzyme inactivation in tomato puree. *Journal of Agricultural Food Chemistry*, 46 (1), 266-270.

Juliano, P., Knoerzer, K., Fryer, P.J., & Versteeg, C. (2009). *C. botulinum* inactivation kinetics implemented in a computational model of a high-pressure sterilization process. *Biotechnology Progress*, 25(1), 163-75.

Koutchma, T., Guo, B., Patazca, E., & Parisi, B. (2005). High pressure high temperature sterilization: From kinetics analysis to process verification. *Journal of Food Process Engineering*, 28(6), 610-629.

Leadley, C., Tucker, G., & Fryer, P. (2008). A comparative study of high pressure sterilization and conventional thermal sterilization: Quality effects in green beans. *Innovative Food Science & Emerging Technologies*, *9*, 70-79.

Ly Nguyen, B., Van Loey, A.M., Smout, C., Özcan, S.E., Fachin, D., Verlent, I., Vu Truong, S., Duvetter, T., & Hendrickx, M.E. (2003). Mild–heat and high–pressure inactivation of carrot pectin methylesterase: A kinetic study. *Journal of Food Science*, 68, 1377–1383.

Maggi, A., Gola, S., Rovere, P., Miglioli, L., Dall'aglio, G., & Lonneborg, N.G. (1996). Effects of combined high pressure-temperature treatments on *Clostridium sporogenes* spores in liquid media. *Industria Conserve*, 71, 8-14.

Margosch, D., Ehrmann, M. A., Gänzle, M. G., & Vogel, R. F. (2004a). Comparison of pressure and heat resistance of *Clostridium botulinum* and other endospores in mashed carrots. *Journal of Food Protection*, 67(11), 2530-2537.

Margosch, D., Gänzle, M.G., Ehrmann, M.A., & Vogel, R.F. (2004b). Pressure inactivation of *Bacillus* endospores. *Applied and Environmental Microbiology*, 70, 7321–7328.

Margosch, D., Ehrmann, M.A., Buckow, R., Heinz, V., Vogel, R.F., & Gänzle, M.G. (2006). High-pressure-mediated survival of *Clostridium botulinum* and *Bacillus amyloliquefaciens* endospores at high temperature. *Applied and Environmental Microbiology*, 72, 3476–3481.

Nguyen, L.T., Tay., A., Balasubramaniam, V.M., Legan, J.D., Turek, E.J., & Gupta, R. (2009). Evaluating the impact of thermal and pressure treatment in preserving textural quality of selected foods. LWT - Food Science and Technology*, In Press*.

Patazca, E., Koutchma, T., & Ramaswamy, H. (2006). Inactivation kinetics of *Geobacillus stearothermophilus* spores in water using high-pressure processing at elevated temperatures. *Journal of Food Science*, 71(3), M110-M116.

Pflug, I.J. (1995). Microbiology and engineering of sterilization processes. Minneapolis: Environmental Sterilization Laboratory.

Rajan, S. (2008). Raw experimental pressure-temperature history during various pressure-assisted thermal process conditions and the corresponding microbial log reductions. Personal communication.

Rajan, S., Ahn, J., Balasubramaniam, V.M., & Yousef, A.E. (2006a). Combined pressure-thermal inactivation kinetics of *Bacillus amyloliquefaciens* spores in egg patty mince. *Journal of Food Protection*, 69(4), 853-860.

Rajan, S., Pandrangi, S., Balasubramaniam, V.M., & Yousef, A.E. (2006b). Inactivation of *Bacillus stearothermophilus* spores in egg patties by pressure-assisted thermal processing. *Food Science and Technology*, 39(8), 844-851.

Ratphitagsanti, W., Ahn, J., Balasubramaniam, V.M., & Yousef, A.E. (2009). Influence of pressurization rate and pressure pulsing on the inactivation of *Bacillus amyloliquefaciens s*pores during pressure-assisted thermal processing. *Journal of Food Protection,* 72 (4), 775–782.

Reddy, N. R., Solomon, H. M., Tetzloff, R. C., & Rhodehamel, E. J. (2003). Inactivation of Clostridium botulinum type A spores by high-pressure processing at elevated temperatures. *Journal of Food Protection*, 66, 1402−1407.

Rovere, P., Gola, S., Maggi, A., Scaramuzza, N., & Miglioli, L. (1998). Studies on bacterial spores by combined pressure-heat treatments: Possibility to sterilize low-acid foods. In High pressure food science, bioscience and chemistry, Isaacs, N.S. (Ed). Cambridge, U.K.: The Royal Society of Chemistry. p 354–63.

Sale, A.J.H., Gould, G.W., & Hamilton, W.A. (1970). Inactivation of bacterial spores by hydrostatic pressure. *Journal of General Microbiology*, 60, 323–34.

Smelt, J.P.P.M. (1998). Recent advances in the microbiology of high pressure processing. *Trends in Food Science and Technology*, 9, 152–158.

Coefficients	$D_{T,P}$	Ln $k_{T,P}$	$n_{T,P}$
a_0	17.63375	11467.4	-2.062
a_1	-0.035	0.642	0.0127
a_2	-0.06628	0.26	-0.017
a_3	1.55E-05	-314.925	-0.000008
a_4	-0.00021	-183.615	0.000146
a_5	1.06E-04	-19.822	-0.0000022
R^2	0.998	0.993	0.888

Table 6.1. Coefficients of regression equation for inactivation kinetics parameters (equations 6.6, 6.7 & 6.8) of *B. amyloliquefaciens* spores based on non-linear regression of the published literature (Rajan et al., 2006a).

Food Matrix		Sample Position	Average holding pressure (MPa)	Temp at different stages during processing (^{o}C)						Time required at different stages during processing (min)		
				T_o	T_1	T_2	T_2-T_3	T_3	T_4	t_o-t_1	t_1-t_2	t_3-t_4
Deionized water	R1	1	606.3 (6.9)	74.4	74.4	114.2	116.4 (0.8)	116.0	82.3	1.36	1.43	1.24
		2		74.4	74.2	104.7	108.6 (1.3)	104.5	78.5			
		3		74.4	74.4	104.8	106.0 (1.2)	104.8	71.7			
	R2	1	599.0 (2.4)	76.9	78.2	117.8	117.4 (0.9)	116.4	83.6	1.04	1.50	1.22
		2		74.9	74.7	105.3	108.8 (1.2)	109.7	79.6			
		3		73.3	73.0	103.0	99.3 (1.7)	98.3	67.2			
	R3	1	602.9 (2.8)	68.7	68.2	101.4	102.2 (1.5)	103.1	74.6	0.71	1.32	1.06
		2		67.3	66.9	98.6	99.6 (1.5)	100.4	73.0			
		3		66.1	66.2	97.8	98.0 (1.1)	98.6	70.5			
Carrot paste	R1	1	606.9 (1.6)	69.1	68.7	97.8	102.6 (1.5)	103.6	75.9	0.72	1.07	1.00
		2		68.4	68.1	97.0	100.9 (1.3)	102.0	74.3			
		3		67.2	67.2	94.5	98.3 (1.2)	99.0	72.1			
	R2	1	609.7 (0.5)	68.2	67.7	97.0	102.3 (1.7)	103.4	75.4	0.69	1.10	1.02
		2		67.2	67.0	95.5	100.0 (1.5)	101.0	72.3			
		3		65.5	65.6	94.5	96.8 (1.1)	96.5	69.0			
	R3	1	598.6 (1.4)	68.5	68.4	97.5	105.4 (2.5)	107.0	78.4	0.58	1.21	1.01
		2		67.8	67.7	96.6	99.7 (1.2)	100.7	71.8			
		3		66.7	66.7	94.4	98.3 (1.4)	99.2	71.5			

T_0: Preprocess; T_1: Immediately before pressurization; T_2: Immediately after pressurization; T_2-T_3: Pressure holding; T_3: Before depressurization; T_4: After depressurization

t_0-t_1: Preprocess; t_1- t_2: Pressure come-up time; t_3-t_4: Depressurization

Table 6.2. Temperature, pressure and time at different stages for independent PATP treatments in pilot scale high pressure machine. R1, R2, R3 designates run number.

			Average holding pressure (MPa)	Temp at different stages during processing (^{o}C)						Time required at different stages during processing (s)			
				T_o	T_1	T_2	T_2-T_3	T_3	T_4	t_o-t_1	t_1-t_2	t_3-t_4	t_{1-4} –t_{2-1}
Single pulse	R1		606.3 (6.9)	74.4	74.4	104.8	106.0 (1.2)	104.8	71.7	1.36	1.43	1.24	-
	R2		602.9 (2.8)	68.7	68.2	101.4	102.2 (1.5)	103.1	74.6	0.71	1.32	1.06	-
	R3		600.0 (5.4)	69.5	69.2	97.6	102.9 (1.9)	104.5	74.3	0.77	1.26	0.91	
Double pulse	R1	1st pulse	601.9 (6.2)	70.5	70.5	99.7	103.4 (1.4)	104.3	77.8	0.93	1.84	0.83	0.22
		2nd pulse	600.6 (7.1)	-	76.9	102.1	104.3 (0.9)	105	76.2	-	1.28	1.26	-
	R2	1st pulse	601.0 (4.7)	73.9	73.1	101.1	104.4 (1.4)	103.5	78.4	0.79	1.25	0.89	0.16
		2nd pulse	601.6 (4.9)	-	77.5	103.1	104.4 (0.6)	104.8	77.0	-	1.11	1.00	-
	R3	1st pulse	606.7 (9.9)	70.0	70.0	97.8	101.3 (1.5)	102.5	75.7	0.78	1.50	0.84	0.21
		2nd pulse	605.9 (1.1)	-	74.9	99.9	101.2 (0.5)	101.6	74.7	0.00	1.04	0.93	-

T_o: Preprocess; T_1: Immediately before pressurization; T_2: Immediately after pressurization; T_2-T_3: Pressure holding; T_3: Before depressurization; T_4: After depressurization

t_o-t_1: Preprocess t_1-t_2: Pressure come-up time; t_3-t_4: Depressurization; t_{1-4} –t_{2-1}: time elapsed between pressure pulses

Table 6.3. Temperature, pressure and time at different stages for independent PATP single- and double-pulse treatments in pilot scale high pressure machine. R1, R2, R3 designates run number.

	Replicate	Sample Position	Accumulated lethality (min)		Log reduction (N/N_0)			Residual	Average residual	MSE	A_f	R^2
					Predicted		Experiment					
			F_T	$F_{P,T}$	TP	PATP	PATP					
Deionized water	R1	1	1.53	1.83	-6.1	-7.3	>-7.1	n/a	**-0.2**	**0.15**	**1.074**	**0.92**
		2	0.16	1.36	-0.6	-5.4	-5.8	-0.4				
		3	0.09	1.25	-0.4	-5.0	-5.4	-0.4				
	R2	1	2.21	1.90	-8.8	-7.6	>-7.1	n/a				
		2	0.16	1.36	-0.7	-5.4	-6.0	-0.6				
		3	0.02	0.89	-0.1	-3.6	-3.6	0.0				
	R3	1	0.03	0.99	-0.1	-4.0	-3.4	0.6				
		2	0.01	0.82	-0.0	-3.3	-3.5	-0.2				
		3	0.01	0.74	-0.0	-3.0	-3.0	-0.1				
Carrot paste	R1	1	0.03	1.02	-0.1	-4.1	-5.1	-1.0	**-0.5**	**0.50**	**1.117**	**0.83**
		2	0.02	0.93	-0.1	-3.7	-4.0	-0.3				
		3	0.01	0.78	-0.0	-3.1	-3.0	0.1				
	R2	1	0.03	1.00	-0.1	-4.0	-4.9	-0.8				
		2	0.01	0.88	-0.1	-3.5	-3.9	-0.4				
		3	0.01	0.70	-0.0	-2.8	-2.7	0.1				
	R3	1	0.06	1.13	-0.3	-4.5	-6.1	-1.5				
		2	0.01	0.84	-0.0	-3.4	-3.7	-0.4				
		3	0.01	0.72	-0.0	-2.9	-3.0	-0.2				

F_T: accumulated lethality considering the thermal effects only

$F_{P,T}$: accumulated lethality considering the combined pressure-temperature effects

TP: log reduction computed based on thermal history only; PATP: log reduction computed based on combined pressure-temperature history

Table 6.4. Modeling performance in pilot scale high pressure machine tested with deionized water and carrot paste. R1, R2, R3 designates run number. Residual was the difference between predicted (PATP) and experimentally determined log reduction under PATP treatments.

	Replicate	Accumulated lethality (min)		Log reduction (N/N_0)			Residual	Average residual	MSE	A_f
				Predicted		Experiment				
		F_T	$F_{P,T}$	TP	PATP	PATP				
Single pulse	R1	0.09	1.25	-0.4	-5.0	-5.4	-0.4	**0.26**	**0.26**	**1.129**
	R2	0.03	0.99	-0.1	-4.0	-3.4	0.6			
	R3	0.02	0.96	-0.1	-3.8	-4.3	-0.2			
Double pulse	R1	0.04	1.07	-0.2	-4.3	-4.3	0.0	**-0.3**	**0.24**	**1.077**
	R2	0.05	1.11	-0.2	-4.4	-5.3	-0.8			
	R3	0.02	0.94	-0.1	-3.7	-3.9	-0.2			

F_T: accumulated lethality considering the thermal effects only

$F_{P,T}$: accumulated lethality considering the combined pressure-temperature effects

TP: log reduction computed based on thermal history only; PATP: log reduction computed based on combined pressure-temperature history

Table 6.5. Modeling performance with double and single pulse high pressure treatment in pilot scale high pressure machine. R1, R2, R3 designates run number. Residual was the difference between predicted (PATP) and experimentally determined log reduction under PATP treatments.

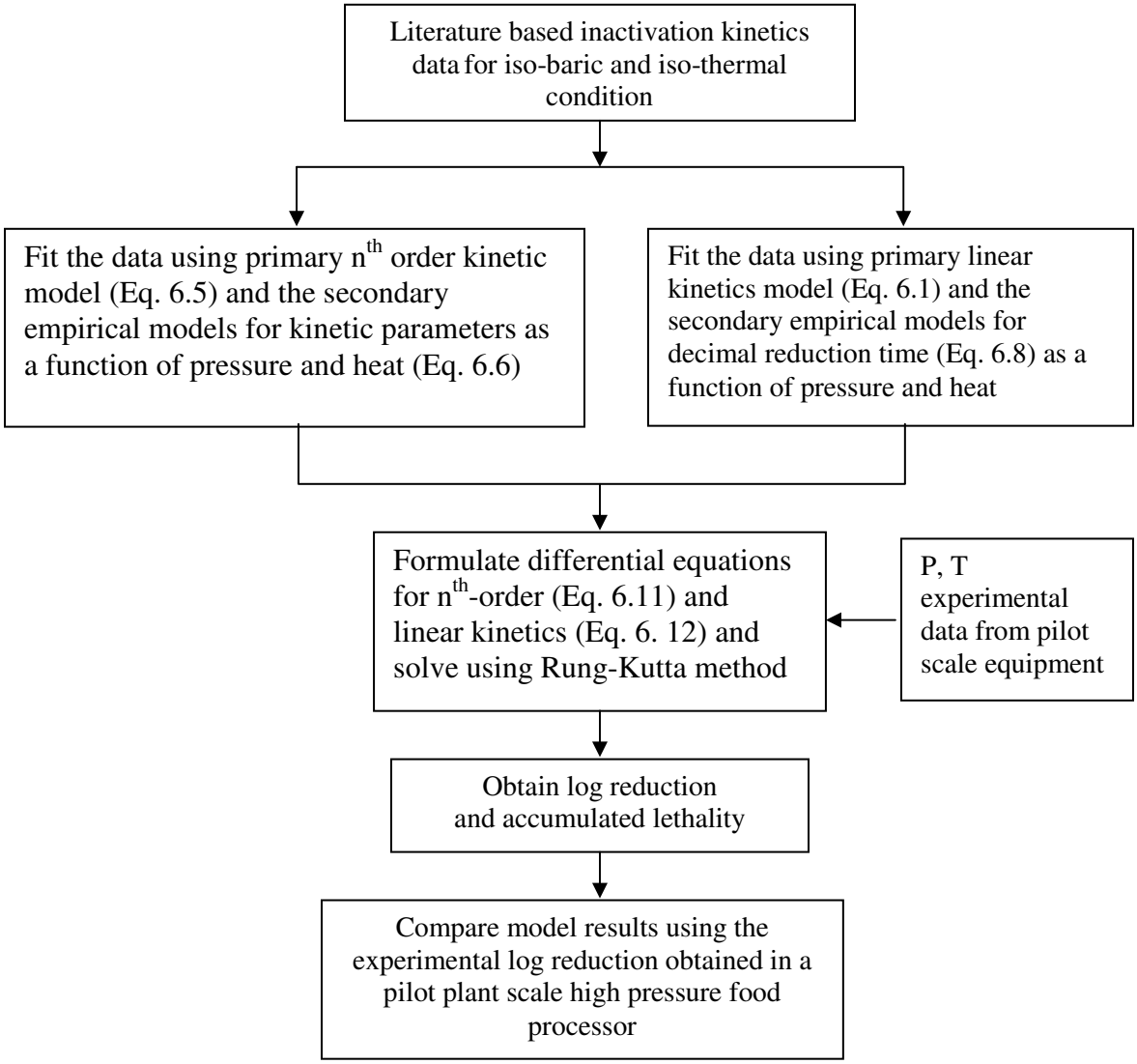


Figure 6.1. Stages used in model development for the determination of accumulated lethality during pressure-assisted thermal processing.

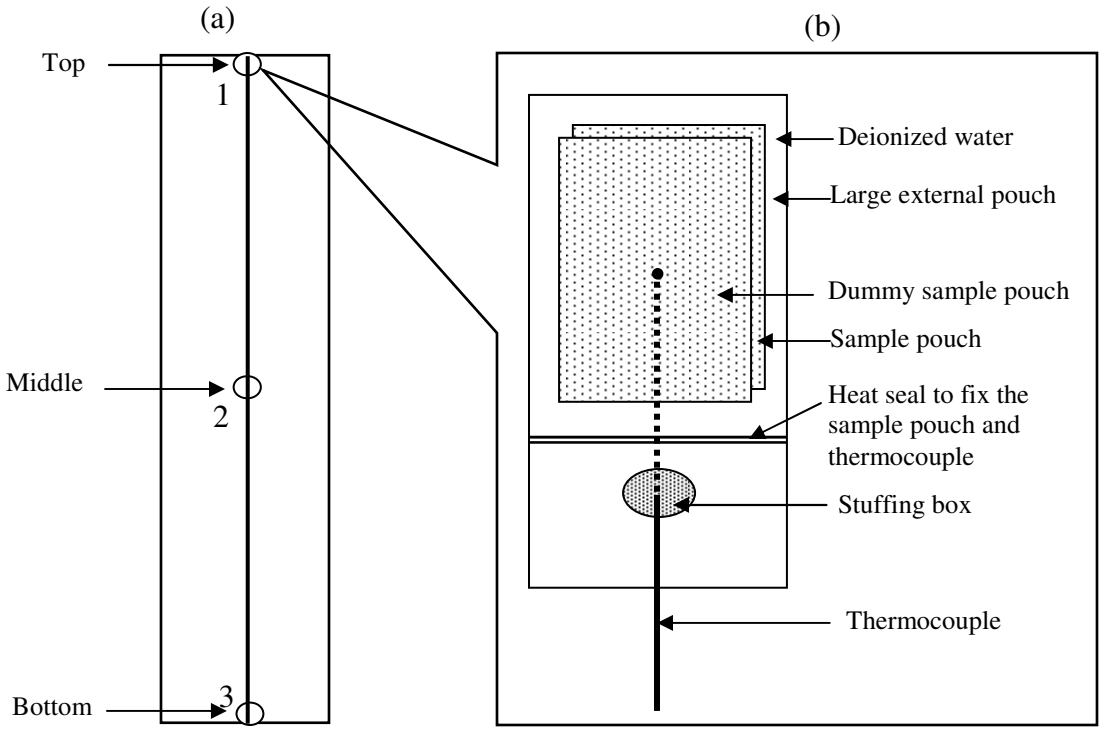
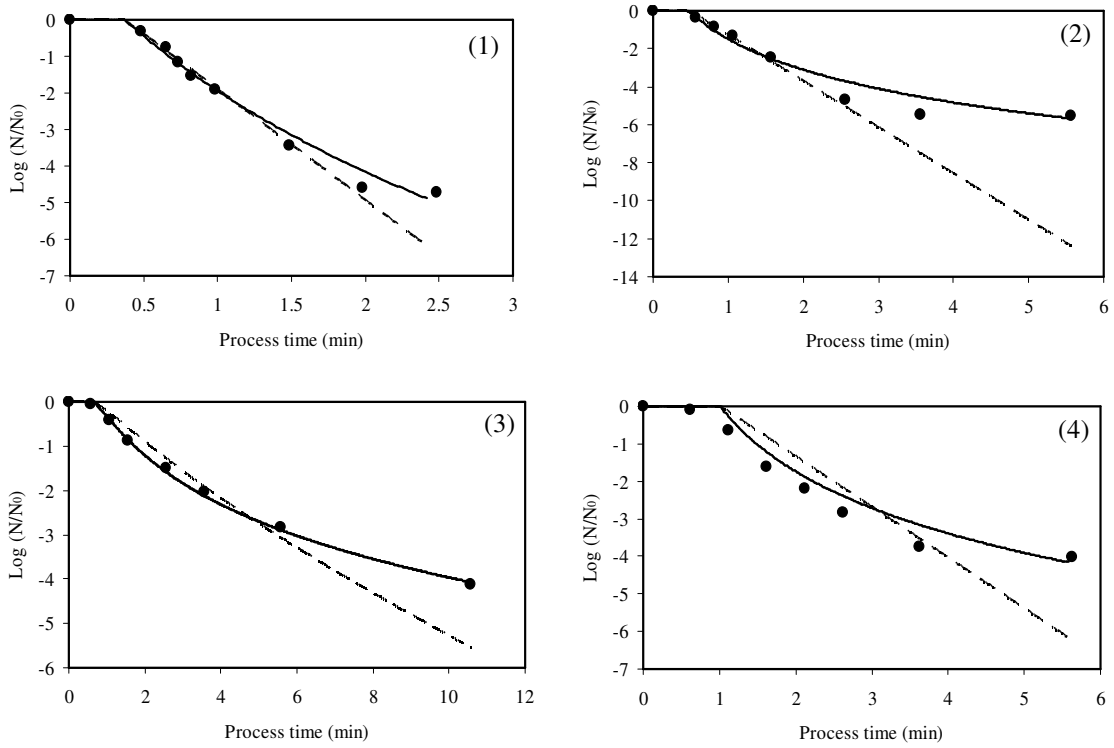


Figure 6.2. Schematic diagram of (a) sample placement in the carrier basket within the pressure vessel for the validation study (b) sample packaging showing thermocouple placement.

(A)

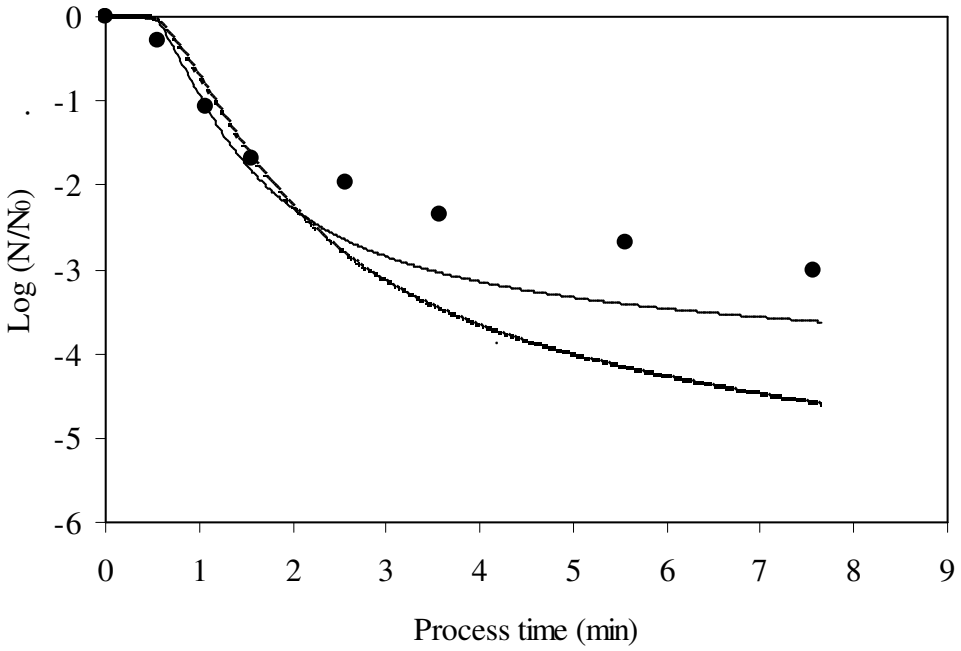


continued

Figure 6.3. (A) Comparison of log reduction computed from developed PATP lethality model vs experimental log reduction values of *Bacillus amyloliquefaciens* spores published by Rajan et al. (2006a). PATP lethality model was tested with both linear (---) and nth order (—) model and utilized pressure-temperature history presented by Rajan (2008). (1) 500 MPa, 121^{o}C; (2) 600 MPa, 110^{o}C; (3) 600 MPa, 95^{o}C and (4) 700 MPa, 95^{o}C. (B) Experimental and predicted inactivation of *Bacillus amyloliquefaciens* spores at 600 MPa under non-isothermal condition. (●) experimental values (Rajan et al., 2006a); computed values from respective T, P data (——) nth order and linear (▬▬) kinetics.

Figure 6.3. continued

(B)



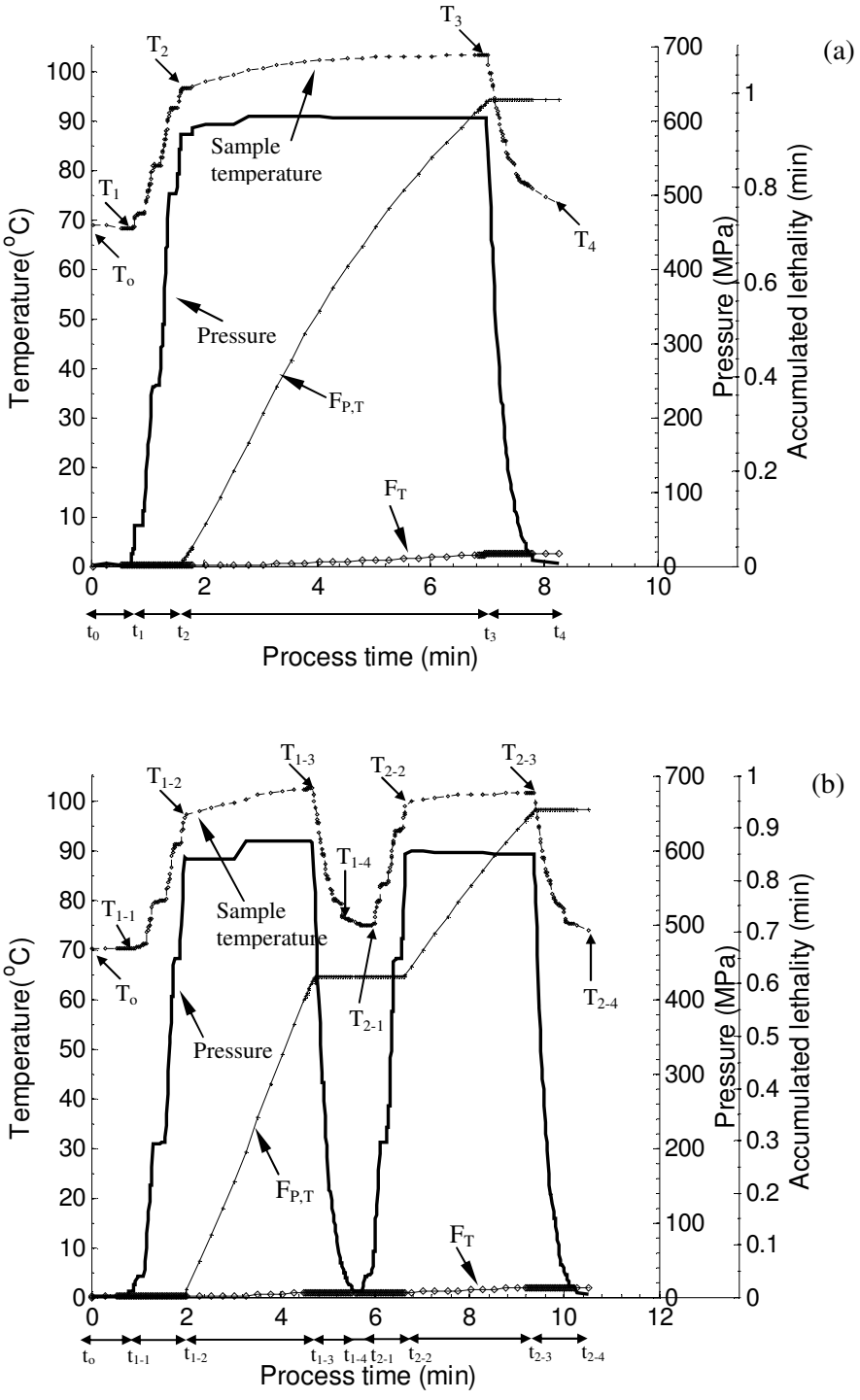


Figure 6.4. Typical pressure and temperature history collected using the pilot scale high pressure machine. a) Single pulse; b) double pulse. Accumulated lethality was computed from the experimental T-P-t data. $F_{P,T}$ and P_T are accumulated lethality based on combined pressure-thermal and thermal treatment, respectively.

Chapter 7: Conclusions

Influence of pressure assisted thermal processing on food quality attributes

- Impacts of pressure-assisted thermal processing (PATP) (500, 700 MPa; 95-121^{o}C) on carrot quality attributes was investigated and compared against that of thermally processed samples with comparable thermal history.
    - Considerable color degradation was observed with thermal treatment and overall color change was maximum at 121^{o}C. PATP degraded product color, but better retained color than TP.
    - Both TP and PATP initially softened the carrot tissue. PATP treated samples retained sample hardness more than TP samples. However, increase in process temperature during PATP (95-121^{o}C) decreased sample hardness. Texture retention of PATP samples was further dependent on pre-process temperature histories. At 121°C, possibly due to exposure to harsher pre-process temperatures as well as due to predominance of thermal effects under pressure, pressure had minimal protective on product hardness. Textural preservation of carrot samples during PATP might have attributed to inhibition of β-elimination reaction either by high pressure-temperature or by the lower degree of esterification of the pectin substances.

- Carotene retention was higher for PATP samples than TP samples at 105^{o}C and no significant difference (P>0.05) in carotene retention was observed among PATP and TP treatments at 121°C.
- Various treatments (TP, HPP, PATP) damaged the structure of the raw sample, but the extent of damage differed by treatments. TP at 105^{o}C severely damaged the carrot microstructure by inducing separation and rupture of the intact cell structure. Further they had non-distinct middle lamella possibly due to degradation of pectinacious material. HPP had the least damage. The extent of thermal damage under PATP conditions was a function of process pressure and temperature, and the cell structure was relatively better preserved.

- Impact of sequential or simultaneous pressure (600 MPa) and heat (105^{o}C) treatment on quality attributes of carrot, red radish, jicama, was investigated.
  - Pressure treatments better retained sample color and texture than thermal treatments and it was product dependent.
  - Pressure treatment followed by thermal processing (HPP-TP) improved textural quality of thermally processed samples.
  - A crunchiness index relating product puncture force and stiffness was developed. The crunchiness index was used for comparing the instrumental textural quality of samples subjected to various process treatments. CI results were in agreement with an industrial sensory panel data.

In-situ determination of thermal properties of food materials under pressure

- A dual needle probe that withstood high pressure treatment conditions was fabricated and used to measure thermal conductivity (k), diffusivity (α), volumetric specific heat (ρC_p) and specific heat (C_p) of selected food materials (tomato puree, soy protein isolate, soybean oil, guacamole, honey, cream cheese and sucrose solution) up to 600 MPa at 25^{o}C.
- Thermal conductivity of tested material increased linearly within the range of pressure at 25^{o}C. Maximum increase in k values under pressure was observed for soybean oil (0.173 -0.256 W/m^{o}C) and honey had the least change (0.324 – 0.396 W/m^{o}C) in thermal conductivity.
- Thermal diffusivity in general increased with pressure and could be described by a second order polynomial equation. Volumetric specific heat derived from thermal conductivity and diffusivity showed no clear trend of pressure dependence.
- Isobaric specific heat of tested foods decreased as pressure increased up to 600 MPa at 25^{o}C. Pressure dependence of specific heat can be expressed by a second and third order polynomial equation.
- The in-situ changes in the measured property values under pressure were temporary for the tested foods. After depressurization, the properties values reverted back close to respective initial values at atmospheric pressure.
- The maximum combined uncertainty in the measurement of k, α, ρC_p and C_p were 3.1, 6.8, 6.6 and 6.9%, respectively.

Determination of accumulated lethality under pressure-assisted thermal processing

- A procedure was developed to determine accumulated lethality of PATP considering lethality contribution of both pressure and heat. The model was validated using a pilot scale high pressure processor.
- Accumulated lethality computed using traditional log linear model overestimated log reduction of the process whereas the process log reduction computed using n^{th}-order kinetic model was in reasonable agreement with experimental data.
- The model was effective in predicting lethality during both static and dynamic pressure conditions (i.e., single and double pulse treatment). The model was able to predict the variation in log reduction due to spatial non-uniform temperature distribution within a pressure vessel.
- The developed model can be further developed into tool for optimization of PATP process conditions for microbial safety and quality.

Bibliography

[AOAC] Association of Official Analytical Chemists. (1990). Official method of analysis Association of Official Analytical Chemists, 15th ed., Arlington, VA 930.04 p. 40,69.

Abdulagatov, I. M., & Magomedov, U.B. (1994). Thermal conductivity of aqueous solutions of NaCl and KCI at high pressures. *International Journal of Thermophysics*, 15, 401– 413.

Ahn, J., Balasubramaniam, V.M., & Yousef, A.E. (2007). Inactivation kinetics of selected aerobic and anaerobic bacterial spores by pressure-assisted thermal processing. *International Journal of Food Microbiology*, 113(3), 321-329.

Akhtar, S., Paredes-Sabja, D., Torres, J.A., & Sarker, M.R. (2009). Strategy to inactivate *Clostridium perfringens* spores in meat products, *Food Microbiology*, 26, 272–277.

Ananta, E., Heinz, V., Schluter, O., & Knorr, D. (2001). Kinetic studies on high-pressure inactivation of *Bacillus stearothermophilus* spores suspended in food matrices. *Innovative Food Science & Emerging Technologies*, (2), 261-272.

Anthon, G.E., & Barrett, D.M. (2004). Comparison of three colorimetric reagents for the determination of methanol with alcohol oxidase. Application of the assay of pectin methylesterase. *Journal of Agricultural and Food Chemistry*, *52*, 3749-3753.

Anthon, G.E., Blot, L., & Barrett, D.M. (2005). Improved firmness in calcified diced tomatoes by temperature activation of pectin methylesterase. *Journal of Food Science*, 70(5), 342-7.

Araya, X.I.T., Hendrickx, M., Verlinden, B.E., Buggenhout, S.V., Smale, N.J., Stewart, C., & Mawson, A.J. (2007). Understanding texture changes of high pressure processed fresh carrots: A microstructural and biochemical approach. *Journal of Food Engineering, 80*, 873-884.

Ardia, A., Knorr, D., & Heinz, V. (2004). Adiabatic heat modeling for pressure build-up during high pressure treatment in liquid-food processing. *Transactions of Institution of Chemical Engineers (IChemE), Part C, Food Bioproduct Process*, *82* (C1), 89-95.

Autio, K. (Ed.). (1998). Fresh novel foods by high pressure. 1998. VTT Symposium 186. Valtion Teknillinen Tutkimuskeskus, VTT Biotechnology and Food Research, Food Technology Biologinkuja Finland.

Avila, I.M.L.B., & Silva, C.L.M. (1999). Modeling kinetics of thermal degradation of color in peach puree. *Journal of Food Engineering*, 39,161–6.

Balasubramaniam, V.M., Farkas, D., & Turek, E. (2008). Preserving Foods through High-Pressure Processing. *Food Technology*, 62(11), 32-38.

Balasubramanian, S., & Balasubramaniam,V.M. (2003). Compression heating influence of pressure transmitting fluids on bacteria inactivation during high pressure processing. *Food Research International*, 36(7), 661-668.

Balasubramanian, V.M., Ting, E.Y., Stewart, C.M., & Robbins, J.A. (2004). Recommended laboratory practices for conducting high pressure microbial inactivation experiments. *Innovative Food Science & Emerging Technologies*, 5(3), 299–306.

Balogh, T., Smout, C., Nguyen, B.L., Van Loey, A.M., & Hendrickx, M.E. (2004). Thermal and high-pressure inactivation kinetics of carrot pectinmethylesterase: From model system to real foods. *Innovative Food Science & Emerging Technologies*, 5, 429-36.

Barbosa, R.D. (2003). High pressure and temperature dependence of thermodynamic properties of model food solutions obtained from in-situ ultrasonic measurement. Dissertation. University of Florida.

Barrett, D. (2007). Personal communication. University of California, Davis, CA.

Basak, S., & Ramaswamy, H. S. (1998). Effect of high pressure processing on the texture of selected fruits and vegetables. *Journal of Texture Studies*, 29, 587–601.

Beck, S.J. (1996). Electron microscopy: a handbook of techniques for the biologist Available from: www.sunynassau.edu/users/becks/Path3f/EM_manual.pdf. Accessed: Sep 15 2006.

Beckerath, A. V., Eberlein, A., Julien, H., Kersten, P., & Kreutzer, J. (1998). Pressure and temperature measurement. *WIKA handbook*. Atlanta: IPD Printing.

Benet, G.U., Schluter, O., & Knorr, D. (2004). High-pressure low temperature processing. Suggested definitions and terminology. *Innovative Food Science and Emerging Technologies*, 5(4), 413-427.

Bigelow, W.D. (1921). The logarithmic nature of thermal death time curves. *Journal of Infectious Diseases*, 29, 528–536.

Black, E. P., Wei, J., Cortezzo, D. E., Koziol-Dube, K., Hoover, D. G., & Setlow, P. (2007) Analysis of factors influencing the rate of germination of spores of *Bacillus subtilis* by very high pressure. *Journal of Applied Microbiology*, 102, 65–76.

Black, E.P., Setlow, P., Hocking, A.D., Stewart, C.M., Kelly, A.L., & Hoover, D.E. (2007). Response of spores to high-pressure processing, *Comprehensive Food Science and Food Safety*, 6, 103-119.

Bourne, M. (2002). Food texture and viscosity: concept and measurement. Second edition. San Diego: Academic Press.

Bourne, M.C. (1978). Texture profile analysis. *Food Technology*, 32 (7), 62–6.

Bridgman, P.W. (1931). The physics of high pressure. London: G. Bells and Sons.

Bridgman, W.P. (1912). Thermodynamic properties of liquid water to 80^{o} and 12,000 kgm. *Proceedings of American Academy of Arts and Sciences*, 48, 309-362.

Bridgman, W.P. (1913). Thermodynamic properties of twelve liquid between 20^{o} to 80^{o} and up to 12,000 kgm. per sq. cm. *Proceedings of American Academy of Arts and Sciences*, 49, 3-114.

Bridgman, W.P. (1923). Thermal conductivity of liquids under pressure. *Proceedings of American Academy of Arts and Sciences*, 59, 141-169.

Bristow, K.L., Kluitenberg, G.J., & Horton, R. (1994). Measurement of soil thermal properties with a dual-probe heat-pulse technique. *Journal of American Society of Soil Science*, 58(5), 1288-1294.

Brown, P., Meyer, R., Cardone, C., & Pocchiari, M. (2003). Ultra-high-pressure inactivation of prion infectivity in processed meat: A practical method to prevent human infection. *Proceeding of National Academy of Science U.S.A.*, 100(10), 6093–6097.

Bubník, Z., Kadlec, P., Urban, D., Bruhns, M. (1995). Sugar Technologists Manual, Bartens, Berlin. p155.

Bull, M.K., Olivier, S.A., van Diepenbeek, R.J., Kormelink, F., & Chapman, B. (2009). Synergistic Inactivation of spores of proteolytic *Clostridium botulinum* strains by high pressure and heat is strain and product dependent. *Applied and Environmental Microbiology*, 75(2), 434–445.

Bundy, F.P. (1961). Effect of pressure on emf of thermocouples. *Journal of Applied Physics*, 32(3), 483-488.

Campanella, O.H., & Peleg, M. (2001). Theoretical comparison of a new and the traditional method to calculate *Clostridium botulinum* survival during thermal inactivation. *Journal of Science of Food and Agriculture*, 81, 1069-1076.

Carslaw, H. S., & Jaeger, J. C. (1959). Conduction of heat in solids. *second ed*. New York: Oxford University Press, pp. 302, 340–341.

Cheftel, J.C. (1995). Review: high pressure, microbial inactivation and food preservation. *Food Science and Technology International*, 1, 75–90.

Chen, B.H., Peng, H.Y., & Chen, H.E. (1995). Changes of carotenoids, colour and vitamin A contents during processing of carrot juice. *Journal of Agricultural and Food Chemistry*, 43, 1912-8.

Chen, H., & Hoover, D. G. (2003). Modeling the combined effect of high hydrostatic pressure and mild heat on the inactivation kinetics of *Listeria monocytogenes* Scott A in whole milk. *Innovative Food Science & Emerging Technologies*, 4, 25–34.

Choi, Y. (1985). Food property prediction as effected by temperature and composition. Dissertation. Purdue University.

Choi, Y., & Okos, M.R. (1983). The thermal properties of tomato juice concentrates. *Transactions of the American Society of Agricultural Engineers*, 26(1), 305-311.

Choi, Y., & Okos, M.R. (1986). Thermal properties of liquid foods-Review. In Physical and chemical properties of food. (pp35-77, (Ed.) M.R. Okos), American Society of Agricultural Engineers, Michigan, USA.

Clark, P.E., Waldeland, C.R., & Cross, R.P. (1946). Specific heat of vegetable oils from 0^{o} to 280 ^{o}C. *Industrial and Engineering Chemistry*, 38, 350-353.

Corradini, M.G., Normand, M.D., & Peleg, M. (2005). Calculating efficacy of heat sterilization processes. *Journal of Food Engineering*, 67, 59-69.

Corradini, M.G., Normand, M.D., & Peleg, M. (2006). Expressing the equivalence of non-isothermal and isothermal heat sterilization processes. *Journal of Science of Food and Agriculture*, 86, 785-792.

Dadarlat, D., Gibkes, J., Bicanic, D., & Pasca, A. (1996). Photopyroelectric (PPE) measurement of thermal parameters in foods products. *Journal of Food Engineering*, 30, 155-162.

De Heij, W.B.C., Van Schepdael, L.J.M.M., Moezelaar, R., Hoogland, H., Matser, A.M., & Van Den Berg, R.W. (2003). High-pressure sterilization: Maximizing the benefits of adiabatic heating. *Food Technology*, 57(3), 37-41.

Denys S, Ludikhuyze LR, Van Loey AM, & Hendrickx, M.E. (2000b). Modelling conductive heat transfer and process uniformity during batch high-pressure processing of foods. *Biotechnology Progress*, 16, 92-102.

Denys, S., & Hendrickx, M.E. (1999). Measurement of the thermal conductivity of Foods at high pressure. *Journal of Food Science*, 64(4), 709-713.

Denys, S., Schluter, O., Hendrickx, M.E., & Knorr, D. (2001). Effects of high pressure on water-ice transitions in foods. In Ultra high pressure treatments of foods, Hendrickx, M.E.G., and D. Knorr (Eds). New York: Kluwer Academic/Plenum Publishers. pp. 215-248.

Denys, S., Van Loey, A.M., & Hendrickx, M.E. (2000a). A modeling approach for evaluating process uniformity during batch high hydrostatic pressure processing: Combination of numerical heat transfer model and enzyme inactivation kinetics. *Innovative Food Science and Emerging Technologies*, 1(1), 5-19.

Dunne, CP. (2005). Killing pathogens: high-pressure processing keeps food safe. http://www.military.com/soldiertech/ 0,14632,Soldiertech_Squeeze,,00.html (last accessed June 15, 2006).

El'yanov B.S., & Hamann, S.D. (1975). Some quantitative relationship for ionization reactions at high pressure. *Australian Journal of Chemistry*, 28, 945-954.

Eshtiaghi, M.N., & Knorr, D. (1993). Potato cube response to water blanching and high hydrostatic pressure. *Journal of Food Science*, 58, 1371–1374.

Farkas, D., & Hoover, D. (2000). High pressure processing. In Special supplement: Kinetics of Microbial Inactivation for Alternative Food processing Technologies. *Journal of Food Science Special Supplement*, 47-64.

Food Processing. (2009). Pressure-assisted thermal sterilization accepted by FDA. http://www.foodprocessing.com/articles/2009/032.html (accessed July 9, 2009).

Ghani, A.G.A., & Farid, M.M. (2007). Numerical simulation of solid–liquid food mixture in a high pressure processing unit using computational fluid dynamics. *Journal of Food Engineering*, 80(4), 1031–1042.

Gola, S., Foman, C., Carpi, G., Maggi, A., Cassarà, A., Rovere., P. (1996). Inactivation of bacterial spores in phosphate buffer and in vegetable cream treated with high pressures. In *High pressure bioscience and biotechnology*, Hayashi, R., Balny, C., (Eds). Amsterdam: Elsevier Science. pp 253–259.

Gonzalez, M.E. (2009). Quantification of cell membrane integrity and its relevance to texture quality of onions: effects of high hydrostatic pressure and thermal processes. Ph.D. Thesis, University of California, Davis, CA, USA.

Gorny, T., & Kader, A. (2008). Post-harvest Technology Research & Information Center. UC Davis, Davis, CA. http://postharvest.ucdavis.edu/index.html last accessed May 24, 2008.

Greve, L.C., Shackel, K.A., Ahmadi, H., McArdle, R.N., Gohlke, J.R., & Labavitch, J.M. (1994). Impact of heating on carrot firmness: Contribution of cellular turgor. *Journal of Agricultural and Food Chemistry*, 42(12), 2896-2889.

Hartmann, C. (2002). Numerical simulation of thermodynamic and fluid-dynamic processes during the high-pressure treatment of fluid food systems. *Innovative Food Science and Emerging Technologies*, 3, 11-18.

Hartmann, C., & Delgado, A. (2002). Numerical simulation of convective and diffusive transport effects on a high-pressure-induced inactivation process. *Biotechnology and Bioengineering*, 79(1), 94-104.

Hartmann, C., & Delgado, A. (2003). The influence of transport phenomena during high-pressure processing of packed food on the uniformity of enzyme inactivation. *Biotechnolgy and Bioengineering*, 82(6), 725-35.

Hartmann, C., & Delgado, A. (2005). Numerical simulation of thermal and fluiddynamical transport effects on a high pressure induced inactivation. *Simulation modeling Practice and theory,* 13, 109-18.

Hartmann, C., Delgado, A., & Szymczyk, Z. (2003). Convective and diffusive transport effects in a high pressure induced inactivation process of packed foods. *Journal of Food Engineering*, 59, 33-44.

Hartmann, C., Delgado, A., & Szymczyk, Z., (2003). Convective and diffusive transport effects in a high pressure induced inactivation process of packed foods. *Journal of Food Engineering*, 59, 33-44.

Hartmann, C., Schuhholz, J.P., Kitsubun, P., Chapleau, N., Le Bail, A., & Degado, A. (2004). Experimental and numerical analysis of the thermo fluid dynamics in a high-pressure autoclave. *Innovative Food Science and Emerging Technologies*, 5, 399-411.

Harvey, A.H., Peskin, A.P., & Klein, S.A. (1996). NIST/ASME Standard Reference database 10, Version 2.2. Boulder, CO: National Institute of Standards and Technology.

Harvey, A.H., Peskin, A.P., & Klein, S.A. (1996). NIST/ASME Standard Reference Database 10. Version 2.2, Boulder, Colo.: National Institute of Standards and Technology.

Hawley, S.A. (1971). Reversible pressure-temperature denaturation of chymotrypsinogen. *Biochemistry*, 10(13), 2436-2442.

Hayashi, R. (Ed). (1991). High Pressure Science for Food. Minamitaisumi-cho Katsura, Nishikyo-ku, Kyoto 615 Japan: San-Ei Publishing Co.

Heinz, V., & Knorr, D. (2001). Effect of high pressure on spores. In Ultrahigh pressure treatment of foods, Hendrickx MEC, & Knorr D, (Eds.). New York: Kluwer Academic/Plenum Publishers. p 77–116.

Heremans, K. (1995). High pressure effects on biomolecules. In High pressure processing of foods. Ledward, D.A., Johnston, D.E., Earnshaw, R.G., & Hasting, A.P.M. (Eds). Nottingham: Nottingham University Press.

Hernández, A., Cano, M.P. (1998). High-pressure and temperature effects on enzyme inactivation in tomato puree. *Journal of Agricultural Food Chemistry*, 46 (1), 266-270.

Hogan, E., Kelly, A.L., & Sun, D.W. (2005). High pressure processing of foods: an overview. In *Emerging technologies for food processing*. Elsevier Academic press. pp. 1-32.

Hoogland, H., de Heij, W., & van Schepdael, L. (2001). High pressure sterilization: novel technology, new products, new opportunities. *New Food*, 4(1), 21-6.

Incropera, F.P, & DeWitt, D.P. (1990). In Fundamentals of heat and mass transfer. John Wiley and Sons, Inc., NY.

Ingersoll, L.R., Zobell, O.J., & Ingersoll, A.C. (1954). Heat conduction with engineering and geological applications. McGrawHill:NewYork. pp 143-147.

Johnson, F.H., Eyring, F.H., & Polissar, M.J. (1954). The kinetics basis of molecular biology. New York: John Wiley and Son.

Juliano P., Toldrág M., Koutchma, T., Balasubramaniam, V.M., Clark, S., Mathews, J.W., Dunne, C.P., Sadlerand, G., & Barbosa-Cánovas, G.V. (2006). Texture and water retention improvement in high-pressure thermally treated scrambled egg patties. *Journal of Food Science*, 71(2), E52-61.

Juliano, P., Knoerzer, K., Fryer, P.J., & Versteeg, C. (2009). *C. botulinum* inactivation kinetics implemented in a computational model of a high-pressure sterilization process. *Biotechnology Progress*, 25(1), 163-75.

Kalichevsky, M.T., Knorr, D., & Lillford, P.J. (1995). Potential food applications of high-pressure effects on ice-water transitions. *Trends in Food Science and Technology*, 6, 253–259.

Kasai, M., Hatae, K., Shimada, A., & Ibuchi, S. (1995). Pressure pre-treatment of vegetables for controlling the hardness before cooking. *Nippon Shokuhin Kagaku Kogaku Kaishi, 42*(8), 594–601.

Kato, N.H., Teramoto, A., & Fuchigami, M. (1997). Pectic substance degradation and texture of carrots as affected by pressurization. *Journal of Food Science*, 62(2), 359-62.

Kestin, J., Sengers, J. V., Kamgar-Parsi, B., & Levelt Sengers, J. M. H. (1984). Thermophysical properties of fluid H_2O. *Journal of Chemical Reference Data*, 13, 175–183.

Kim, Y.S., Park, S.J., Cho, Y.H., Park, J. (2001). Effects of combined treatment of high hydrostatic pressure and mild heat on the quality of carrot juice. *Journal of Food Science*, 66(9), 1355-60.

Kirup, L., & Frenkel, R.B. (2006). An introduction to uncertainty in measurement using the GUM (Guide to the expression of uncertainty in measurement), (pp. 35-161). Cambridge: Cambridge University Press.

Koutchma, T., Guo, B., Patazca, E., & Parisi, B. (2005). High pressure high temperature sterilization: From kinetics analysis to process verification. *Journal of Food Process Engineering*, 28(6), 610-629.

Kovarskii, A. L. (1993). High-pressure chemistry and physics of polymers. Boca Raton, Florida: CRC press, Inc.

Krebbers, B., Matser, A. M., Hoogerwerf, S. W., Moezelaar, R., Tomassen, M. M. M., & Van DenBerg, R. W. (2003). Combined high-pressure and thermal treatments for processing of tomato puree: evaluation of microbial inactivation and quality parameters. *Innovative Food Science & Emerging Technologies*, *4*(4), 377–85.

Krebbers, B., Matser, A. M., Koets, M., & Van Den Berg, R. W. (2002). Quality and storage stability of high-pressure preserved green beans. *Journal of Food Engineering*, *54*(1), 27–33.

Kumar, P., Coronel, P., Simunovic, J., Sandeep, K.P. 2008). Thermophysical and dielectric properties of salsa con queso and its vegetable ingredients at sterilization temperatures. *International Journal of Food Properties*, 11(1), 112-126

Kunugi, S., & Hayashi, R. (Ed.). (1998). High pressure biotechnology. San-Ei Publishing Co,. 30 Minamitaisumi-cho Katsura, Nishikyo-ku, Kyoto 615 Japan.

Lau, M. H., & Turek, E. J. (2007). Determination of quality difference in low-acid foods sterilized by high pressure versus retorting. In Doona, C. J., & Feeherry, F. E, High pressure processing of foods. (pp.195-217). Blackwell publishing & IFT press.

Lawson, A.W., Lowell, R., & Jian, A.L. (1959). Thermal conductivity of water at high pressures. Journal of Chemical Physics, 53, 643-647.

Leadley, C., Tucker, G., Fryer, P. (2008). A comparative study of high pressure sterilization and conventional thermal sterilization: Quality effects in green beans. *Innovative Food Science & Emerging Technologies*, *9*, 70-79.

Ledward, D.A., Johnston, D.E., Earnshaw, R.G., & Hasting, A.P.M. (Eds). (1995). High pressure processing of foods. Sutton Bonington Campus, Loughborough, Leicestershire: Nottingham University Press.

Lee, C.Y., Bourne, M.C., Buren, J.P. (1979). Effect of blanching treatment on the firmness of carrots. *Journal of Food Science*, 44, 615-6.

Lopez, J.A.B., Mandelis, A. (2003). Self-consistent photothermal techniques: Application for measuring thermal diffusivity in vegetable oils. *Review of Scientific Instruments*, 75(1), 700-702.

Luechapattanaporn, K., Wang, Y., Wang, J., Al-Holy, M., Kang, D.H., & Tang, J. (2004). Microbial safety in radio frequency processing of packaged foods. *Journal of Food Science*, 69(7), 201–6.

Ly Nguyen, B., Van Loey, A.M., Smout, C., Özcan, S.E., Fachin, D., Verlent, I., Vu Truong, S., Duvetter, T., & Hendrickx, M.E. (2003). Mild–heat and high–pressure inactivation of carrot pectin methylesterase: A kinetic study. *Journal of Food Science*, 68, 1377–1383.

Maggi, A., Gola, S., Rovere, P., Miglioli, L., Dall'aglio, G., & Lonneborg, N.G. (1996). Effects of combined high pressure-temperature treatments on *Clostridium sporogenes* spores in liquid media. *Industria Conserve*, 71, 8-14.

Margosch, D., Ehrmann, M. A., Gänzle, M. G., & Vogel, R. F. (2004). Comparison of pressure and heat resistance of *Clostridium botulinum* and other endospores in mashed carrots. *Journal of Food Protection*, 67(11), 2530-2537.

Margosch, D., Ehrmann, M.A., Buckow, R., Heinz, V., Vogel, R.F., & Gänzle, M.G. (2006). High-pressure-mediated survival of *Clostridium botulinum* and *Bacillus amyloliquefaciens* endospores at high temperature. *Applied and Environmental Microbiology*, 72, 3476–3481.

Margosch, D., Gänzle, M.G., Ehrmann, M.A., & Vogel, R.F. (2004b). Pressure inactivation of *Bacillus* endospores. *Applied and Environmental Microbiology*, 70, 7321–7328.

Matser, A. M., Krebbers, B., van den Berg R. W., & Bartels P. V. (2004). Advantages of high pressure sterilization on quality of food products. *Trends in Food Science and Technology, 15*(2), 79-85.

Meyer, R., Cooper, K. L., Knorr, D., & Lelieveld, H. L. M. (2000). High pressure sterilization of foods. *Food Technology, 54* (11), 67–72.

Min, S, Sastry, S., & Balasubramaniam, V.M. (2009). Variable volume piezometer for measurement of volumetric properties of materials under high pressure. *International Journal* of *High Pressure Research*, 29(2), 278-289.

Min, S., Sastry, S.K, Balasubramaniam, V.M. (2009). Compressibility and density of select liquid and solid foods under pressures up to 700 MPa. *Journal of Food Engineering*, 96(4), 568-574.

Min, S.K. (2008). Properties of food and buffer solutions during high pressure processing: In-situ measurement of density, compressibility, electrical conductivity and reaction volume. Dissertation. The Ohio State University.

Mohsenin, N. (1970). Physical properties of plants and animal materials: structure, physical characteristics and mechanical properties. New York: Gordon and Breach, Science Publishers, Inc.

Murakami, E.G., Sweat, V.E., Sastry, S.K., & Kolbe, E., Hayakawa, K., & Datta, A. (1996). Recommended design parameters for thermal conductivity probes for non-frozen food materials, *Journal of Food engineering*, 1, 93-113.

Narayama, K.B., & Murthy, M.V.K. (1981). Heat and mass transfer characteristics and the evaluation of thermal properties of moist food materials. *Transactions of the American Society of Agricultural Engineers*, 24(3), 789-793.

Nguyen, L. T., Rastogi, N. K., & Balasubramaniam, V. M. (2007). Evaluation of instrumental quality of pressure-assisted thermally processed carrots. *Journal of Food Science*, *72*, E264-E270.

Nguyen, L.T., Tay., A., Balasubramaniam, V.M., Legan, J.D., Turek, E.J., & Gupta, R. (2009). Evaluating the impact of thermal and pressure treatment in preserving textural quality of selected foods. *LWT - Food Science and Technology, In Press*.

Niassar, M.S., Hozawa, M., & Tsukada, T. (2000). Development of probe for thermal conductivity measurement of food materials under heated and pressurized conditions. *Journal of Food Engineering*, 43, 133-139.

Nilsson, O., Sandberg, O., & Bäckström. (1986). dc-ac hot-wire procedure for determining thermophysical properties under pressure. *Review of Scientific Instrumen*t, 57(9), 2303-2309.

Nix, G.H., Lowery, G.W., Vachen, R.I., & Tanger, G.E.. (1967). Direct determination of thermal diffusivity and conductivity with a refined line-source technique. In: Heller, G.G., (Ed). *Progress in astronautics and aeronautics*. Academic Press, New York, pp. 113–116.

Nix, G.H., Vachon, R.I., Lowery, G.M., & McCurry, A.T. (1969). The line-source method: procedure and iteration scheme for combined determination of conductivity and diffusivity. *Proceedings of 18th Conference on Thermal Conductivity*, 999-1008

Norton, C. R. T., Mitchell, J. R., & Blanshard, J. M. V. (1998). Fractal determination of crispy or crackly textures. *Journal of Texture Studies, 29*, 239-253

Oey, I., Lille, M., Van Loey, V., & Hendrickx, M. (2008). Effects of high pressure processing on colour, texture and flavor of fruit and vegetable-based food products: a review. *Trends in Food Science and Technology 19*, 320-328.

Ohlsson, T. (1996). High pressure processing of food and food components, a literature survey and bibliography. SIK, Box 5401, Gtoborg, Sweden.

Otero, L., & Sanz, P.D. (2003). Modeling heat transfer in high pressure food processing: a review. *Innovative Food Science and Emerging Technologies*, 4, 121-134.

Otero, L., Molina-Garcıa, A. D., & Sanz, P. D. (2000). Thermal effect in foods during quasi-adiabatic pressure treatments. *Innovative Food Science and Emerging Technologies*, 1, 119–126.

Otero, L., Ousegui, A., Benet, G.U., de Elvira, C., Havet, M., Le Bail, A., & Sanz, P.D. (2007). Modeling industrial scale high-pressure-low-temperature processes. *Journal of Food Engineering,* 83, 136-141.

Patazca, E., Koutchma, T., & Balasubramaniam, V.M. (2007). Quasi-adiabatic temperature increase during high pressure processing of selected foods. *Journal of Food Engineering*, 80(1), 199–205.

Patazca, E., Koutchma, T., & Ramaswamy, H. (2006). Inactivation kinetics of *Geobacillus stearothermophilus* spores in water using high-pressure processing at elevated temperatures, *Journal of Food Science*, 71(3), M110-M116.

Pfister, M.K.H., Butz, P., Heinz, V., Dehne, L.I., Knorr, D., & Tauscher, B. (2001). Influence of high pressure treatment on chemical alterations in foods. A literature review. *Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin*, Tabellen, Berlin.

Pflug, I.J. (1995). Microbiology and engineering of sterilization processes. Minneapolis: Environmental Sterilization Laboratory.

Povey, M.J.W. (1998). Ultrasonics of food. *Contemporary Physics*, 39(6), 467-478.

Rajan, S. (2008). Raw experimental pressure-temperature history during various pressure-assisted thermal process conditions and the corresponding microbial log reductions. Personal communication.

Rajan, S., Ahn, J., Balasubramaniam, V.M., & Yousef, A.E. (2006). Combined pressure-thermal inactivation kinetics of *Bacillus amyloliquefaciens* spores in egg patty mine. *Journal of Food Protection*, 69(4), 853-860.

Rajan, S., Pandrangi, S., Balasubramaniam, V.M., & Yousef, A.E. (2006b). Inactivation of *Bacillus stearothermophilus* spores in egg patties by pressure-assisted thermal processing, *Lebensmittel-Wissenschaft* und-*Technologie*, 39(8), 844-51.

Ramaswamy, R., Balasubramaniam, V.M., & Sastry, S.K. (2005). Properties of food materials during high pressure processing. In Encyclopedia of Agricultural, Food, and Biological Engineering, Heldman, D.R. (Ed). New York: Marcel Dekker Inc.

Ramaswamy, R., Balasubramaniam, V. M., & Sastry, S. K. (2007). Thermal conductivity of selected liquid foods at elevated pressures up to 700 MPa. *Journal of Food Engineering*, 83, 444-451.

Ranganna, S. (1986). Handbook of analysis and quality control for fruit and vegetable products. 2nd ed. New Delhi: Tata McGraw Hill Publishing Co Ltd.

Rasanayagam, V., Balasubramanaiam, V.M., Ting, E., Sizer, C.E., Bush, C., & Anderson, C. (2003). Compression heating of selected fatty food materials during high pressure processing. *Journal of Food Science*, 68(1), 254-259.

Rastogi, N.K., Nguyen, L.T., & Balasubramaniam, V.M. (2008). Effect of pretreatments on carrot texture after thermal and pressure-assisted thermal processing. *Journal of Food Engineering*, *88*, 541-547.

Rastogi, N.K., Niranjan, K. (1998). Enhanced mass transfer during osmotic dehydration of high pressure treated pineapples. *Journal of Food Science,* 63(3), 508-11.

Rastogi, N.K., Rangarao, K.S.M.S., Balasubramaniam, V.M., Niranjan, K. & Knorr, D. (2007). Opportunities and challenges in high pressure processing of foods. *Critical Reviews in Food Science and Nutrition*, 47, 69–112

Ratphitagsanti, W., Ahn, J., Balasubramaniam, V.M., & Yousef, A.E. (2009). Influence of pressurization rate and pressure pulsing on the inactivation of *Bacillus amyloliquefaciens s*pores during pressure-assisted thermal processing. *Journal of Food Protection*, 72 (4), 775–782.

Reddy, N. R., Solomon, H. M., Tetzloff, R. C., & Rhodehamel, E. J. (2003). Inactivation of Clostridium botulinum type A spores by high-pressure processing at elevated temperatures. *Journal of Food Protection*, 66, 1402–1407.

Reddy, N.R., Tetzloff, R.C., Solomon, H.M., & Larkin, J.W. (2006). Inactivation of *Clostridium botulinum* nonproteolytic type B spores by high pressure processing at moderate to elevated high temperatures. *Innovative Food Science & Emerging Technologies*, 7, 169-175.

Riedel, L. (1949). Thermal conductivity measurement on sugar solutions, fruit juices and milk. *Chemie-Ingenieur-Technik*, 21(17), 340-341.

Roeck, A. D., Sila, D. N., Duvetter, T., Van Loey, A., & Hendrickx, M. (2008). Effect of high pressure/high temperature processing on cell wall pectic substances in relation to firmness of carrot tissue. *Food Chemistry*, *107*, 1225-1235.

Rovere, P., Gola, S., Maggi, A., Scaramuzza, N., & Miglioli, L. (1998). Studies on bacterial spores by combined pressure-heat treatments: Possibility to sterilize low-acid foods. In High pressure food science, bioscience and chemistry, Isaacs, N.S. (Ed). Cambridge, U.K.: The Royal Society of Chemistry. p 354–63.

Rovere, P., Maggi, A., Scaramuzza, N., Gola, S., Miglioli, L., Carpi, G., & Dall'Aglio, G. (1996). High-pressure heat treatments: Evaluation of the sterilizing effect and of thermal damage. *Industria Conserve*, *71*, 473-483.

Rovere, P., Squarcina, N., Gola, S., Sandei, L., Iametti, S., & Carpi, G. (2000). Effect of thermal treatment under high pressure on the quality of a meat sauce. *High Pressure Research*, 19, 99–107.

Safarov, M.M., Usupov, S.T., & Tagoev, S.A. (1999). Thermophysical properties of vegetable oils in a wide range of temperatures and pressures. *High Temperature High Pressure*, 31, 43-48.

Sale, A.J.H., Gould, G.W., Hamilton, W.A. (1970). Inactivation of bacterial spores by hydrostatic pressure. *Journal of General Microbiology*, 60, 323–34.

San Martin, M.F., Barbosa-Canovas, G.V., & Swanson, B.G. (2002). Food processing by high hydrostatic pressure. *Critical Reviews in Food Science and Nutrition* 42, 627-645.

Short, B.E., & Bartlett, L.H. (1944). The specific heat of foodstuffs. The University of Texas, Publication No. 4432. Engineering Research Series No. 40.

Sila, D.N., Smout, C., Elliot, F., Van Loey, A., & Hendrickx, M. (2006). Non-enzymatic depolymerization of carrot pectin: Toward a better understanding of carrot texture during thermal processing. *Journal of Food Science*, *71*(1), E1–E9.

Sila, D., Smout, C., Truong, V., & Hendrickx, M. (2004). Effects of high pressure pretreatment and calcium soaking on the texture degradation kinetics of carrots during thermal processing. *Journal of Food Science*, *69*, E205–E211.

Sila, D., Yue, X., Van Buggenhout, S., Smout, C., Van Loey, A., & Hendrickx, M. (2007). The relation between (bio-)chemical, morphological, and mechanical properties of thermally processed carrots as influenced by high-pressure pretreatment condition. *European Food Research Technology*, *226*, 127-135.

Smelt, J.P.P.M. (1998). Recent advances in the microbiology of high pressure processing *Trends in Food Science and Technology*, 9, 152–158.

Sopade, P.A., Halley, P.J., & D'Arcy, B.R. (2006). Specific heat capacity of Australian honeys from 35 to 165°C as a function of composition under differential scanning calorimetry. *Journal of Food Processing and Preservation*, 30, 99-109.

Sweat, E.V., & Parmelee, C.E. (1978). Measurement of thermal conductivity of dairy products and margarines. *Journal of Food Process Engineering*, 2, 187–197.

Sweat, V.E. (1986). Thermal properties of foods. In Engineering properties of foods, Rao, M.A., & Rizvi, S.S.H. (Eds). NewYork: Marcel Dekker, 49-87.

Taylor, B. & Kuyatt, C. (1994). Guidelines for evaluating and expressing uncertainty of NIST measurement results. NIST Technical Note, 1297.

Thakur, B.R., & Nelson, P.E. (1998). High pressure processing and preservation of foods. *Food Reviews International*, 14(4), 427–447.

Ting, E., Balasubramaniam, V.M., & Raghubeer, E. (2002). Determining thermal effects in high-pressure processing. *Food Technology*, 56(2), 31–35.

Torres, J.A., & Velásquez, G. (2005). Commercial opportunities and research challenges in the high pressure processing of foods. *Journal of Food Engineering*, 67(1), 95-112

Touloukian, Y.S., Liley, P.E., & Saxena, S.C. (1970). Thermophysical properties of matter, Vol. 3: Thermal conductivity, nonmetallic liquids and gases. IFI/Plenum, New York.

Van Buren, J.P.S. (1979). The chemistry of texture in fruits and vegetables. *Journal of Texture Studies*, *10*, 1-23.

Vu, T.S., Smout, C., Sila, D.N., Ly Nguyen, B., Van Loey, A.M.L., & Hendrickx, M.E.G. (2004). Effect of preheating on thermal degradation kinetics of carrot texture, *Innovative Food Science & Emerging Technology*, 5, 37-44.

Werner, M., Baars, A., Eder, C., Delgado, A. (2008). Thermal conductivity and density of plant oils under high pressure. *Journal of Chemical Engineering Data*, *53*, 1444-1452.

Werner, M., Baars, A., Werner, F., Eder, C., Delgado, A. (2007). Thermal conductivity of aqueous solutions under high pressure. *International Journal of Thermophysics*, 28, 1161-1180.

Zhu, S., Marcotte, M., Ramaswamy, H., Shao, Y., & Le-Bail, A. (2008). Evaluation and comparison of thermal conductivity of food materials at high pressure. *Food and Bioproduct Processing*, 86, 147-153.

Zhu, S., Naim, F., Marcotte, M., Ramaswamy, H., & Shao, Y. (2008). High-pressure destruction kinetics of *Clostridium sporogenes* spores in ground beef at elevated temperatures. *International Journal of Food Microbiology*, *126*(1-2), 86-92.

Zhu, S., Ramaswamy, H. S., Marcotte, M., Chen, C., Shao, Y., & Le Bail, A. (2007). Evaluation of thermal properties of food materials at high pressures using a dual-needle line-heat source method. *Journal of Food Science*, 72(2), E49-E56.

Appendix A: Matlab Code for Texture Analysis (Chapter 4)

```
clear
clc

%Determine the size of the raw data table
for n=1:1;
   TXX = xlsread('Puncturejicama-ctrl',n);
   [m10, n10]=size(TXX) ;

%Transfer force and distance to a separate array
for i=1:m10
   TX(i,1)=TXX(i,1);
   TX(i,2)=TXX(i,2);
end

%Determine Fmax and different force values on the F-D curve
      [C1,I1]=max(TX);
      Fs10=0.1*TX(I1(1),1);
      Fs20=0.2*TX(I1(1),1);
      Fs30=0.3*TX(I1(1),1);
      Fs40=0.4*TX(I1(1),1);
      Fs50=0.5*TX(I1(1),1);
      Fs60=0.6*TX(I1(1),1);
      Fs80=0.8*TX(I1(1),1);
      Fs70=0.7*TX(I1(1),1);

%Determine the position of the force values on the F-D curve
for i=1:I1(1)
      Fse3(i)=abs(Fs10-TX(i,1));
      Fse2(i)=abs(Fs20-TX(i,1));
      Fse4(i)=abs(Fs30-TX(i,1));
      Fse5(i)=abs(Fs40-TX(i,1));
      Fse6(i)=abs(Fs50-TX(i,1));
      Fse7(i)=abs(Fs60-TX(i,1));
      Fse1(i)=abs(Fs70-TX(i,1));
      Fse8(i)=abs(Fs80-TX(i,1));
end
      [C2,I2]=min(Fse1);
      [C3,I3]=min(Fse2);
      [C4,I4]=min(Fse3);
```

```
        [C5,I5]=min(Fse4);
        [C6,I6]=min(Fse5);
        [C7,I7]=min(Fse6);
        [C8,I8]=min(Fse7);
        [C9,I9]=min(Fse8);

% Transfer values from F= 0 to F =80% x F max
for i=1:I9
        TXfx(i)=TX(i,2);
        TXfy(i)=TX(i,1);
end

%Fit the 3-order polynimial to the F-D curve and determine slope at different deformation.
            p=polyfit(TXfx,TXfy,3);
            k=polyder(p);%(derivative of F-D curve)
            grad10(n)=polyval(k,TX(I4, 2));
            grad20(n)=polyval(k,TX(I3, 2));
            grad70(n)=polyval(k,TX(I2, 2));
            grad30(n)=polyval(k,TX(I5, 2));
            grad40(n)=polyval(k,TX(I6, 2));
            grad50(n)=polyval(k,TX(I7, 2));
            grad60(n)=polyval(k,TX(I8, 2));
            Fmax(n)=C1(1);
% Print out results
    fprintf(1,' %2.5f\t',n);
    fprintf(1,'  %2.5f\t',Fmax(n));
    fprintf(1,'  %2.5f\t',grad10(n));
    fprintf(1,'  %2.5f\t',grad20(n));
    fprintf(1,'  %2.5f\t',grad30(n));
    fprintf(1,'  %2.5f\t',grad40(n));
    fprintf(1,'  %2.5f\t',grad50(n));
    fprintf(1,'  %2.5f\t',grad60(n));
    fprintf(1,'  %2.7f\t\n',grad70(n));
clear
end
```

Appendix B: Matlab Code for Thermal Property Determination (Chapter 5)

```
clear
clc
Ce=0.5772157; %Euler constant
r=2.0*10^-3; % Distance of the diffusivity TC from the heat source
R=6.8; % heating wire resistance
l=0.105; % heating wire length
N1=50;
N2=150;

display('  ToC        P          k          alfa(x 10^6)          Cp')
%Read the data from Excel worksheet
%Extract the data of linear part of ln(t) vs t curve

for j=1:6

DT=xlsread('kNepo7cheese-01afterP',j);
   n=1;
      for i=1:135
         if DT(i,1)> 3 && DT(i,1)<15.0
         DTT(n,:)=DT(i,:);
         n=n+1;
         end
      end
   %Point temperature
   TT(j)=(DTT(n-1,3)+DTT(1,3))/2;
   %Plot the curve
   %line(log(DTT(:,1)),DTT(:,3));
   % Fitting the curve with linear equation
   coff=polyfit(log(DTT(:,1)),DTT(:,3),1);
   %Plot the fitted data against measured data
   y2=polyval(coff,log(DTT(:,1)));
   plot(log(DTT(:,1)),DTT(:,3),'o',log(DTT(:,1)),y2), grid on
   %axis([0 3 20 22]);
   % Extract the slope of the curve
   b=coff(1);
   % Calculate the power stregth and thermal conductivity
   Q(j)=(DTT(10,5)/1000)^2/(R*l);
   k(j)=Q(j)/(b*4*3.1416);
```

```
end

for j=1:6
      DT=xlsread('Nepo7cheese-01afterP',j);
      sumdiff=0;
      for i=N1:N2
         G=-2*3.1416*k(j)*(DT(i,4)-DT(1,4))/Q(j);

         x=10^-10;
         epsilon=1;
               while epsilon>10^-4
                  f1=-Ce/2-log(x);
                  df1=-1/x;
                  f2=0; df2=0;
                   for m=2:2:100
                     f2=f2+(-1)^((m+2)/2)*(x^m)/(m*factorial(m/2));
                     df2=df2+(-1)^((m+2)/2)*(x^(m-1))/factorial(m/2);
                  end
                  x1=x-(G+f1+f2)/(df1+df2);
                  epsilon=abs((x-x1)*100/x);
                  x=x1;
               end
         diff(i)=r^2/(4*x^2*(DT(i,1)));
         sumdiff=sumdiff+diff(i);
         %fprintf(1,'  %2.10f\t\n',diff(i));
      end
      AVGDIFF(j)=sumdiff/(N2-N1);
      Cp(j)=k(j)*(10^-6)/AVGDIFF(j);

   fprintf(1,'  %2.2f\t',TT(j));
   fprintf(1,'  %2.2f\t',Q(j));
   fprintf(1,'  %2.4f\t',k(j));
   fprintf(1,'  %2.4f\t',10^6*AVGDIFF(j));
   fprintf(1,'  %2.4f\t\n',Cp(j));
end
```

Appendix C: Matlab Code for Accumulated Lethality Determination (Chapter 6)

```
%function main

clc; clear;
TP{4}='10149CUTTdr';
for i=4;
   [logSt01, Fo1, logSt02, Fo2]=ode_RK4_3(TP{i});
      fprintf(1,'  %2.5f\t\n',logSt01);
      fprintf(1,'  %2.7f\t\n',Fo1);
      fprintf(1,'  %2.5f\t\n',logSt02);
      fprintf(1,'  %2.7f\t\n',Fo2);
end

%function ODE-RK3

function [logSt01, Fo1, logSt02, Fo2]=ODE_RK4_1(x)
% Loading Temperature and pressure profile data from Spread sheet
N0=1.4*10^8;
n0=1.131227;
P0=0.21*0.2388;
T0=121.1+273.15;

function [k,n]= coefficientODE1(T,P)
T1=T+273.15; P1=P*0.2388;

k=exp(11467.4033*T1^-1+0.642348599*T1^-1*((P1-P0)^2)+0.260270539*(T1^-1)*((P1-
P0)*(T1-T0))-314.9248236*(T1^-1)*(T1*(log(T1/T0)-1)+T0)-183.6150664*(T1^-1)*(P1-P0)-
19.82177208*(T1^-1)*(T1-T0));

n=  -2.061571713+0.012739616*P-0.017035659*T-7.97465*10^(-06)*P^2+0.000146465*T^2-
2.19264*10^(-05)*P*T;
end

function [b, n]= coefficientODE2(T,P)
      b= 10^(-14.066+0.1211*T);
      n= 1;
end

function [f]=f(logSt, k, n)
      f=-(k*(N0^(n-1))/log(10))*10^((n-1)*logSt);
end
```

```
function [ff]=ff(logSt, b, n)
    ff=-b*n*(-logSt/b)^((n-1)/n);
end

TP = xlsread(x);

% Calculate the average temperature for each segment
N=length(TP);
for i=1: N;

   if i==1;
      %Average T, P of first segment
      TP(i,3)=TP(i,3)*6.89476;
      TPAV(i,1)=TP(1,1);
      TPAV(i,2)=TP(i,2);
      TPAV(i,3)=TP(i,3);
      TPAV(i,4)=TP(i,2);
      TPAV(i,5)=TP(i,3);
   else
      % Average T,P of the second segment onward
      TP(i,3)=TP(i,3)*6.89476;
      TPAV(i,1)=TP(i,1);
      TPAV(i,2)=(TP(i,2)+TP(i-1,2))/2;
      TPAV(i,3)=(TP(i,3)+TP(i-1,3))/2;
      TPAV(i,4)=TP(i,2);
      TPAV(i,5)=TP(i,3);
    end
end


for i=1:N
   logSt1(i)=-0.01;
   logSt2(i)=-0.0001;
   F01(i)=0;
   F02(i)=0;
end

for i=1:N-1;

  if (TPAV(i,2)>=95) & (TPAV(i,3)>500);
     h=(TPAV(i+1,1)-TPAV(i,1));
     [k,n]=coefficientODE1(TPAV(i+1,2),TPAV(i+1,3));
     f1=f(logSt1(i), k, n);
     f2=f(logSt1(i)+f1*h/2, k, n);
     f3=f(logSt1(i)+f2*h/2, k, n);
     f4=f(logSt1(i)+f3*h, k, n);
     logSt1(i+1)=logSt1(i)+(h/6)*(f1+2*f2+2*f3+f4);
     logSt1(i)=logSt1(i+1);
     F01(i+1)= -logSt1(i+1)*0.25;
```

```
  else
     logSt1(i+1)=logSt1(i);
     logSt1(i)=logSt1(i+1);
     F01(i+1)= -logSt1(i+1)*0.25;

  end
 end


for i=1:N-1;
[b,n]=coefficientODE2(TPAV(i+1,2),TPAV(i+1,3));
 if (b>=0) & (TPAV(i,2)>=95)% & (TPAV(i,3)>500);
     h=(TPAV(i+1,1)-TPAV(i,1))/60;
     ff1=ff(logSt2(i), b, n);
     ff2=ff(logSt2(i)+ff1*h/2, b, n);
     ff3=ff(logSt2(i)+ff2*h/2, b, n);
     ff4=ff(logSt2(i)+ff3*h, b, n);
     logSt2(i+1)=logSt2(i)+(h/6)*(ff1+2*ff2+2*ff3+ff4);
     logSt2(i)=logSt2(i+1);
     F02(i+1)= -logSt2(i+1)*0.25;
    else
     logSt2(i+1)=logSt2(i);
     logSt2(i)=logSt2(i+1);
     F02(i+1)= -logSt2(i+1)*0.25;
  end
 end

Fo1=F01(length(F01));
logSt01=logSt1(length(logSt1));
Fo2=F02(length(F02));%F01(length(F01));
logSt02=logSt2(length(logSt1));%logSt1(length(logSt1));

function plotlogSt(X,Y)
      figure('units','normalized',...
     'DefaultAxesXMinorTick','on','DefaultAxesYminorTick','on');
      plot(X/60,Y);
      xlabel('Process time (min)','FontSize',12)
      ylabel('Log reduction-log(N/No)','FontSize',12)
end

function plotlethality(t,T,P,F0)
           figure('units','normalized',...
          'DefaultAxesXMinorTick','on','DefaultAxesYminorTick','on');
           xlabels{1}= 'Process time (min)';
           ylabels{1} = 'Temperature( ^oC)';
           ylabels{2} = 'Pressure (MPa)';
           ylabels{3} = 'Accumulated lethality (min)';
```

```
        hl(1) = line(t/60,T,'Color','k','linestyle',':', 'linewidth', 0.5, 'marker', 'd', 'markersize',2);
        cfig = get(gcf,'color');
        ax1 = gca;
        pos=[0.1 0.15 0.7 0.75];
        offset = pos(3)/8;
        pos(1)=pos(1)+offset;
        pos(3)=pos(3)-offset;
        limy1=get(ax1,'ylim');limy1(1)=0;
        set(ax1,'ylim', limy1, 'XColor','k','YColor','k','position',pos, 'box', 'off','fontsize',11);


        pos=get(ax1,'position');
       %Determine the position of the third/fourth axes
        pos3= [pos(1) pos(2) pos(3)+offset pos(4)];
        %Determine the proper x-limits for the third and fourth axes
        scale3 = pos3(3)/pos(3);
        limx1 = get(ax1,'xlim');
        limx3=[limx1(1) limx1(1)+scale3*(limx1(2)-limx1(1))];
        ax2 = axes('Position',pos,'box','off',...
        'Color','none','YColor','k',...
         'xtick',[],'xlim',limx1,'yaxislocation','right','fontsize',11);
        ax3 = axes('Position',pos3,'box','off',...
           'Color','none','XColor',cfig, 'YColor','k',...
           'xtick',[],'xlim',limx3,'yaxislocation','right','fontsize',11);
        hl(2) = line(t/60, P,'Parent',ax2);
        set(hl(2), 'linestyle', '-', 'color', 'k', 'linewidth', 1.5);
        limy2=get(ax2,'ylim');limy2(1)=0;
        set(ax2,'ylim', limy2);
        hl(3) = line(t/60,F0,'Color','k','Parent',ax3);
        set(hl(3), 'color', 'k', 'linewidth', 0.9, 'marker', '*', 'markersize',2);
        %lghandle=legend(hl,'T', 'P', 'Lethality', 4);
        %set(lghandle,'fontsize', 8, 'box', 'off');
        set(get(ax1,'xlabel'),'string',xlabels{1}, 'fontsize',12);
        set(get(ax1,'ylabel'),'string',ylabels{1},'fontsize',12);
        set(get(ax2,'ylabel'),'string',ylabels{2},'fontsize',12);
        set(get(ax3,'ylabel'),'string',ylabels{3},'fontsize',12);

end

plotlogSt(TPAV(:,1),logSt2);
plotlethality(TPAV(:,1), TPAV(:,4), TPAV(:,5), F02);
end.
```