# THERMAL BEHAVIOR OF FOOD MATERIALS DURING HIGH PRESSURE PROCESSING

#### DISSERTATION

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By

Raghupathy Ramaswamy, M.E.(Ag.)

\*\*\*\*

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Dissertation Committee:

Professor V.M. Balasubramaniam, Advisor

Professor Sudhir K. Sastry

Professor Ahmed E. Yousef

Professor Valente B. Alvarez

Advisor Food Science and Nutrition Graduate Program

Approved by

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#### ABSTRACT

Knowledge about temperature and pressure history is important for evaluating process uniformity during high pressure processing (HPP). Process uniformity is further influenced by the food's thermal properties. This study was conducted to estimate thermal conductivity and heat of compression of selected materials under pressure to evaluate thermal behavior of foods under pressure.

Thermal conductivity (*k*) of selected foods was determined using a line heat source probe. The probe was calibrated using distilled water. Probe specific calibration factors were developed by comparing experimental data against National Institute of Standards and Technology (NIST) data for water. Thermal conductivity of selected liquid (apple juice, canola oil, clarified butter, honey and high fructose corn syrup) and solid foods (carrot, cheddar cheese, guacamole, chicken breast and chicken fat) were determined at pressures between 0.1 and 700 MPa. The process temperatures used were 25°C for liquids and 25, 50 and 75°C for solid foods. Thermal conductivity increased linearly for all foods with increasing pressures. Among the liquids tested, water and apple juice had the highest *k* (0.82 W/m°C), while fatty foods had the lowest (0.4 W/m°C) at 700 MPa. In solid foods, *k* increased with increasing moisture content and process temperature and decreased with increasing fat content. Carrot had the highest *k* (0.90

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W/m°C), while chicken fat had the lowest k (0.43 W/m°C) at 700 MPa and 75°C. The combined uncertainty in the measured k values ranged from 0.6% (canola oil) to 4.2% (chicken fat). Effect of polarity and molecular structure on heat of compression ( $\delta$ ) was analyzed in a separate study. While polar liquids showed a linear trend with the  $\delta$ , non-polar liquids exhibited a nonlinear relationship. Heat of compression decreased with increasing polarity index (8.8 °C per100 MPa for chloroform to 3 °C per100 MPa for water). Change in carbon chain length (C<sub>2</sub> to C<sub>4</sub>) and degree of saturation (C<sub>18:1</sub> to C<sub>18:3</sub>) of selected fatty acids had effect on  $\delta$  only at elevated pressures. Empirical relationships were developed for predicting k and the maximum rise in temperature under pressure.

Dedicated to my father, wife and kids

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## VITA

1989	B.E.(Ag.),Tamil Nadu Agricultural University, Coimbatore, India
1991	M.E.(Ag.), Tamil Nadu Agricultural University, Coimbatore, India
1992 - 1994	. Senior Research Fellow, Tamil Nadu Agricultural University, India
1994 - 1997	. Assistant Professor, University of Agricultural Sciences, Dharwad, India
1997 - 2003	. Assistant Professor, Tamil Nadu Agricultural University, India
2003 – present	Graduate Research Associate, The Ohio State University

## **PUBLICATIONS**

#### **Research Publications**

- 1. Raghupathy Ramaswamy, V.M. Balasubramaniam and S.K. Sastry. 2007. Thermal conductivity of selected liquid foods at elevated pressures up to 700 MPa. *Journal of Food Engineering*, 83 (3), 444-451.
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#### **Book chapters**

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### FIELDS OF STUDY

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#### CHAPTER 1

#### **INTRODUCTION**

High pressure processing (HPP) is a novel food processing technique where elevated pressures (up to 700 MPa) can be used to preserve food without significant thermal impact on food quality. HPP has been applied in food processing to inactivate microorganisms and enzymes while preserving quality (vitamins, pigments and flavor), changing functionality by affecting proteins, or increasing rates of freezing and thawing. The process is also known as high hydrostatic pressure processing (HHP) and ultra highpressure processing (UHP). HPP products currently marketed worldwide are primarily distributed refrigerated. The products include jams, jellies, oyster, meat products, salad dressing, juices, yogurt and guacamole. Low acid, shelf-stable products such as soups are not commercially available.

Pressure treatment can be a batch or a semi-continuous process. Most of the commercial equipment are batch in nature. In a typical batch process, the product is packaged in a flexible high barrier container (usually a pouch or plastic bottle) and is loaded into a high pressure chamber filled with a pressure-transmitting (hydraulic) fluid. The hydraulic fluid (normally water) in the chamber is pressurized with a pump, and this

pressure is transmitted through the package into the food. Pressure is applied for a specific time, usually 3 to 5 minutes. The processed product is then removed and stored/distributed in the conventional manner. Because the pressure is transmitted uniformly (in all directions simultaneously), food generally retains its shape, even at extreme pressures. Products containing excess air may be deformed under pressure due to difference in compressibility between the product and the air.

Knowledge on thermal and pressure history is necessary to evaluate potential process non-uniformities during high pressure processing. During high pressure processing, water, a major constituent in the food material, is compressed to about 15-20%. Further due to compression during HPP, the temperature of the food materials under pressure also increases. The magnitude of this temperature rise depends on target pressure, temperature and food composition. While pressure is assumed to be distributed quasi-uniformly through the entire processed volume, heat transfer between the food material, pressure transmitting fluid, and pressure chamber needs to be considered in determining cold-spot (location which received the least process treatment). Thus, study on thermal and physical properties (such as thermal conductivity, specific heat, heat of compression, density. etc.) of food material under pressure will be helpful to document the extent of process non-uniformity during pressure treatment.

Methods for measuring properties of foods under atmospheric conditions have been reviewed by many prior researchers. Determination of properties at elevated pressure conditions through conventional techniques is hampered by practical instrumentation problems and reported values are scarce. Determination of thermal properties of foods under HPP will help in developing and evaluating numerical conductive heat transfer models, capable of predicting temperature evolution throughout food products undergoing batch HPP processes (i.e. the temperature rise observed during the compression step and the subsequent temperature evolution during holding time). The past literature primarily focused on food safety aspects of high pressure pasteurization. Uniform heating during pressurization and immediate cooling during depressurization reduces quality degradation due to thermal effects. Relatively limited studies focused on unique quality benefits of pressure-treated products.

The primary objective of this dissertation research was to determine thermal behavior of food materials during HPP as influenced by process temperature and food composition. The central hypothesis is that properties and behavior of food materials change with pressure and temperature, and food composition. The specific objectives of this dissertation are:

- 1. To estimate the thermal conductivity of selected liquid foods under elevated pressures up to 700 MPa at 25°C.
- 2. To estimate the thermal conductivity of selected solid foods under combined pressure and temperature conditions.
- 3. To evaluate the role of polarity and molecular structure on the heat of compression of selected polar and non-polar components.
- 4. To evaluate the effect of high pressure pretreatment on hydration characteristics of navy beans.

#### **CHAPTER 2**

# HIGH PRESSURE PROCESSING – BASIC PRINCIPLES, EFFECT ON PROPERTIES AND MECHANISMS OF MICROBIAL INACTIVATION

#### 2.1. Introduction

High Pressure Processing (HPP) is a method of food processing wherein the food is subjected to elevated pressures (pressures up to 900 MPa or 9000 atm) with or without the addition of heat to achieve microbial inactivation or to alter food attributes in order to achieve consumer-desired qualities. High pressure processing is also called as high hydrostatic pressure processing (HHP), ultra high pressure processing (UHP), or sometimes pressure assisted thermal processing (PATP). The amount of pressure used in high pressure applications is 7-20 times greater than the pressure at the deepest ocean (Knorr, 1999; Moshaev et al., 1996). Compared to other non-thermal technologies such as pulsed electric field (PEF) processing, ionizing radiation and ultraviolet radiation (UV), HPP was found to be more suited for wholesome treatment of most of the food products including solid foods (Lado & Yousef, 2002). PEF processing is suited only for liquid (pumpable) foods and irradiation is yet to overcome the social stigma. A number of food products minimally processed using HPP and stored under refrigerated conditions are currently marketed worldwide. This include jams, jellies, fish, oyster, meat, salad dressing, rice cake, juices, smoothies, and guacamole (traditional Mexican sauce made with avocado puree, onion, salt and other ingredients). Other potential applications of HPP include processing shelf-stable foods, blanching, pressure extraction, pressure assisted freezing and thawing. Thermally induced off-flavors are minimized by application of HPP. HPP can be used to process both liquid and water containing solid foods. Batch processing of pre-packaged foods being the current trend, the technology has been upgraded to process liquid foods (juice-like) in a semicontinuous manner without packaging (Farkas & Hoover, 2000; Patterson, 2005).

Knowledge about temperature and pressure histories is important for evaluating process uniformity during HPP. Process uniformity is further influenced by properties of food materials under pressure. This information will be useful in microbial and enzyme kinetics studies and in improving our understanding on interactions among the various food constituents. This improved understanding will help food processors to extend the application of HPP technology to a wide variety of foods and create new market opportunities for processed foods. However, reliable data on pressure-temperature effects on physical transport and thermodynamic properties of food materials are not readily available. This chapter focuses on the governing principles of high pressure processing, effect of HPP on properties of food components and the mechanisms behind high pressure inactivation of microorganisms.

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#### **2.2.** Governing principles of HPP

High pressure processing is governed by two fundamental principles (Smelt, 1998): Isostatic pressure rule and Le Chatelier's principle. According to the isostatic pressure rule, pressure transmission through the food product is instantaneous and uniform irrespective of the size and geometry of the food. According to Le Chatelier's principle, pressure enhances any phenomenon that results in a decrease of volume. The phenomenon may be any chemical reaction, phase transition or change in molecular configuration (Butz & Tauscher, 2002).

#### **2.3.** Thermal effects during high pressure processing

Efficacy of high pressure processing in microbial inactivation and food preservation have been extensively studied (Balasubramaniam, 2003; Cheftel, 1995; Farkas & Hoover, 2000) but very limited emphasis was given on controlling thermal effects during HPP. All compressible substances change temperature during physical compression and this is an unavoidable thermodynamic effect (Figure 2.1) (Ting, Balasubramaniam & Raghubeer, 2002). The pressure increase during the come-up time from P<sub>i</sub> to P<sub>1</sub> increases the temperature from its initial value T<sub>i</sub> to a maximum value T<sub>1</sub>. The magnitude of this change depends mainly on the compressibility of the substance, thermal properties, initial temperature, and target pressure (Rasanayagam, Balasubramaniam, Ting, Sizer, Bush & Anderson, 2003; Ting et. al., 2002). The maximum product temperature at target process pressure is independent of compression rate as long as heat transfer to the surroundings is negligible. It is further interesting to note that while the rate of temperature increase of aqueous substances readily follow the rate of pressurization, maximum temperature ( $T_1$ ) of fatty substances slightly lag (30-60 sec) behind the maximum target pressure ( $P_1$ ) (Rasanayagam et. al., 2003). This is attributed to the difference in their respective molecular structure. During pressure holding time ( $P_1$  to  $P_2$ ), the temperature of the product decreases from  $T_1$  to  $T_2$  due to thermal exchange through pressure vessel. Immediately after depressurization, product temperature drops to  $T_f$ , which is lower than its initial temperature value ( $T_i$ ). Thus HPP provides a unique opportunity to uniformly heat the product with minimal thermal degradation effects during treatment and cool down the product immediately after treatment.

#### **2.4.** Compression heating of food materials

Substances change temperature during physical compression. Gases experience significant compression during pressurization. In contrast, liquids are far less compressible than gases, and solids have the lowest compressibility. The compression behavior of water under pressure has been well-documented (Bridgman, 1912; Bridgman, 1923; Bridgman, 1931). However, limited information is available on compressibility of food materials.

Compression heating (i.e., instantaneous temperature change in materials during pressurization or depressurization) can be theoretically calculated using the equation (Ardia, Knorr & Heinz, 2004; Kalichevsky, Knorr & Lillford, 1995).

$$\left(\frac{\partial T}{\partial p}\right)_{s} = \frac{\beta}{\rho . C_{p}} . T$$
(2.1)

where  $\beta$ , T,  $\rho$  and C<sub>p</sub> represent the thermal expansion coefficient, temperature, density and heat capacity at constant pressure respectively.

Equation (2.1) is strictly applicable only to small pressure changes and Otero, Molina-Garcia & Sanz, (2000) used it in an iteration-based method to calculate compression heating of water for larger pressure differences. The main constraint is the calculation of volume under pressure, which cannot be taken as constant under elevated pressure conditions. Alternatively, researchers often experimentally estimated compression heating values by directly monitoring temperature change in the substance during pressurization (Rasanayagam et. al., 2003) or depressurization (Otero et. al., 2000). Compression heating value of water increases with increase in its initial temperature (Figure 2.2). Since water is the main ingredient in most foods, compressionheating behavior exhibited by most foods (Table 2.1) (Rasanayagam et. al., 2003; Kesavan, Balasubramaniam, Adhikari, Narayanaswamy & Parulekar, 2002) is very similar to that of water. To date, water seems to be the lowest heating component under pressure and fats and oils seem to have the highest compression heating (up to 9°C per 100 MPa). This difference in thermal response of water, fats and oils could be attributed to their respective molecular structure and phase transition characteristics. Compression heating values of fats and oils are not much influenced by its initial temperature. Knowing compression heating factors  $(CH_m)$  for food constituents and food composition (M), the apparent temperature of the test sample at the beginning of pressure holding can be estimated using simple mixture rule (Rasanayagam et. al., 2003):

$$T_{1} = T_{i} + \left(\frac{\sum_{i} (CH_{m} * M_{f})}{M}\right)(\Delta P)$$
(2.2)

#### 2.5. Properties of foods under pressure

After the pioneering work of Bridgman, the properties of water under pressure (Table 2.2) were well documented and the data are available from the International Association for the Properties of Water and Steam (IAPWS, 1996). This formulation is valid in the stable fluid region of water from the melting pressure curve to 1000°C at pressures up to 1000 MPa (Otero et. al., 2000). A software implementation of IAPWS work can be obtained from the U.S. National Institute of Standards and Technology (NIST) (Harvey, Peskin & Klein, 1996). Since most foods mainly contain water, and due to lack of information on properties of food materials under pressure, they are assumed to have similar values as that of free water. However, a note of caution: in a food sample, water may exist in different possible forms and the properties of bound water are significantly different from that of free water.

#### 2.5.1. Thermal conductivity

Determination of thermal conductivity under high pressure is hampered by practical problems and reported values are scarce. A line heat source probe technique based on the unsteady-state method was used by Denys and Hendrickx (1999) for determining the thermal conductivity of water and other homogenous and uniform liquid foods. The probe differed from the line heat source (hot-wire) technique by having two separate wires for heater and temperature sensor instead of one. Thermal conductivity of materials increased with increase in pressure and further influenced by the amount of moisture present in the food material (Shariaty-Niassar, Hozawa & Tsukada, 2000). The pressure dependency of thermal conductivity values was higher at lower moisture

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contents than at higher moisture contents. This may be due to the smaller percentage of incompressible water and higher porosity of the sample at lower moisture contents.

A primary source of error in the line heat source probe technique is the change in resistivity of heating elements under pressure. The error may be minimized by calibrating the probes individually at specific operating conditions. It has been recognized that high pressures of interest do not influence the type K thermocouple readings at temperatures below 500°C (Bundy, 1961; Cheng, Allen & Lazarus, 1975).

#### 2.5.2. Specific heat

Determination of specific heat of foods at atmospheric pressure is simple using conventional methods such as the method of mixtures or differential scanning calorimetry (DSC) techniques. Specific heat of food materials has commonly been assumed constant regardless of the applied pressure. This assumption is not valid for the elevated pressuretemperature conditions encountered during high pressure processing. The data on specific heat of pure water as a function of elevated pressure and temperature are readily available through the NIST data base (Harvey et. al., 1996) and presented in Table 2.2. These values are approximately ten percent lower than those estimated at ambient pressures. Often researchers ignore the effect of pressure on specific heat in heat transfer calculations (Denys, Van Loey & Hendrickx, 2000).

#### 2.5.3. Thermal expansivity

Efforts were also made to determine the thermal expansion coefficient of various products (apple sauce, tomato paste and agar gel) at different conditions of pressure and

temperature (Denys et. al., 2000). Experiments were conducted at an initial uniform temperature and the temperature increase due to known increase in pressures was measured. The thermal expansion coefficient,  $\beta_{TP}$ , was then calculated using:

$$\beta_{TP} = \frac{\Delta T \ C_p}{\Delta P \ T \ V}$$
(2.3)

where T and P are the average values during the measured period of pressure build up. The values of thermal expansivity of products tested were lower when compared to the values for pure water.

#### 2.5.4. Density

Density of a product at atmospheric pressure may be measured as the ratio of its mass and volume. A similar principle could be used for the measurement of sample density under pressure. This involves the estimation of sample volume change at the target pressure. Volume change in sample plus surrounding pressure transfer fluid can be measured by converting the volume change into a linear expansion through the use of a bellows. The linear change in the bellows is measured with a linear velocity differential transducer (LVDT) (Bridgman, 1931; Chang & Moldover, 1996). Stick/slip jumps caused by frictional loss during displacement should be considered. Another approach is using pressure-dependent acoustic methods (Kovarskii, 1993). Denys et. al., (2000) used the bulk volume displacement method for estimating density of apple sauce and tomato paste. The pressure relation of product density was determined after immersion of the sample in the pressure vessel and measuring the amount of pressure transmitting medium to be pumped into the system for compressing it to a particular pressure. After compression and pressure stabilization, pressure was released from the vessel and the surplus pressure medium (pumped in the vessel during the compression step) was collected and weighed. The pressure relation of the density of the product was then calculated using the expression:

$$\rho_{product} = \frac{M_{product}}{V_{product}}$$
(2.4)

where

$$V_{product} = V_{vessel} - \left(\frac{M_{medium} + \Delta M_{medium}}{\rho_{medium}}\right)$$
(2.5)

where  $\rho$  is the density of the product (kg/m<sup>3</sup>), M is the mass (kg), V is the volume (m<sup>3</sup>),  $\Delta$ M is the mass of the pressure medium collected upon decompression.

#### 2.6. Process uniformity assessment

It is generally accepted that pressure is transmitted uniformly and quasiinstantaneously throughout the sample volume. Accordingly, if one considers pressure effects alone, there are no significant process non-uniformity issues. On the other hand, thermodynamically it would be difficult to separate pressure and thermal effects due to compression heating of materials during high pressure processing. Due to difference in compression heating of materials, the temperature of a product processed inside a pressure chamber can change as a result of heat exchange to or from the pressure transmitting fluid, the pressure vessel and the environment (De Heij, Va Schepdael, & Van der Berg, 2001; Ting et. al., 2002) The resulting temperature distribution within a pressure chamber (Figure 2.3) depends on the thermophysical properties of food, pressure transmitting fluid, and those of the pressure chamber material. Since metals have negligible compression heating values, upon pressurization the interior metal surface of the pressure chamber is likely to be at a lower temperature than that of the sample being processed and the pressure transmitting fluid. Hartmann and Delgado (2002) used mathematical modeling to investigate heat transfer effects during high pressure processing of packaged foods. They reported that by changing the properties of the packaging material, a marked temperature gradient could be induced.

The temperature gradient within different regions of the processed volume would result in a pronounced non-uniformity effect on enzyme and/or microbial inactivation, nutritional and/or sensorial quality degradation (Denys et. al., 2000). Makita (1992) emphasized that temperature gradients in the pressure chamber are almost unavoidable, even if a thermostatic jacket is equipped around the pressure vessel. The author suggested that stirring the pressure medium could reduce the gradient but may be technically difficult under pressures higher than 300 MPa. Denys et. al., (2000) proposed applying an appropriate heat source at the boundary of the product to prevent the temperature gradients (in anticipation of the temperature increase of the compressed product). The unwarranted thermal effects could be further minimized by controlling variables such as initial temperature of the product, pressure transmitting fluid, and pressure chamber, ratio of pressurizing fluid to product in the pressure chamber and pressure hold time (Balasubramaniam & Balasubramaniam, 2003). Choosing a proper insulation material for the pressure chamber could also reduce the heat exchange between the sample and the environment (Meyer, Cooper, Knorr & Lelieveld, 2000).

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#### 2.7. Effect of high pressure on microbial cells

High pressure processing is one of the promising non-thermal alternative technologies whose efficacy against pathogenic and spoilage food-borne vegetative microorganisms has been estimated (Hendrickx & Knorr, 2001). Its application in eliminating the spores is being currently investigated. High pressure combined with temperature and high pressure applied in pulses hold promise in achieving shelf-stable products (Balasubramaniam, 2003; Meyer et al. 2000). The mechanisms of microbial inactivation during HPP are still not fully understood. However, HPP was reported to induce changes to the cell membranes, cell morphology and affect biochemical components and other genetic mechanisms (Hoover et al., 1989; Patterson, 2005). The extent of inactivation depends on the type of microorganism, the pressure level, the process temperature and time, the pH, and the composition of the food (Smelt, 1998).

The cell membrane of vegetative bacteria is made up of a phospholipid bilayer with associated proteins (Fig. 2.4) (Neidhardt, Ingraham & Schaechter, 1990). The associated proteins are membrane-penetrating with amphiphilic structure (Kato & Hayashi, 1999). The highly polar or ionic groups (hydrophilic) are on the outer membrane in contact with the surrounding aqueous phase and the nonpolar groups (hydrophobic) are buried in the interior of the bilayer (Neidhardt et al., 1990). Increasing pressure at constant temperature increases the thickness of the bilayer caused primarily by the change in their molecular assembly (Kato & Hayashi, 1999). Increasing pressure reduces the volume and cross-sectional area of acyl chains. This induces decreases in cell membrane fluidity and phase transitions resulting in breakage of the membrane followed by denaturation of membrane-associated proteins (Kato & Hayashi, 1999). High pressure

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treatment also solubilizes intra-cellular substances in the order of adenosine triphosphate (ATP) or UV-absorbing compounds, amino acids, and metals with increasing pressure of up to 600 MPa (Shimada et al., 1993). This allows the extra-cellular substances to permeate into cells and tissues (Kato & Hayashi, 1999). This is accompanied by the breakdown of sub-cellular organelle membranes. The various structural and functional changes occurring in vegetative microorganisms during the pressure treatment can be summarized as below (Hoover et al., 1989; Lado & Yousef, 2002).

Cell wall is less affected by high pressure than the membrane (Patterson, 2005). Pressure supplies the energy needed for the biochemical reactions that lead to a reduction in volume (ex., high compressibility of fatty acids) while retarding the reactions that lead to a volume increase (e.g., keeping the water unfrozen at sub-zero temperatures). Reduction in volume due to permeability changes in the cell membrane leads to a reduction in the cross-sectional area of the phospholipid layers (Farkas & Hoover, 2000). While pressure influences hydrophobic and electrostatic interactions in protein, the hydrogen bonds are not much influenced (Mozhaev et al., 1996). The  $\alpha$ -helical and  $\beta$ -pleated sheet forms of protein and the genetic structure of DNA helix and nucleic acids are not much affected by pressure. However, DNA replication and transcription, and translation into proteins are inhibited by high pressure as it inactivates the associated enzymes (Cheftel, 1995). Covalent bonds remain unaffected thereby preventing any damage to the sensory and nutritional quality of foods (Tauscher, 1998).

Among the vegetative bacteria, Gram-positive bacteria is more resistive to HPP than Gram-negative bacteria due to the presence of rigid teichoic acids in the peptidoglycan layer of their cell wall (Shigehisa et al., 1991). Smaller size and coccoidal shape bacteria offer more resistance to HPP than the large rod-shaped ones because of their reduced surface area for cell leakage. In the microbial growth cycle, midexponential phase growth cells are more susceptible to pressure treatment than stationary phase cells as they cannot reseal their membranes damaged by pressure (Mañas & Mackey, 2004).

Bacterial spores are the most resistive form of microorganisms to HPP (Cheftel, 1995). Their resistance is mainly due to the protective effect of membranes and coat layers surrounding the core, low water-activity in the core and due to the presence of dipicolinic acid (Fig. 2.4) (Setlow, 2003). The inactivation of spores is achieved either by a combination of high temperature with high pressure (Heinz & Knorr, 2001) or by applying pressure in stages (Furukawa, Shimoda & Hayakawa, 2003). The pre-treatment (sub-lethal pressure or thermal shock) germinates the spores followed by the pressure treatment that inactivates and kills the germinated spores (Setlow, 2003). Germination by low pressures (100-200 MPa) is supposedly caused by the activation of the germinant receptors which initiates an enzymatic chain reaction resulting in the degradation of the peptidoglycan cortex (Black et al., 2007; Heinz & Knorr, 1998). High pressures (400-800 MPa) were reported to cause the release of pyridine-2,6-dicarboxylic acid (dipicolinic acid (DPA)), leading to the hydrolysis of the cortex and hydration and expansion of the spore's core (Setlow, 2003). The germinated spores are then inactivated or killed by the mechanisms as explained before for the vegetative bacteria.

#### 2.8. Pressure-induced denaturation of proteins

Protein denaturation is the unfolding of polypeptide structure or any modification in secondary, tertiary or quaternary conformation of proteins. During pressure treatment of proteins, the primary structure remains intact because of covalent bonds (Mozhaev et al., 1996). The peptide bonds of the primary structure remain intact. However, hydrogen bonds of the secondary structures get ruptured by the high pressure treatment. While lower pressures produce reversible denaturation, higher pressures cause irreversible denaturation (Heremans, 1998). The phase diagram of proteins under pressure follows a typical elliptical curve indicating a lowering of the denaturation pressure at lower and higher temperatures than 20°C (Knorr, 1999). The protein is in its native state at low pressures and low or high temperatures (Fig. 2.6). The denaturation at these conditions is reversible or elastic. At high pressures and at low or high temperatures, protein undergoes irreversible or plastic denaturation (Heremans & Smeller, 1998).

Pressure denaturation results in the incorporation of water into the protein as against the transfer of nonpolar groups into water by heat denaturation (Hummer et al., 1998). The efficiently packed residual interior of protein is more hydrophobic than the surface. But when the water molecules are forced into the protein interior by the increasing hydrostatic pressure, the protein structures break apart resulting in its denaturation.

For a system under equilibrium,

$$\Delta G = -R T \ln K = \Delta E + p \Delta V - T \Delta S \qquad (2.6)$$

where  $\Delta G$ ,  $\Delta E$ ,  $\Delta V$ , and  $\Delta S$  are the changes in Gibbs free energy, internal energy, volume and entropy; K is the equilibrium constant governing the process, T the temperature, p the pressure, and R the gas constant (Mozhaev et al., 1996). Application of pressure only affects the volume of the system ( $\Delta V$ ) i.e., changes in the volumes of the protein molecule and water structure as against the effect of temperature which brings in changes in both the internal energy and the volume. The volume change ( $\Delta V$ ) upon denaturation or unfolding is positive at low pressures (100-200 MPa) due to the attraction of new water molecules by the newly surface-exposed amino acid residues (Farkas & Hoover, 2000). However, due to the disruption of electrostatic and hydrophobic interactions and disappearance of left out voids in the protein,  $\Delta V$  becomes negative at high pressures. The extent of hydrophobicity of a protein determines the extent of protein denaturation at any given pressure (Jaenicke, 1981). In some organisms, denaturation of key enzymes by high pressure, especially membrane-bound ATPases plays an important role in their destruction (Farkas & Hoover, 2000). Various factors which affect enzyme inactivation under pressure are pH, substrate concentration and intramolecular structure of the enzyme.

#### 2.9. Conclusions

Understanding thermal effects that occur during high pressure processing is very important as many of the reactions (such as gelation, protein denaturation, and microbial inactivation, etc.) that occur in food during processing are not only pressure dependent but also temperature dependent. Among the food constituents, water exhibited the lowest thermal effects as a result of pressurization while fats and oils exhibited highest compression heating effects. The resulting process non-uniformity due to thermal exchange between sample, pressure transmitting fluid, pressure chamber and the environment should be considered in microbial and enzyme inactivation studies. Data on properties of model and real food substances are scarce and more studies are essential to improve our understanding and process optimization.

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Fig.2.1. Typical temperature-pressure history during high pressure processing



Fig.2.2. Compression heating values of water [experimental (dashed lines) vs. predicted (continuous lines) using NIST/ASME software] at different initial temperatures.



Fig.2.3. Schematic diagram illustrating temperature distribution and heat transfer effects during high pressure processing (a) Products preheated to uniform initial temperature, (b) Products and pressure transmitting fluid reach different final temperature at the end of pressurization depending on their respective compressibility and thermal properties, (c) Extended pressure holding time results in heat exchange between vessel, pressure transmitting fluid and the products.



Fig. 2.4. Structural details of Gram-positive and Gram-negative bacteria (Adopted from: www.kcom.edu/.../Website/Lects/Bacteria.htm)



Fig. 2.5. Structural details and components of a spore which get affected during high pressure processing (Setlow, 2003).



Fig. 2.6. Phase diagram of proteins under pressure (h,p and c represents heat, pressure and cold denaturation respectively) (Heremans, 1998).

Substance at 25°C	Temperature change per 100 MPa	
Water, juice, tomato salsa, 2% fat milk and	3.0	
other water like substances		
Tofu	3.1	
Egg Albumin	3.0	
Mashed potato	3.0	
Voghurt	3.1	
Heney	3.2	
Honey	3.2	
Salmon	4.5	
Chicken fat	4.8 to <3.7 <sup>a</sup>	
Water/Glycol (50/50)	6.3	
Beef fat	8.7 to <6.3 <sup>a</sup>	
Olive oil	9.1 to <6.2 <sup>a</sup>	
Soy oil	12.01	
Silicone oil	18.5	

<sup>a</sup> Substances exhibited decreasing temperature rise as pressure increased.

Table 2.1. Compression heating factors for various food substances

Properties/ Pressure	0.1 MPa	100 MPa	200 MPa	500 MPa
Thermal conductivity W/m K	0.607	0.651	0.715	0.759
Specific heat kJ/kg K	4.18	3.99	3.83	3.79
Density kg/m <sup>3</sup>	997	1038	1101	1150

<sup>a</sup> Source: NIST/ASME Standard Reference Database 10. Version 2.2. (Harvey et. al., 1996)

Table 2.2. Properties of water (25°C) at different pressures <sup>a</sup>

Pressure (MPa)	Pressure influenced structural and functional changes
0.1	Atmospheric pressure
50	Inhibition of protein synthesis; reduction in the number of ribosomes
100	Reversible protein denaturation; compression of gas vacuoles
200	Membrane damage; Signs of cell contents leakage
300	Irreversible protein denaturation; Leakage of cell contents

Table 2.3. Structural and functional changes in vegetative microorganisms during high pressure processing

# **CHAPTER 3**

# THERMAL CONDUCTIVITY OF SELECTED LIQUID FOODS AT ELEVATED PRESSURES UP TO 700 MPa

# ABSTRACT

Thermal conductivity (*k*) of selected liquid foods during high pressure processing (HPP) was studied using a line heat source probe. The probe was calibrated using distilled water and probe specific calibration factors were developed by comparing experimental data against published data from National Institute of Standards and Technology (NIST) for water. *k* of commercially available apple juice, canola oil, clarified butter, honey and high fructose corn syrup (HFCS) were then determined using a custom made high pressure experimental setup for various pressures (0.1, 100, 300, 500 and 700 MPa) at 25°C. Results indicated that material *k* increased linearly with increasing pressures up to 700 MPa. Water and water like substances (apple juice) were found to have the highest *k* values (up to 0.82 W/m°C at 700 MPa), while fatty foods such as canola oil and clarified butter had the lowest (0.29 to 0.4 W/m°C respectively at 700 MPa) values. Honey and HFCS had intermediate values. The combined uncertainty

(including Type A and Type B) in the measurement of k values of various liquid foods ranged from 0.6 (canola oil) to 3.8% (HFCS).

#### **3.1. Introduction**

High pressure processing (HPP) is emerging as a novel alternative to thermal processing in preserving fresh like quality attributes. In a typical process, elevated pressures up to 700 MPa are used either with or without the addition of heat to preserve food without significant thermal impact on food quality (Farkas & Hoover, 2000; Sizer, Balasubramaniam & Ting, 2002). Some of the HPP products commercially available include juices, jams, jellies, yogurt, smoothies, guacamole, oysters, poultry, and meat products. Other potential applications of HPP include processing of shelf-stable products, hydration and blanching and pressure assisted freezing and thawing (Otero & Sanz, 2003; Ramaswamy, Balasubramaniam & Sastry, 2005a). All these applications require that the entire food material is subjected to uniform processing conditions to achieve safety and quality. However, thermal gradients within the processed volume may still exist under pressure affecting the uniformity of the process. The complex interdependence of thermo physical properties may create regions of hot and cold zones resulting in non-uniform effects on enzyme and/or microbial inactivation, nutritional and/or sensory quality degradation (Otero & Sanz, 2003). The undesired thermal effects could be minimized by controlling variables such as initial temperature of the product, pressure transmitting fluid, and pressure chamber, ratio of pressurizing fluid to product in the pressure chamber and pressure hold time (Ting, Balasubramaniam & Raghubeer, 2002; Otero & Sanz, 2003).

To understand process uniformity during pressure treatment, especially the thermal distribution within the processed volume, data on various thermal properties of the products is needed (Denys, Van Loey, & Hendrickx, 2000; Ramaswamy, Balasubramaniam, & Sastry, 2005b). With the growing interest in exploiting HPP as a commercially viable alternative to conventional thermal processing of foods, it becomes imperative to determine and document thermophysical properties of food materials under high pressure.

Extensive literature has documented thermal conductivity (k) of various food materials under atmospheric conditions (0.1 MPa) (Mohsenin, 1980; Nesvadba, 1983; Sweat, 1986; Murakami & Okos, 1988), and under retort-like pressure conditions (Choi and Okos, 1986). Except for the pioneering research by Bridgman (1923) on determining the effect of extreme pressure on k of water and some chemicals, very limited information is available on k of food materials. Bridgman (1923) proposed a theoretical approach for estimating thermal conductivity of pure liquids. The approach was based on the hypothesis that molecules are arranged in coherent columns and rows and energy is transferred by thermal vibration. Considering the center to center molecular spacing in a cubical lattice structure, Bird, Stewart, & Lightfoot (2002) reported the following relationship based on the Bridgman theory,

$$k = 3\left(\frac{N}{V}\right)^{\frac{2}{3}} K v_s \tag{3.1}$$

where N is the number of molecules in a mole represented by Avagadro's number, V is the molar volume in  $m^3/kg$ -mole, K is Boltzmann's constant in J/K, and  $v_s$ , the velocity of sound in m/s. Sonic velocity  $(v_s)$  data is available only for a few organic liquids and can be calculated from compressibility values using the expression,

$$v_{s} = \sqrt{\frac{1}{\rho(\frac{1}{\rho})(\frac{\partial\rho}{\partial p})_{T}}}$$
(3.2)

where  $(\frac{1}{\rho})(\frac{\partial \rho}{\partial p})_T$  is the isothermal compressibility and  $\rho$ , the density of the liquid. For most food materials, such data does not exist, so direct experimental determination of *k* values of foods under pressure is required.

Denys & Hendrickx (1999) studied *k* of tomato paste and apple pulp at pressures up to 400 MPa. Shariaty-Niassar et al., (2000) reported *k* of gelatinized potato starches at pressures up to 10 MPa. Most authors relied upon the line heat source probe technique for estimating *k* under pressure. This method is also a method of choice for estimating *k* values in thermally processed food samples due to convenience, speed of measurement, sample size, and limited influence of sample geometry on measurement (Sweat & Haugh, 1974; Sweat, 1986; Murakami & Okos, 1988; Murakami et. al., 1996b). The objective of the current research was to determine *k* for selected liquid foods under pressures up to 700 MPa at 25°C and to develop mathematical relationships to predict thermal conductivity under pressure.

#### 3.2. Materials and methods

#### 3.2.1. Experimental set-up

A custom fabricated high pressure test system (Harwood Engineering Co. Inc., Massachusetts; 26190) was used for the experiments. The system was capable of pressurizing to 1000 MPa with a pressurization rate of approximately 20 MPa per second. Temperature within the pressure chamber could be isothermally controlled using an outer jacket connected to a water/oil bath circulator (Busch Electronics LLC, Minnesota). A mixture of 50% propylene glycol (Safe-T-Therm, Houghton Int. Inc., Pennsylvania) in distilled water (Ohio State University Chemistry store) was used as the pressure transmitting fluid. The top closure of the pressure chamber had provisions for attaching insulated thermocouple and heater feed-through wires (Fig 3.1a). Entrapped air within the pressure transmitting fluid was purged through a purging mechanism attached to the top closure.

#### **3.2.2.** Thermal conductivity probe and data acquisition system

A line heat source probe technique designed to withstand elevated pressures (up to 700 MPa) was custom fabricated (Fig. 3.1b) by adapting the design guidelines proposed by Murakami, Sweat, Sastry, Kolbe, Hayakawa, & Datta (1996b). The probe's length-to-diameter ratio was 60 to minimize the axial heat flow error (Sweat, 1986; Murakami et. al., 1996b). A K-type thermocouple (response time <0.1s) was chosen as the temperature sensor, since high pressures do not influence type K thermocouple readings below 500°C (Bundy, 1961). The thermocouple wires (TFCY-003; TFAL-003; Omega Engineering, Stamford, Connecticut; diameter: 0.076mm) along with the

insulated constantan heater wire (TFCC-003; Omega Engineering, Stamford,

Connecticut; diameter: 0.076mm) were inserted inside a stainless steel hypodermic needle tube (VITA Gauge 20, Needham, Massachusetts; outer diameter:0.71mm; thickness: 0.15mm). Care was taken to position the thermocouple junction in the middle of the probe tube by physical measurement. The wires were insulated to avoid any short circuits. They were connected to the power source (BK precision, Mouser Electronics Inc., Texas; 615-1621A) and data acquisition system (Agilent Technologies, Palo Alto, California; 34970A; 20 bits) using appropriate lead wires less than 1 m long. The internal digital multimeter of the data acquisition system used 6 digits (20 bits) resolution with slow mode filter (3-Hz) for noise reduction. The pressure chamber, the power source and data acquisition system were grounded to the same source to minimize the measurement error in data collection. The electrical contact junctions in the end closure and wire feed-throughs were insulated with epoxy to avoid short circuits. The extension or lead wires from the thermocouple and heater wires were twisted and then wrapped with a grounded foil sheath to minimize induced voltages in the loops.

#### **3.2.3.** Sample holder

A 19 mm diameter polycarbonate sample holder (US Plastics, Lima, Ohio) with a movable piston was used to suspend liquid samples (Fig. 3.1a). The thermal conductivity probe (TCP) was aligned approximately in the central axis of the sample holder. Air bubbles present in the sample holder were released through a central hole in the piston before the commencement of pressurization experiments. The sample holder was

subsequently closed using a metallic screw against an O-ring on the piston. The O-ring also prevented the pressure transmitting fluid from mixing with the liquid food sample.

#### 3. 2.4. Probe calibration

Preliminary experiments were carried out with distilled water at various power levels (up to 10 W/m) to choose a power level with minimal convection effects. Microcarrier beads (LSG1007-2135, SoloHill Engineering Inc., Ann Arbor, Michigan) of specific gravity 1.006 were suspended in distilled water inside the transparent polycarbonate sample holder. A known power was supplied to the heater wire and the corresponding bead movement in response to thermal convection during power application was videotaped. Visual examination of video tape recording and analysis of recorded experimental data (sample temperature and applied power) were used to choose the optimum power level.

The TCP was calibrated with distilled water at various pressures (0.1, 100, 300, 500 and 700 MPa) and at 25 °C using the selected power level (4.7 W/m). The sample holder was filled with the calibration fluid and then loaded into the pressure chamber. During high pressure experiments, first, the heat of compression gained by the sample (Fig 3.2; region A-B) was given sufficient time (120 to 1200 s) to dissipate so that the test sample reached the desired process temperature (Fig 3.2; region C-D). The external circulating water jacket attached to the pressure chamber helped control temperature. At the desired equilibrium temperature ( $25\pm1$ °C), a constant direct current (DC) power (*Q*) was applied to the probe. The temperature in the close proximity to the heater wire (Fig 1b) was recorded at 1 s time (*t*) intervals for 60 s (Fig 3.2, region D-E). In addition,

voltage (*V*), current (*I*), pressure (*P*) were also recorded. The thermal conductivity of water was then calculated from the slope  $(4\pi k/Q)$  of the linear portion of the logarithm of time versus temperature plot based on the cylindrical coordinate solution of Fourier equation for unsteady-state radial heat conduction in an infinite medium (Carslaw & Jaeger, 1959; Murakami, Sweat, Sastry & Kolbe, 1996a; Denys & Hendrickx, 1999; Murakami et al., 1996b):

$$k = \frac{Q}{4\pi\,\Delta T} \left[ \ln\left(\frac{t_2}{t_1}\right) \right] \tag{3.3}$$

where k is the thermal conductivity of the sample (W/m°C) and  $\Delta T$ , the temperature difference between time  $t_1$  and  $t_2$ . The experimentally determined k data ( $k_{experiment}$ ) of water were then compared against NIST/ASME steam properties database ( $k_{standard}$ ) (Harvey, Peskin & Klein, 1996) (Fig.3.3a). Probe specific calibration factors corresponding to each pressure level were then calculated using eqn. (3.4).

$$X_{cal,p} = \frac{k_{\text{standard}}}{k_{\text{experiment}}}$$
(3.4)

The calibration experiments were repeated for three times at each pressure level and the mean value was considered for estimating k of selected liquids.

# **3.2.5.** Food materials

Thermal conductivity of selected liquid foods including canola oil, clarified butter, honey, high fructose corn syrup (HFCS) and filtered apple juice were determined at pressures up to 700 MPa as per the procedure described for water. The samples were purchased from a local supermarket (Wild Oats, Columbus, Ohio). HFCS was obtained from ADM Co., Decatur, Illinois. The samples chosen were without any additives and their atmospheric pressure k values were available in literature (Table 3.1). Fresh food samples were used for all the experiments. Experimentally measured k value at each pressure level was multiplied by the corresponding calibration factor to obtain final k value. The experiments were repeated for five times. The mean values and standard deviations were calculated for each of the liquids at each of the pressure levels.

# **3.2.6.** Uncertainty analyses

The sources of measurement errors and the uncertainty of the measured thermal conductivity values were analyzed based on GUM (Guide to the Expression of Uncertainty in Measurement) recommendations of the International Standards Organization (Taylor & Kuyatt, 1994; Kirkup & Frenkel, 2006). The total standard uncertainty (including Type A and Type B) during *k* measurement was estimated. Type A uncertainty component associated with the input quantity  $X_i$ ,  $u(x_i)$  was estimated by calculating the standard deviation of the mean  $(\overline{X_i})$  of *n* number of independent observations  $X_{i,k}$  of  $X_i$  at each of the same measurement conditions:

$$u(x_i) = \left(\frac{1}{n(n-1)} \sum_{k=1}^n \left(X_{i,k} - \overline{X_i}\right)^2\right)^{1/2}$$
(3.5)

Type B uncertainty was estimated based on scientific judgment of the various factors influencing the experimental output. This include measurement errors associated with temperature, pressure, power and time as well as the non-measurement errors associated with the theoretical assumptions made in k estimation.

Considering the measurement variables as mutually uncorrelated, the combined standard uncertainty,  $u_c(k)$  was estimated as the positive square root of the estimated variance  $u_c^2(k)$  obtained using the law of propagation of uncertainty:

$$u_c^{2}(k) = \sum_{i=1}^{N} \left(\frac{\partial k}{\partial x_i}\right)^2 u^{2}(x_i)$$
(3.6)

where  $u(x_i)$  indicates the standard uncertainty component associated with the input estimate  $x_i$  of either Type A or Type B.

#### **3.3. Results and Discussion**

Fig. 3.2 presents the time-temperature response of the sample during a typical HPP treatment. During the pressure treatment, sample temperature increased due to the heat of compression (Fig. 3.2, region A-B). Among the liquids tested water had the lowest heat of compression (3 C per 100 MPa) while oils had the highest heat of compression (7-8 C /100 MPa) (Rasanayagam, Balasubramaniam, Ting, Sizer, Bush & Anderson, 2003). Due to the differences in thermal properties (including heat of compression) (Table 3.2), different liquids required different times for thermal equilibration. Within the experimental conditions, thermal equilibration time was minimum for water (approximately 120 s) and maximum for canola oil (about 1200 s).

# 3.3.1. Calibration

During the calibration experiments, lower power yielded better linear fit of logarithmic time vs temperature data than the higher power levels. Based on the review of the recorded video images and analysis of sample temperature and applied power data (not shown), approximately 4.7 W/m was found to give a smooth time-temperature response (Fig.3.2; region D-E) with reasonable  $\Delta T$  for all the liquid foods studied.

The temperature rise after the first 5 s  $(t_1)$  of application of power was linear. Hence, the portion of the curve after 5 s was considered for analysis to reduce the truncation error (Murakami et al., 1996a). A sample probe specific calibration factor curve is presented in Fig. 3.3b. The calibration factors were related to applied pressures using a third degree polynomial. The observations were similar to the findings of Denys & Hendrickx (1999). Calibration factors close to 1.0 are highly desirable; however due to limitations of manual fabrication of the probe, calibration factors tend to vary between 0.81 and 1.1. Whenever a new probe was used, the calibration procedure was repeated and a new set of probe-specific calibration factors was developed and used to adjust the raw k values. One key difference between this study and previously reported work (Denys & Hendrickx, 1999) was the use of water as the calibration standard instead of agar gel. This was done as the influence of pressure treatment on the gelation of agar gel was uncertain and not fully characterized. Further, the reported NIST/ASME k values were available only for water (Harvey, Peskin & Klein, 1996). Potential errors due to natural convection were minimized using a low power input – still, it is possible that nonmeasurement errors might have occurred.

# **3.3.2.** Thermal conductivity of liquid foods under pressure

Experimental *k* values for filtered apple juice, canola oil, clarified butter, honey and high fructose corn syrup (HFCS) are given in Fig. 3.4 and Table 3.1. Values at atmospheric pressure were reasonably in agreement with published values (Table 3.1).

Any variability between the literature and experimental data may be due to differences in their biological source, sample temperature and method of measurement. The *k* value of the test substances under pressure increased linearly ( $R^2>0.90$ ) with increasing pressure (Fig. 3.4). When pressure increased from 0.1 to 700 MPa, *k* of water increased from 0.61 to 0.82 W/m°C, while for canola oil the values changed from 0.20 to 0.29 W/m°C. Filtered apple juice (88% water content) values were found to be very close to that of water. Honey and HFCS, the two carbohydrate solutions tested also showed a linear trend, but had intermediate *k* values between water and oil. The *k* of liquid food substances tested in this study can be correlated with pressure using a simple linear empirical relationship of the form

$$k_{\text{liquid}} = \alpha + \beta P \tag{3.7}$$

where  $\alpha$  is the y intercept of the least-square fit and  $\beta$  is the slope. Values of  $\alpha$  and  $\beta$  for different liquid foods estimated at various pressure levels are summarized in Table 3.1. In the absence of theoretical models for predicting *k* values of food materials under pressure, empirical relationships provided in Table 3.1 could be used for estimating *k* values within the range of experimental conditions studied. Extrapolation of the results beyond the experimental conditions is not advised as it might result in erroneous values.

At elevated pressures, water and other substances become compressible. For example, water, a polar compound is compressed by 15 to 20% at 600-700 MPa (Harvey, Peskin & Klein, 1996). Accordingly, the molecules are held closer reducing the length of free molecular movement and hence increasing the k value consistent with the theory proposed by Bridgman (1923). Table 2 shows that among the products tested, clarified butter had the highest increase (106%) in k under pressure and water had the lowest increase (35%). Water and aqueous-based materials have lower compressibility (Bridgman, 1923) than fat-based foods and their k values under pressure changed to a lesser extent. Amount of moisture present in the food product also influenced the k values under pressure (Shariaty-Niassar et al., 2000). The estimated k values of all substances in this study were higher than k values of materials under atmospheric pressure signifying faster thermal equilibrium under pressure.

#### **3.3.3. Uncertainty analysis**

#### **3.3.3.1.** Type A uncertainty

The standard deviation of replicate measurements provided estimates of Type A uncertainties. For each of the selected liquids over the selected pressure range these uncertainties were: apple juice (1.0-2.5%); honey (1.0-2.3%); HFCS (1.6-3.8%); clarified butter (0.6-1.6%) and canola oil (0.5-2.1%).

# **3.3.3.2.** Type B uncertainty

#### 3.3.3.2.1. Temperature measurement

Type K thermocouple used in the study had 0.4% error (Omega Engineering, Stamford, CT). The data acquisition manufacturer (Agilent Technologies, Palo Alto, CA; 34970A) specified that the uncertainty related to thermocouple *emf* measurement was about 0.05%. Therefore the combined uncertainty of the temperature measurement was estimated to be 0.45%. Since this uncertainty was mainly systematic (carried out throughout the experimentation) and k was calculated using slope of the temperature rise vs logarithm of time evolution, researchers often considered the uncertainty in temperature measurement during k estimation as negligible (Labudova & Vozarova, 2002). Therefore, a temperature uncertainty value of 0.1% was used in subsequent calculations.

#### **3.3.3.2.2.** Pressure, power, and time measurements

The uncertainties related to the pressure, power and the time measurements were based on the operating characteristics of the data acquisition system (Agilent technologies, Palo Alto, CA; 34970A). The combined influence of these parameters on the uncertainty of k measurement was assumed to be 0.1%. The estimate included 0.005% measurement error for DC voltage (for pressure and power), 0.05% error for DC current (for power) and 0.01% for time. At elevated pressures, the resistivity of the heating element may also change. Earlier researchers (Bridgman, 1970; Jansen, 1997) reported this source to be negligible. In this study, the experimental errors were further minimized by individually calibrating the TCPs and using the probe specific calibration factor in estimating k.

#### **3.3.3.2.3.** Non-measurement errors

The theoretical solutions for k considered ideal experimental conditions, some of which might be difficult to be put into practice. For example, the TCP has finite rather than negligible thermal mass and finite instead of infinite length. Such deviations could contribute to errors in k measurement. Similarly, thermal contact resistance between TCP

and the sample, thermocouple and the heater wire may also influence k measurement. Such errors were minimized as much as possible by using a very thin wire, making the TCP length-to-diameter ratio >25 and by following other design recommendations of Murakami et al. (1996b). Also, to minimize the error associated with finite length of the heater wire, temperature was measured at the half-length of the heater wire. Since k values were estimated based on least-square fit of the temperature rise vs logarithmic time data, such errors in temperature measurement could also be considered as a part of random uncertainty (Type A). Currently very limited knowledge is available on heat transfer in food materials under pressure (such as natural and forced convection as a result of change in density or viscosity of liquid material under pressure). In the present study, such errors were considered to be part of the random uncertainty error (Type A).

#### **3.3.3.3. Combined uncertainty**

Independently considering all components of Type A and Type B uncertainties and using the law of propagation (eqn.6), the combined uncertainty of the thermal conductivity measurement under pressure was estimated to be in the range of (1.0-2.5%) for apple juice, (1.0-2.3%) for honey; (1.6-3.8%) for HFCS, (0.7-1.6%) for clarified butter and (0.6-2.1%) for canola oil over the pressure range studied.

#### **3.4.** Conclusions

The line heat source probe technique was successfully used to measure k of selected liquid foods. k of tested liquid food materials increased linearly with increasing pressures up to 700 MPa. Composition and compressibility characteristics of the foods

were found to significantly influence k values. The uncertainty analysis indicated a maximum uncertainty of 3.8% of the measured value for HFCS and a minimum uncertainty of 0.6% for canola oil. Further research is needed to determine and document k for a range of food products as a function of pressure and temperature.

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Figure 3.1. Schematic diagram of the high pressure experimental set-up (a) and thermal conductivity probe (b).



Figure 3.2. Sample time-temperature curve observed during the thermal conductivity measurement (P=100 MPa). The rise A-B is due to heat of compression, and D-E due to probe power input.



(a)



(b)

Figure 3.3. (a) Experimental versus NIST thermal conductivity data for water at 25°C (b) Sample probe specific calibration factors curve as a function of applied pressure (data points with error bars indicate mean±standard deviation).



Figure 3.4. Thermal conductivity values of selected liquid foods under high pressure (data points with error bars indicate mean±standard deviation).

Liquid food	Literature k (W/m°C)	Experimental $k (W/m^{\circ}C)$ at	Linear r (eqn	egression equation 7) coefficients	
tested	at 0.1 MPa	0.1 MPa	α	β	$R^2$
			(W/m°C)	(W/m°C-	
				MPa)	
Water	$0.61^{a}, 0.61^{b^{*}}$	0.61-0.65	0.6164	0.000293	0.99
Apple juice (filtered)	$0.56^{b\ddagger}, 0.56^{c}$	0.59-0.64	0.6003	0.000329	0.92
High fructose corn syrub	0.35 <sup>b**</sup>	0.33-0.35	0.3145	0.000256	0.97
Honey	0.46 <sup>b†</sup>	0.38-0.40	0.3584	0.000160	0.90
Clarified butter	$0.21^{b_{*}}, 0.23^{d}$	0.22-0.23	0.2356	0.000293	0.91
Canola oil	0.16 <sup>b0</sup>	0.22-0.23	0.1987	0.000176	0.99

<sup>a</sup> at 25°C (Harvey et al., 1996)
<sup>b</sup> at \*27°C; <sup>‡</sup> 20°C; \*\* 27°C; <sup>†</sup> 21°C; \* 10°C; <sup>◊</sup> 20°C (Choi & Okos, 1986)
<sup>c</sup> at 28°C (Bhumbla, Singh & Singh, 1989)
<sup>d</sup> at 30°C (Tavman & Tavman, 1999)

Table 3.1. Linear regression of thermal conductivity (k) values in response to pressure

Liquid food	Compressibility <sup>a</sup> per MPa (βx10 <sup>6</sup> )	Compression heating factor <sup>b</sup> (°C/100 MPa)	Specific heat <sup>d</sup> KJ/kg°C (T=20°C)	Density <sup>d</sup> kg/m <sup>3</sup> (T=20°C)	Thermal conductivity (present study) W/m°C
Water	4.9 (20°C; 1.3 MPa)	2.6-3.0	4.180	1000	0.61
Canola oil	5.9 (20°C; 0.5 MPa)	6.9-8.7 <sup>c</sup>	1.91	910	0.22

<sup>a</sup> Perry, Green & Maloney (1984)
<sup>b</sup> Rasanayagam et al. (2003)
<sup>c</sup> Values assumed to be equivalent to other oils (Olive and soybean oil)
<sup>d</sup> Choi & Okos (1986)

Table 3.2. Comparison of thermo physical properties of water and canola oil at atmospheric pressure.

# **CHAPTER 4**

# THERMAL CONDUCTIVITY OF SELECTED SOLID FOODS DURING HIGH PRESSURE PROCESSING AS INFLUENCED BY PROCESS TEMPERATURE AND FOOD COMPOSITION

# ABSTRACT

Thermal conductivity (k) of selected foods (carrot, cheddar cheese, chicken breast, chicken fat and guacamole) was measured during high pressure processing (HPP) using a line heat source probe. The probe was calibrated using published k data from National Institute of Standards and Technology (NIST) for water under pressure. Experiments were conducted at pressures up to 700 MPa and at process temperatures of 25, 50 and 75°C. The effect of pressure, temperature and sample composition (moisture and fat content) on k was evaluated. Results indicated that k increased linearly with increasing pressure up to 700 MPa for all foods studied. While k under pressure increased with increase in moisture and temperature, it decreased with increasing fat content. Among the products tested, carrot had the highest k at 700 MPa and 75°C (0.90 W/m°C), while chicken fat had the lowest k (0.43 W/m°C) under similar conditions. Empirical regression equations were developed to predict k as a function of pressure and
temperature. The combined uncertainty (including Type A and Type B) in the measured k values ranged from 1.7% (carrot) to 4.2% (chicken fat).

# 4.1. Introduction

Thermal conductivity (k) is one of the important thermal properties considered in many engineering applications. In most biological materials, data on k along with other relevant thermo-physical properties are being used in control of transport processes, product and process development and optimization. Values of k of various foods at atmospheric pressure were extensively studied (Buhri & Singh 1993; Lentz, 1961; Liang, Zhang, & Ge, 1999; Sweat, 1974; Tavman & Tavman, 1999; Willix, Lovatt, & Amos, 1998;). Comprehensive reviews and compilation of k data are available for various raw and processed food products (Mohsenin, 1980; Nesvadba, 1983; Okos, 1986; Polley, Snyder, & Kotnour, 1980). Line heat source probe (k-probe) method is one of the commonly used methods for estimation of k values, due to its convenience, relative simplicity, short measurement time and small sample requirements (Murakami, Sweat, Sastry, & Kolbe, 1996a; Sweat, 1995). Thermal conductivity of food materials was reportedly influenced by temperature and food composition (Baghe-Khandan, Okos, & Sweat, 1982; Choi & Okos, 2003; Magerramov, Abdulagatov, Abdulagatov, & Azizov, 2006). Limited information is available on k of solid foods at elevated temperatures (Gratzek & Toledo, 1993; Nije, Rumsey, & Singh, 1998; Pan & Singh, 2001).

Recently, high pressure pasteurization and sterilization are being studied for potential commercial adoption. A number of authors stressed the importance of estimating thermal properties such as k, thermal diffusivity ( $\alpha$ ), volumetric heat capacity  $(C_p)$  and the heat of compression ( $\delta$ ) during HPP (Otero, Molina-Garcia, & Sanz, 2000; Ramaswamy, Balasubramaniam, & Sastry, 2005; Rasanayagam, Balasubramaniam, Ting, Sizer, Bush, & Anderson, 2003). It will help in process modeling and design (Denys, Van Loey, & Hendrickx, 2000; Baars, Rauh, & Delgado, 2007). Properties of water under pressure were extensively studied and the data are available through National Institute of Standards and Technology (NIST) steam properties database (Harvey, Peskin, & Klein, 1996). Very limited studies evaluated the combined pressure-thermal effects on thermo-physical properties of foods due to the practical difficulties in their in-situ estimation under pressure (Denys & Hendrickx 1999; Ramaswamy, Balasubramaniam, & Sastry, 2007; Zhu, Ramaswamy, Marcotte, Chen, Shao, and Le Bail, 2007). Denys and Hendrickx (1999) studied k of tomato paste and apple pulp for pressures up to 400 MPa at 25°C. Similarly, Zhu et al. (2007) studied k values of potato and cheddar cheese up to 350 MPa at 5°C. In general, k was reported to increase linearly with increasing pressure. Ramaswamy et al. (2007) reported k of different liquid foods (apple juice, honey, high fructose corn syrup, canola oil, clarified butter) at pressures up to 700 MPa at 25°C. Authors reported that the k values linearly increased with pressure and the food composition influenced the magnitude of k values.

The objective of the present study was to determine k of selected solid foods *insitu* under combined pressure (up to 700 MPa) and temperature (25-75°C) conditions. The influence of food composition (moisture and fat content) on k was also evaluated.

#### 4.2. Materials and methods

#### **4.2.1.** High pressure equipment and accessories

A custom fabricated high-pressure experimental system (Harwood Engineering Co. Inc., Walpole, Massachusetts, U.S.A.; Model No. 26190) capable of pressurizing to 1000 MPa at the rate of 20 MPa/s was used in the study. The top closer has an in-built purging mechanism for air removal. The outer jacket of the pressure chamber was attached with an external oil bath circulator (Busch Electronics LLC, Minneapolis, Minnesota, U.S.A.). This facilitated temperature control within pressure chamber up to 100±1°C. Propylene glycol (Safe-T-Therm, Houghton Int. Inc., Valley Forge, Pennsylvania, U.S.A.) and distilled water (Chemistry store, The Ohio State University, Columbus, Ohio, U.S.A.) mixed in the ratio of 1:1 was used as the pressure transmitting fluid. The high pressure system was connected with an external DC power supply system (BK precision, Mouser Electronics Inc., Mansfield, Texas, U.S.A.; 615-1621A) within 1m distance from it. A data acquisition system (Agilent technologies, Palo Alto, California, U.S.A.; 34970A; board resolution: 20 bits) with an in-built 3-Hz slow mode filter was also connected within 1m distance. The extension lead wires from the top closure to the power source and the data acquisition system were insulated, twisted and foil sheath covered to avoid induced voltages. All system components were grounded to the same source to minimize measurement error. Additional details of the experimental set-up are available in Ramaswamy et al. (2007).

#### 4.2.2. Thermal conductivity probe and its calibration

Thermal conductivity probes were custom fabricated based on the recommendations of Murakami, Sweat, Sastry, Kolbe, Hayakawa, & Datta (1996b). Ktype thermocouple (response time < 0.1 s) was used in the study as it was reported to be least influenced by high pressure conditions (Bundy, 1961). The K-type thermocouples used in the experiment were calibrated between fixed point references of ice-water bath and boiling water with a high-precision thermocouple calibrator (NIST-traceable certified for calibration to a resolution of 0.1°C) (OMEGA CL20; Omega Engineering, Stamford, Connecticut, U.S.A). Loops of insulated constantan heater wire (TFCC-003; Omega Engineering, Stamford, Connecticut, U.S.A.; diameter: 0.076mm) and K-type thermocouple wire (TFCY-003; TFAL-003; Omega Engineering, Stamford, Connecticut, U.S.A.; diameter: 0.076mm) with the thermocouple junction positioned in the middle of the loop were inserted inside a stainless steel hypodermic needle tube (VITA Gauge 20, Needham, Massachusetts, U.S.A.; outer diamter:0.71mm; thickness: 0.15 mm). The ends of wires were glued to the needle tube with epoxy (Devcon 2 Ton epoxy, Riviera beach, Florida, U.S.A; S-31/31345). The length-to-diameter (L/D) ratio of the k probe was 60. This should be >25 to minimize axial heat flow error (Murakami et al., 1996b; Sweat, 1995).

The *k* probe uses the cylindrical coordinate solution of Fourier's equation (Eq.4.1) for unsteady-state radial heat conduction in an infinite medium by measuring the temperature in close proximity to the heater wire over a period of time (Carslaw & Jaeger, 1959; Murakami et al., 1996b; Sweat, 1995):

$$k = \frac{Q}{4\pi\,\Delta T} \left[ \ln\left(\frac{t_2}{t_1}\right) \right] \tag{4.1}$$

where *k* is the thermal conductivity of the sample (W/m°C), Q is the heat flux of the line source (W/m) and  $\Delta T$ , the temperature difference (°C) between time  $t_1$  and  $t_2$  (s). The *k* probe was positioned in the middle of a polycarbonate sample holder (19 mm x 90 mm; US Plastics, Lima, Ohio, U.S.A.) and both the probe and the sample holder were fixed to the top closure with epoxy. A movable polycarbonate piston with an o-ring arrangement suitably positioned within the sample holder was used to transfer the pressure to the sample.

Preliminary experiments were conducted with distilled water at various process temperatures (25, 50, 75°C) and at various power levels (up to 10 W/m) to choose a power level with minimum convection effects (Ramaswamy et al., 2007). Microcarrier beads (LSG1007-2135, SoloHill Engineering Inc., Ann Arbor, Michigan, U.S.A.) of specific gravity 1.006 were suspended in distilled water inside the transparent sample holder. The bead movement during power application was videotaped to document thermal convection effects. Based on visual examination of the video and analysis of sample temperature data, an optimum power level (4.7 W/m) was chosen for the experiments.

Probe-specific calibration factors were calculated at various pressure-temperature conditions to improve accuracy of the measurand. The *k* probe was calibrated with distilled water at 100 MPa intervals up to 700 MPa and at 25, 50 and 75°C. Current study utilized published NIST *k* values of water (Harvey et al., 1996) under pressure as calibration standard. Agar gel (Denys & Hendrickx 1999; Zhu et al., 2007) was not used

because of uncertainty regarding its behavior under high pressure conditions. After thermal equilibrium was achieved between the test sample, pressure transmitting fluid and the jacket surrounding the chamber (Fig. 4.1), a chosen power (Q) was applied to the probe. The temperature (T) increase was recorded at 1 s time (t) intervals for 60 s (Fig. 4.1, region D-E). In addition, voltage (V), current (I) and pressure (P) at various process temperatures were also recorded. Thermal conductivity of water was then calculated from the slope ( $4\pi k/Q$ ) of the linear portion ( $R^2>0.99$ ) of the logarithm of time versus temperature plot after the first 3 s of the measurement (to minimize truncation error) (Gratzek & Toledo 1993; Murakami et al., 1996a). The experimentally determined *k* for water was then compared with that of the NIST steam properties database. The probe and process specific calibration factors ( $X_{cal, p}$ ) were estimated as the ratio of  $k_{standard}$  to  $k_{experiment}$ . Calibration experiments were replicated five times at each of the process conditions. The mean values were used for estimating *k* of selected food materials.

# 4.2.3. Food samples

Thermal conductivity of baby carrots, guacamole, cheese and chicken were determined over various combinations of pressures (up to 700 MPa) and temperatures (25, 50, and 75°C). These samples were selected to represent different (vegetables, dairy, and poultry) products containing varied levels of moisture and fat content. Availability of k data at atmospheric conditions for the products at different process temperatures was another consideration. Baby carrot and cheddar cheese were obtained from local super market (Wild Oats, Columbus, Ohio, U.S.A.). Semi-solid guacamole (avocado based relish) (Trader Joes, Columbus, Ohio, U.S.A.) was also tested considering the widely

popular commercial application of high pressure technology in guacamole processing. Fresh chicken (*pectoralis major*) samples were obtained from a local butcher on the day of the experiment. Breast meat and separable fat from the breast area were carefully separated before the experiments. A 19 mm diameter cork borer (No.12) was used to prepare the samples. Chicken samples were cut to arrange the fibers parallel to the axis of the cylindrical probe and sample holder so that the heat from the line source flowed perpendicular to the fibers (Sweat, Haugh, & Stadelman, 1973).

The food samples selected for the study were analyzed for their moisture content using a vacuum oven at 95°C till constant weight (AOAC, 2002). Fat content of chicken samples and guacamole was determined by solvent extraction procedure using petroleum ether, while the Babcock method of fat estimation was used for cheddar cheese (AOAC, 2002). Apparent density and porosity of the solid food samples were measured by liquid displacement using a picnoflask (Abhayawick, Laguerre, Tauzin, & Duquenoy, 2002).

# 4.2.4. High pressure processing experiments

Thermal conductivity experiments were conducted after thermal equilibrium was achieved pressure between the sample and the surrounding pressure transmitting fluid at the targeted process (Fig. 4.1). Heat of compression of the sample and pressure transmitting fluid were considered in selecting the initial loading temperature of the sample (Rasanayagam et al., 2003). To ensure thermal equilibrium within samples and with the surrounding, preliminary experiments were conducted to document the sample temperature in the centre and surface (1-2 mm from the surface). Depending upon the type of food material, after loading into pressure vessel, samples took up to 20 minutes to reach thermal equilibrium, before the power could be applied for *k* measurement. Temperature gradient within the sample was < $0.2^{\circ}$ C at equilibrium and small sample size also helped to minimize this. Further to maintain the system at the desired process temperature and minimize heat loss to the surroundings, the outer bath was also maintained at the desired process temperature. Upon reaching equilibrium process conditions, a constant DC voltage (4.7 W/m) was supplied to the line-heat source and the resulting change in temperature was recorded at 1 s intervals for 60 s. Thermal conductivity was then estimated by using Eq.4.1 and as per the procedure described in the calibration section. The experimentally measured *k* value at each process condition was multiplied by the corresponding calibration factor to obtain the final *k* value. Empirical regression equations as a combined function of pressure and temperature (Eq. 4.2) were developed to predict *k* of the selected foods within the experimental conditions:

$$k = a + b P + c T + d (P*T)$$
 (4.2)

where a,b,c are empirical regression coefficients.

#### 4.2.5. Uncertainty analysis

The reasons for deviation of the measured *k* values from actual *k* value may be numerous. Analysis of uncertainties (Kirkup & Frenkel, 2006 and Taylor & Kuyatt, 1994) can help identify and potentially minimize sources of error. Type A uncertainty related to components of uncertainty that are determined by statistical methods based on the experimental values. Standard deviation of the mean ( $\overline{X_i}$ ) of *n* number of independent observations  $X_{i,k}$  of any input quantity  $X_i$  at each of the measurement conditions was considered as Type A uncertainty:

$$u(x_i) = \left(\frac{1}{n(n-1)} \sum_{k=1}^n \left(X_{i,k} - \overline{X_i}\right)^2\right)^{1/2}$$
(4.3)

Type B uncertainty relates to both measurement and non-measurement errors (Labudova & Vozarova, 2002) estimated based on scientific judgment of factors affecting the experimental output. For thermal conductivity measurement, this includes measurement errors associated with temperature, pressure, power, time, as well as non-measurement errors associated with the theoretical assumptions made in *k* estimation. This is different from Type A in that the calculation of the uncertainty component is not based on a statistical analysis of data. Considering the measurement variables as mutually uncorrelated, the combined standard uncertainty,  $u_c(k)$  was estimated as the positive square root of the estimated variance  $u_c^{-2}(k)$  obtained using the law of propagation of uncertainty:

$$u_c^{2}(k) = \sum_{i=1}^{N} \left(\frac{\partial k}{\partial x_i}\right)^2 u^{2}(x_i)$$
(4.4)

where  $u(x_i)$  indicates the standard uncertainty component associated with the input estimate  $x_i$  of either Type A or Type B.

#### 4.3. Results and Discussion

#### 4.3.1. Probe calibration

Earlier researchers (Denys & Hendrickx, 1999; Zhu et al., 2007) reported the line heat source probe method as the fastest and most accurate way of obtaining thermal conductivity of food materials at high-pressure. Use of various power levels (6 to 8 W/m, Denys & Hendrickx, 1999; 12.4 to 13.4 W/m, Zhu et al., 2007) were reported during high pressure calibration experiments. In the current study, a power level of 4.7 W/m was found to produce appreciable change in temperature ( $\Delta T$ >3°C at all process temperatures in <30 s) with minimum convection effects. Additional precautions to be taken during calibration experiments were also provided by Ramaswamy et al. (2007).

Thermal conductivity of water estimated with the line heat source probe at each process pressure (0.1-700 MPa) and temperature (25, 50 and 75°C) was compared with the published values of the NIST steam properties database (Fig. 4.2). The estimated values were found to be in good agreement with the NIST data and the calibration factors were estimated to be in the range of 0.90 to 1.12. The calibration factors remained close to 1.0 irrespective of the pressure and temperature used in the experiments indicating the stability of the probe under the varied operating conditions.

#### **4.3.2.** Thermal conductivity of solid foods at atmospheric pressure

Thermal conductivity values of selected foods at atmospheric pressure (0.1 MPa) and ambient temperature (25°C) determined using the line-heat source probe are presented in Table 4.1. The data were reasonably in good agreement with the published

literature. Any deviations between published and experimental values may be possibly due to biological variability, process conditions and method of measurement.

### 4.3.3. Influence of process pressure on thermal conductivity of solids

Thermal conductivity of all the tested food materials increased linearly with increasing process pressure (Fig. 4.3-4.6). Compression of a material decreases the average intermolecular distance between adjacent molecules. At elevated pressures, up to 15% reduction in volume is reported for water (Harvey et al., 1996). This resulted in about 34% increase in *k* of water from 0.61 W/ m°C (0.1 MPa) to 0.82 W/m°C (700 MPa) (Fig 4.2). In solid foods, elevated pressures also deformed the solid structure (Wang & Sun, 2002) and air pockets present in the food matrices likely collapsed. Thermal conductivity is further influenced by food composition. Thermal conductivity values of carrot samples at various pressure-temperature combinations were very close to that of water (Fig 4.2 & 4.3) possibly because of its high moisture content (86%). Water is the predominant constituent of various food materials. Since water has the highest *k* value at atmospheric pressure condition, it has the greatest effect on thermal properties of food material (Sweat et al., 1973). During high pressure processing, water continues to play such a role in impacting thermal behavior of food materials.

Among the food materials tested, guacamole, cheddar cheese, and chicken fat samples had lower moisture content (68.4 to 17.2%) and higher fat content (10.4 to 76.4%) than carrot. Accordingly, their respective thermal conductivity values (Fig. 4.4, 4.5, 4.6) were much lower than that of water or carrot samples at various combinations of pressure-temperatures tested. These observations were similar to that of Zhu et al. (2007), who reported lower thermal conductivity values for cheddar cheese samples (0.38 W/m°C) than potato (0.67 W/m°C) at 350 MPa and 5°C. Similarly, Denys & Hendrickx (1999) reported that thermal conductivity of tomato paste and apple pulp at 35 and 65°C up to 400 MPa exhibited positive linear relationship with pressure, and the magnitude of k values were reported to be lower than that of water.

Thermal conductivity values of meat samples above freezing were reported to be 10% below that of water at atmospheric pressure (Lentz 1960; Sweat 1973). Such observations held good for chicken breast samples used in the current study at ambient conditions, but at 700 MPa, both chicken breast and water had similar thermal conductivity values at the various process temperatures tested (Fig.4.2, 4.6).

### **4.3.4.** Influence of process temperature on thermal conductivity of solids

As expected, at constant pressure, *k* of all the tested foods increased with increasing process temperature. Magnitude of this increase was less pronounced than that for increasing pressure and was dependent on the composition of the material tested. For example, the percentage increase in *k* due to change in pressure (0.1 to 700 MPa) over the process temperatures tested was relatively constant for water ( $\approx$ 33-35%), guacamole ( $\approx$ 48-50%), carrot ( $\approx$  36-43%) and chicken fat ( $\approx$  43-46%) at 25, 50 and 75°C (Fig 2-6). Gratzek and Toledo (1993) reported *k* value of carrot (90% moisture content) at about 0.67 W/m°C at 130°C and retort pressure conditions (estimated  $\approx$  0.2 MPa). On the contrary, higher *k* (0.90 W/m°C) of carrot samples (86% moisture content) at 75°C and 700 MPa was observed in the present study, signifying the dominance of pressure over temperature in increasing the *k*. Process temperature appears not to play a significant role in k values of semi-solid guacamole and chicken fat (Fig. 4.4, 4.6). On the other hand, elevated process temperatures resulted in higher k values for cheddar cheese at 50 and  $75^{\circ}$ C (Fig. 4.5). Due to experimental limitations, the phase change characteristics of cheese samples under pressure were not tested. For chicken breast, temperature was found to have maximum influence at atmospheric pressure, but the thermal effect diminished at elevated pressures (Fig 4.6). This may be attributed to the complex meat structure and denaturation of meat proteins due to pressure and temperature. At elevated temperatures, the chicken sample softened and had weaker structural rigidity (Bhattacharya & Mahajan, 2003; Pan & Singh, 2001). Bhattacharya et al., (2003) reported organic change and shrinkage of sheep collagen tissues and diminished thermal effect at about 55°C. Breakdown of connective tissue during long holding time at elevated temperatures reported to increase thermal conductivity values of beef (Gratzek and Toledo, 1993). Chicken myofibrils were reported (Iwasaki, Noshiroya, Saitoh, Okano & Yamamoto, 2006) to be disrupted at pressures above 200 MPa reducing the concentration of solubilized protein in them. The resulting dispersion of myofilaments may be the cause for low density and decreased effect of pressure on k. Temperature effect remained constant for chicken fat (Fig. 4.6) and guacamole (Fig. 4.4) at all process pressures. More studies are needed to characterize the influence of food structure on thermal conductivity of food materials as a function of pressure and temperature.

### **4.3.5.** Prediction of k values

Simple empirical regression equations were developed to predict *k* of tested food materials as a function of pressure (0.1-700 MPa) and temperature (25, 50 and 75°C):

 $k_{carrot} = 0.573 + 0.000254 * P + 0.0006397 * T + 1.777 \times 10^{-6} * P * T (R^{2} = 0.99; SE = 0.01)$ (4.5)  $k_{guacamole} = 0.378 + 0.000277 * P + 0.000494 * T - 5 \times 10^{-7} * P * T (R^{2} = 0.97; SE = 0.01)$ (4.6)  $k_{cheddar cheese} = 0.256 + 0.000102 * P + 0.001939 * T + 5.07 \times 10^{-6} * P * T (R^{2} = 0.96; SE = 0.03)$ (4.7)  $k_{chicken breast} = 0.413 + 0.000591 * P + 0.002593 * T - 2.3 \times 10^{-6} * P * T (R^{2} = 0.98; SE = 0.02)$ (4.8)  $k_{chicken fat} = 0.239 + 0.000165 * P + 0.000738 * T + 4.82 \times 10^{-7} * P * T (R^{2} = 0.98; SE = 0.01)$ (4.9) A note caution, extrapolating the results of the empirical relationship beyond the experimental range may likely produce erroneous results.

# **4.3.6.** Uncertainty analysis

Type A uncertainty ranged from 0.15 to 3.66 (carrot (0.22-2.45); guacamole (0.32-3.66); cheddar cheese (0.77-2.81); chicken breast (0.15-2.71); chicken fat (0.26-4.24)). Measurement errors of Type B uncertainties were estimated to be 0.1% for temperature related measurements and another 0.1% for pressure, power and time measurements. These errors were considered systematic throughout the experiments. The non-measurement errors of Type B uncertainties (based on assumptions made in the theory and design of the *k*-probes) were considered as random and were assumed to be part of the Type A uncertainty. Using the law of propagation (Eq. 4), the combined uncertainty in the *k* measurement of the selected solid foods was estimated to be in the range of: carrot (0.26-2.45) for carrot; (0.35-3.66) for guacamole; (0.78-2.81) for cheddar cheese; (0.21-2.71) for chicken breast and (0.30-4.24). Chicken fat sample had the maximum uncertainty ( $u(k)_{max}$ ) of 4.2%.

# 4.4. Conclusions

The line heat source probe method was effectively used to estimate thermal conductivity of selected solid foods during high pressure processing up to 700 MPa and 75°C. Within the range of experimental conditions k of foods tested linearly increased with pressure, but process temperature had weaker influence on k values. Depending on the pressure, temperature, moisture content and food material type, thermal conductivity varied from 0.25 to 0.90 W/m°C. Generally, differences in measured data and responses to both temperature and moisture content were attributed to differences in structural characteristics and composition. The uncertainty associated with the measurements was less than 4.2%. The finding of this study will be of interest for mathematical modeling of high pressure processing of food materials, and would aid in the development of optimal process conditions.

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Figure 4.1. Pressure-temperature history of carrot sample during thermal equilibration under pressure (P=500 MPa; T=50 $^{\circ}$ C). The rise A–B is due to heat of compression, and D–E due to probe power input.



Figure 4.2 Comparison between experimental and published (NIST) thermal conductivity values of water during high pressure processing at three different process temperatures (lines denote NIST predicted data; markers denote experimental data)



Figure 4.3. Thermal conductivity of carrots under pressure as influenced by process temperature (data points with error bars indicate mean  $\pm$  standard deviation).



Figure 4.4. Thermal conductivity of guacamole under pressure as influenced by process temperature (data points with error bars indicate mean  $\pm$  standard deviation).



Figure 4.5. Thermal conductivity of cheddar cheese under pressure as influenced by process temperature (data points with error bars indicate mean± standard deviation)



Figure 4.6. Thermal conductivity of chicken breast and chicken fat under pressure as influenced by process temperature (data points with error bars indicate mean  $\pm$  standard deviation)

Sample material	Properties				Literature k (W/m°C)	Experimental k (W/m°C)
	Moisture (%wb)	Fat (%)	Density (kg/m <sup>3</sup> )	Porosity (%)	(0.1 MPa; @ 25°C)	(0.1 MPa; 25°C)
Carrot	86.1	0.1	1069	7.2	$0.56^{a}, 0.61^{b}$	0.58
Guacamole	68.4	10.4	1010	6.5	NA	0.38
Cheddar cheese	38.1	35.0	1096	8.7	$0.35^{\rm c}, 0.35^{\rm d}$	0.32
Chicken breast	72.5	2.6	1080	7.7	$0.48^{\rm e}, 0.49^{\rm f}$	0.48
Chicken fat	17.2	76.4	1012	1.5	0.21 <sup>°</sup> ,	0.26
<sup>a</sup> Buhri & Singh, 1993 <sup>b</sup> Sweat, 1974 <sup>c</sup> Willix et al., 1998 <sup>d</sup> Tavman & Tavman, 1999 <sup>e</sup> Sweat et al., 1973 <sup>f</sup> Walters & May, 1963						

Table 4.1. Thermal conductivity of the selected foods at atmospheric conditions (0.1 MPa; @25°C)

# **CHAPTER 5**

# EFFECT OF POLARITY AND MOLECULAR STRUCTURE OF SELECTED LIQUIDS ON THEIR HEAT OF COMPRESSION DURING HIGH PRESSURE PROCESSING

### ABSTRACT

During high-pressure processing (HPP) of food materials, water and fatty food components showed lowest and highest heat of compression ( $\delta$ ) values, respectively. A study was conducted to evaluate the relationship between  $\delta$  of selected liquids under pressure and their polarity index. The influence of carbon chain length and degree of unsaturation on the  $\delta$  values was also evaluated. While polar liquids showed a linear trend with the  $\delta$ , non-polar liquids exhibited a nonlinear relationship.  $\delta$  values decreased with increasing polarity index (8.8 °C per100 MPa for chloroform to 3 °C per100 MPa for water). Change in carbon chain length (C<sub>2</sub> to C<sub>4</sub>) and degree of saturation (C<sub>18:1</sub> to C<sub>18:3</sub>) of selected fatty acids were found to have effect on the  $\delta$  only at elevated pressures. The study would aid in improving our understanding of thermal non-uniformities during high pressure processing.

# **5.1. Introduction**

High pressure processing (HPP) is gaining importance in pasteurization and sterilization of heat sensitive foods. Elevated pressures up to 700 MPa are used either with or without the addition of heat to preserve food without significant thermal impact on food quality (Rajan, Ahn, Balasubramaniam & Yousef, 2006). All the compressible substances increase in temperature as a result of pressurization. The importance of considering the temperature rise during compression and temperature drop during decompression was stressed by many prior researchers (Kalichevsky, Knorr & Lillford, 1995; Otero, Molina-Garcia & Sanz, 2000; Rasanayagam, Balasubramaniam, Ting, Sizer, Bush & Anderson, 2003; Shimuzu, 1992; Ting, Balasubramaniam & Raghubeer, 2002). Temperature change due to heat of compression ( $\delta$ ) may vary between the various components of foods subjected to HPP. The magnitude of  $\delta$  depends mainly on their thermophysical properties. A thorough understanding of the compression heating behaviour of food components will help us evaluate potential process non-uniformities during HPP especially on an industrial scale. Compression heating behaviour of water under pressure was reported as early as 1931 by Bridgman. Recent reports on thermal effect of the  $\delta$  for various components of food include those for water (Houska, Kubasek, Strohalm, Landfeld & Kamarad, 2004; Otero et. al., 2000; Rasanayagam et. al., 2003), fatty substances (Houska et. al., 2004; Otero et. al., 2000; Rasanayagam et. al., 2003; Shimuzu, 1992), and carbohydrates (Ardia, Knorr, & Heinz, 2004).

Fats and oils were reported to show approximately three times higher  $\delta$  values than that of water (Houska et. al., 2004; Patazca, Koutchma, & Balasubramaniam, 2007;

Rasanayagam et. al., 2003). It was also observed that the temperature change as a result of  $\delta$  was more in milk which was more non-polar than in water which is a polar component (Otero et. al., 2000). Higher temperature rise observed in olive and soybean oil when compared to beef fat was attributed to the difference in the degree of unsaturation in those components (Rasanayagam et. al., 2003). Hence, this study was carried out with the aim of understanding the  $\delta$  behaviour of selected liquids with varying polarity index and pure fatty acids of varying degree of unsaturation and carbon chain length.

#### **5.2.** Experimental methods and materials

# **5.2.1.** Experimental set-up

Experiments were conducted using a custom-made high-pressure kinetic tester (pressure test unit PT-1, Avure Technologies, Inc., Kent, WA) capable of pressurizing to 700 MPa at the rate of 19 MPa.s<sup>-1</sup> (Rajan et. al., 2006). A high-pressure intensifier (M-340A, Flow International, Kent, WA) was used to achieve the intended pressure in the 54 ml stainless steel (0.02 m internal diameter) vertical pressure chamber. The high pressure cylindrical chamber was immersed in a temperature controlled bath (Haake DC30 Immersion circulator, Fisher Scientific Co., IL) so that isothermal conditions could be maintained. Propylene glycol (>99% pure; Houghto-safe 620-TY, Houghton International Inc., PA;  $\delta = 4.2$  to 4.7 °C per100 MPa) was used as the pressure transmitting fluid. A 10ml plastic syringe (internal diameter 0.014m, height 0.065m, thickness 0.001m; 14-823-2A; Fisher Scientific Co., IL) insulated with 3 layers of CVS sports tape (CVS/Pharmacy, Columbus, OH) was used as the sample holder. A K-type thermocouple probe (SCASS- 062U-7, Omega Engineering, Stamford, CT) attached to the pressure chamber top closer was used as the temperature sensor. The insulated sample tube was attached to the top closer end cap with an adapter so that the thermocouple junction was positioned approximately in the middle of the sample. In a separate set of experiments, K-type thermocouple was also positioned in the pressure transmitting fluid within the pressure chamber as well as in the temperature controlled glycol bath to measure respective temperatures. A data acquisition system (Daq-Board/2000; IOtech, Inc., Cleveland, OH) equipped with the software (DasyLab 7.00.04; National Instruments Corp., Austin, TX) was used to record the sample temperature, bath temperature, pressure and time data at 1s intervals.

#### **5.2.2.** Test materials

The liquids selected for evaluating the effect of polarity on the heat of compression had a wide range of polarity index (Table 1). These were HPLC grade solvents purchased from the Chemistry store of The Ohio State University, Columbus, OH, USA. In addition, non-polar alkanes varying in their hydrocarbon chains, short chain fatty acids with varying carbon chain length and long chain fatty acids with varying degree of unsaturation (Table 2) were also tested for their  $\delta$ . The fatty acids chosen were based on their purity and availability in liquid form at atmospheric conditions.

### 5.2.3. High pressure experiments

Prior to  $\delta$  experiments, all the test samples were equilibrated in a water bath at the desired initial temperature (T±0.5 °C) and then transferred to the pressure chamber. The

pressure chamber was suspended vertically in a temperature controlled glycol bath maintained at the same initial temperature. Samples were pressurized to 700 MPa (pressure come-up time  $\approx 37$  s) and held for 30 s. Pressure holding time was limited to 30 s to minimize subsequent heat loss to the environment. Upon depressurization ( $\approx$ 4 s), the sample was removed from the pressure chamber and the sample was inspected to ensure no loss (through evaporation) or gain (glycol infusion) in the test material. All the experiments were repeated three times using fresh samples each time.

The  $\delta$  values of the test samples were calculated using equation 5.1 as the difference between the initial temperature before commencement of pressurization and the maximum temperature of the material at the target pressure.

$$\delta = \frac{T_P - T_0}{\Delta P} X 100 \tag{5.1}$$

where  $\delta$  is the heat of compression (°*C*/100*MPa*),  $T_p$  is the maximum sample temperature (°C) at the applied pressure,  $T_0$  is the initial sample temperature (°C) at atmospheric pressure and P is the applied pressure in MPa. The laboratory scale pressure equipment had a rapid pressurization rate of 19 MPa.s<sup>-1</sup> and the ratio between pressure transmitting fluid pumping capacity in the system and the volume of the sample to be pressurized was very high. Temperature of the pressure transmitting fluid (glycol) with and without the samples within the pressure chamber indicated that there was no appreciable heat exchange between the test sample and the pressure transmitting fluid during pressure holding time (≈30 s). Thus, it was reasonable to assume that quasiadiabatic conditions prevailed during the experiments (Houska et. al., 2004; Rasanayagam et. al., 2003).

#### 5.3. Results and Discussion

### **5.3.1.** Liquids with varying polarity index

Compression heating reflects the behaviour of material compressibility under pressure (Ting et. al., 2002). It is a thermodynamic effect. Under compression, the internal energy of the system increased resulting in a rapid rise in temperature (Rasanayagam et. al., 2003). Sample curves illustrating the effect of compression and decompression on water and other liquids of varying polarity index during high pressure processing are presented in Fig. 5.1. Temperature curve of the polar substance gradually increased with pressure as a result of physical compression. Upon depressurization, the temperature dropped back close to its initial value. The estimated  $\delta$  value of water was approximately 2.99 °C per 100 MPa (Fig. 5.2). This was in agreement with previously reported results (Otero et. al., 2000; Rasanayagam et. al., 2003; Harvey, Peskin, & Klein, 1996). The polar materials like water and methanol could retain their closer atomic grouping because of hydrogen bonds (Bridgman, 1935; Hemley, 2000) and the  $\delta$  values remained constant or increased minimally over the tested pressure range. It was further interesting to note that the  $\delta$  values of water increased with increase in its initial temperature (Fig. 5.2). Increasing initial temperature of water from 25 to 50 °C increased its δ values from about 2.99 °C to 3.86 °C per 100 MPa. Bridgman (1935) (Weast & Astle, 1982) reported that the presence of an oxygen atom anywhere in the molecule results in low compressibility and hence the lower  $\delta$  values. It was also reported that most of the hydrogen bonds remain intact over a wide range of temperatures in polar liquids (Bridgman, 1935).

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With increased non-polarity, non-polar substances showed sharp temperature increase with increasing pressure (Fig. 5.1). For example, chloroform (polarity index 4.4) reached 87 °C (a rise of 62 °C above the initial 25 °C) with the highest  $\delta$  values (8.82 °C per 100 MPa at 700 MPa) (Fig. 5.2). The non-linear change in  $\delta$  with pressure can be empirically expressed by a regression equation of the form

$$\delta = \alpha + \beta P + \chi P^2 \tag{5.2}$$

where P is the target pressure in MPa (Table 5.3). It is worth to note that equation 2 is valid for  $\delta$  estimated at a specific initial temperature. The final temperature T<sub>f</sub> of the selected liquids can be estimated using,

$$T_f = T_i + \left(\frac{\delta^* \Delta P}{100}\right) \tag{5.3}$$

where  $\delta$  is the heat of compression value at the target pressure (P) for which final temperature T<sub>f</sub> is to be predicted.

Bridgman (1935) reported that the addition of hydrocarbon chain (CH<sub>2</sub>) links to the molecules results in high compressibility and hence the higher  $\delta$  values. Interestingly, the  $\delta$  of various alkane hydrocarbons tested in this study did not present such a trend indicating the need for further study for correlating the  $\delta$  with the structural arrangement. Sample temperature history during pressurization and pressure holding time was also influenced by its properties such as specific heat, density, thermal expansion and sample temperature (Equation 5.4; Table 5.1 and 5.2) and the heat transfer characteristics of the specific equipment used. The very low specific heat capacity of chloroform (0.97 kJ. kg<sup>-1</sup>.°C<sup>-1</sup>) may be the reason for the temperature of the chloroform dropping quickly during the experiment. Schottky's theorem relates the average internal kinetic and potential energies as a function of pressure and volume (Weast & Astle, 1982). Initial increase in pressure rapidly removes the 'slack' between the molecules resulting in high compressibility. Further increase in pressure results in compression of molecules themselves at their atomic level resulting in closer atomic grouping and shrinkage of atoms. Thus the decrease in the  $\delta$  of non-polar compounds at higher pressures may be attributed to the orbital shrinkage experienced by them influenced by their thermal properties (Equation 5.4). Decrease in the heat of compression with increasing pressure and increasing fat content was reported earlier using decompression measurements (Otero et. al., 2000).

Effect of sample initial temperature on the  $\delta$  was more pronounced at lower pressures than at elevated pressures. This may be due to the pressure effect overcoming the temperature effect at higher pressures for non-polar compounds. Various spectroscopic techniques, such as Raman, X-ray, neutron scattering and high-pressure NMR have been used recently for studying the effect of pressure and temperature on the hydrogen bond strength and structure (Hemley, 2000). Further studies may be needed to correlate the chemical structures with the  $\delta$  of liquids of varying polarity.

# 5.3.1. Short chain fatty acids with varying carbon chain length

Within the range of experimental conditions, fatty acids with fewer carbon chains had higher  $\delta$  values (Figure 5.3). Among the three materials tested, acetic acid had the highest  $\delta$ . It was further worth to note that  $\delta$  markedly increased with increasing pressure (8.27±0.33 to 11.44±1.51 °C per100 MPa) beyond 300 MPa. Similar observations were reported earlier (Rasanayagam et. al., 2003) for ethanol. This may be due to the molecules of these compounds getting arranged in infinite hydrogen-bonded chains that adopt a symmetrical structural conformation in terms of hydrogen-bond lengths and bond angles at high pressure (Matsumoto & Gubbins, 1993). It was further noted that acetic acid and ethanol molecular chains may also reorient themselves in puckered molecular layers with less strain at elevated pressures. This may have resulted in a more efficient molecular packing due to a modified methyl-methyl interaction between adjacent molecular chains. It was further noted that increased intermolecular repulsions in the larger monocarboxylic acids (with more than one carbon in the tail of carboxyl group) led to excessive strain in the hydrogen bonds for chain formation. Accordingly, as the pressure increased from 100 MPa to 700 MPa,  $\delta$  of propionic and butyric acids decreased from 8.54±0.07 to 6.66±0.04°C per 100 MPa and 5.68±0.16 to 4.65±0.19 °C per 100 MPa respectively.

#### **5.3.2.** Long chain fatty acids with varying degree of unsaturation

At lower pressures, the degree of unsaturation was found to have no significant effect (p < 0.05) on the  $\delta$  (Figure 5.4). However, at elevated pressures (>500 MPa), difference in the  $\delta$  behaviour was observed among the substances tested. The initial decrease in the  $\delta$  may be attributed to the curtailment of free flight of the molecules due to pressure (Wallen, Palmer, Garrett, & Yonker, 1996). It was reported that pressure forces a closer packing of the lipid chains resulting in decreased number of *gauche bonds* and kinks in the chains. It was also reported by the same author that the application of high pressures can lead to the formation of additional gel phases, particularly with acyl chain lengths  $\geq$ C16. A non-observable phase change and crystallization at pressures more than 500 MPa may be a possible reason for the reversal of the  $\delta$  behavior of the long chain fatty acids.

# 5.4. Prediction of maximum temperature rise

Heat of compression of the materials can be theoretically estimated using a thermodynamic relation,

$$\frac{\partial T}{\partial P} = \frac{T\alpha}{C_p \rho} \tag{5.4}$$

where *T* is temperature (K), *P* is pressure (Pa),  $\rho$  is the density (kg.m<sup>-3</sup>),  $C_p$  is the heat capacity of the substance at constant pressure (J.kg<sup>-1</sup>.K<sup>-1</sup>), and  $\alpha$  is the thermal expansion coefficient (K<sup>-1</sup>). Often properties of materials under pressure are scarce (Allen & Clark, 1999). Under such circumstances, from the knowledge of pressure-temperature curves of the test samples (Fig. 5.1), the maximum rise in temperature during compression can be empirically estimated by using an integral of equation 5.4 (Houska et. al., 2004).

$$\Delta T_{\max}(T_0, P) = T_0 \cdot C(T_0, 0) \cdot \left| (C(T_0, P) / C(T_0, 0)) \cdot dP \right|$$
(5.5)

where C(T, P) is the pressure parameter which takes care of the unknown values of the heat capacity and the volume thermal expansion of the studied material at the specified temperature (K) and pressure (MPa). The empirical relationships for the maximum rise in temperature under pressure for all the liquids studied are presented in Table 5.3. Under negligible heat transfer between the sample and the surroundings, the final liquid temperature ( $T_f$ ) at any target pressure can then be estimated using the equation

$$T_f = T_i + \Delta T_{\max} \tag{5.6}$$
where  $T_i$  is the initial temperature in °C,  $\Delta T_{max}$  is the maximum rise in temperature due to the heat of compression estimated using equation 5.5.

Equation 2 for the heat of compression and the equation 5 for the maximum temperature rise were empirically derived. A note of caution, the empirical relationships developed in this study are valid only within the range of experimental conditions (100-700 MPa at 25°C) and extrapolating beyond may result in erroneous results. Both the equations did not adequately predict the unique compression heating behaviour of acetic and oleic acid. For all other materials tested, the above equations reasonably predicted the temperature (with maximum deviation of  $\pm 4^{\circ}$ C) of the tested substances under pressure. Thus, the equations can be used to estimate the final temperature under pressure of the tested material, provided the heat loss with the surrounding is negligible (Rajan et. al., 2006; Houska et. al., 2004). Use of higher order polynomials in equations 5.2 and 5.5 may improve the accuracy of prediction but may lead to more complex equations.

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Liquids with their molecular formula	Polarity index	Specific heat <sup>†</sup> [19], (kJ.kg <sup>-1</sup> .°C <sup>-1</sup> )	Density <sup>†</sup> [20], (g.ml <sup>-1</sup> )	Thermal expansion coefficient <sup>†</sup> [20] (K <sup>-1</sup> )	Compressibility per MPa <sup>*</sup> [19], β X 10 <sup>5</sup>
Water (H <sub>2</sub> O)	10.2	4.18	1.000	0.00018	43
Methanol (CH <sub>3</sub> OH)	6.6	2.51	0.791	0.00119	95
Acetone (CH <sub>3</sub> COCH <sub>3</sub> )	5.4	2.26	0.791	0.00143	61
Chloroform (CHCl <sub>3</sub> )	4.4	0.97	1.483	0.00128	83
<sup>†</sup> At 25°C and 0.1 MPa					

<sup>a</sup> At 25°C

Table 5.1. Properties of selected liquids of varying polarity index.

Category of liquids	Density at 0.1 MPa <sup>†</sup> (g.ml <sup>-1</sup> )	Specific heat at $0.1 \text{ MPa}^{\dagger}$ $(\text{kJ.kg}^{-1}. \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	Heat of compression <sup>*</sup> (℃ per 100 MPa)
Short chain fatty acids			
Acetic acid (CH <sub>3</sub> COOH) Propionic acid (CH <sub>3</sub> CH <sub>2</sub> COOH)	1.049 0.990	2.04 2.49	$11.44 \pm 1.51$ 6.66±0.04
Butyric acid (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH)	0.959	2.29	4.65±0.19
Long chain fatty acids			
Oleic acid (C <sub>18</sub> H <sub>34</sub> O <sub>2</sub> )	0.863	2.05	8.47±0.19
Linoleic acid (( $C_{18}H_{32}O_2$ )	0.903	N/A	$6.42 \pm 0.08$
Linolenic acid (C <sub>18</sub> H <sub>30</sub> O <sub>2</sub> )	0.916	N/A	6.88±0.27
Alkane hydrocarbons			
Pentane [CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>3</sub> -CH <sub>3</sub> ]	0.626	2.40	8.33±0.03
Hexane $[CH_3-(CH_2)_4-CH_3]$	0.659	2.21	6.12±0.07
Heptane [CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub> ]	0.684	2.00	7.77±0.01
Octane $[CH_3-(CH_2)_6-CH_3]$	0.703	1.71	7.67±0.01

<sup>†</sup> Fisher Scientific Co., IL MSDS 2006 (Acetic acid: S70048; Propionic acid: AC14930-0010; Butyric acid: AC10811-0010; Oleic acid: ICN 10295801;Linoleic: ICN 19469510; Linolenic acid: ICN 10218880)

\* Estimated from experiments done at 25 °C and 700 MPa

Table 5.2. Properties of selected liquids (Short-chain fatty acids of varying carbon chain length, long-chain fatty acids of varying degree of unsaturation and alkanes of varying hydrocarbon chains) used in the experiments (25 °C).

Classification	Name of the liquid	Empirical relationship for $\delta$ (equation 2)	Empirical relationship for $\Delta T_{max}$ (equation 5) at T <sub>0</sub> =25°C.
Organic liquids varying in polarity index	Water Methanol Acetone Chloroform	0.0014 P+1.985 -0.0034 P+7.960 -0.0045 P+9.997 -0.0086 P+15.497	0.022287 (P+0.000503 P <sup>2</sup> ) 0.077931(P-0.000457 P <sup>2</sup> ) 0.094499 (P-0.000478 P <sup>2</sup> ) 0.175752(P-0.000726 P <sup>2</sup> )
Short chain fatty acids with varying carbon chain length	Acetic acid Propionic acid Butyric acid	0.0053 P+7.267 -0.0031 P+9.013 -0.0017 P+5.896	0.150967 (P-0.000237 P <sup>2</sup> ) 0.094046 (P-0.000452 P <sup>2</sup> ) 0.059728 (P-0.000351 P <sup>2</sup> )
Long chain fatty acids with varying degree of unsaturation	Oleic Linoleic Linolenic	1E-05 P <sup>2</sup> -0.0073 P+8.576 2E-06 P <sup>2</sup> -0.0028 P+7.690 -0.0021 P+7.847	0.078338 (P-0.000115 P <sup>2</sup> ) 0.081477 (P-0.000372 P <sup>2</sup> ) 0.071329 (P-0.000103 P <sup>2</sup> )
Alkanes with varying hydrocarbons	Pentane Hexane Heptane Octane	-0.0108 P+15.989 -0.0102 P+13.309 -0.0069 P+12.766 -0.0056 P+11.819	0.162123 (P-0.000751 P <sup>2</sup> ) 0.139734 (P-0.000843 P <sup>2</sup> ) 0.133297 (P-0.000652 P <sup>2</sup> ) 0.124849 (P-0.000598 P <sup>2</sup> )

Table 5.3. Empirical relationship for the heat of compression ( $\delta$ ) and maximum temperature rise ( $\Delta T_{max}$ ) under pressure for the selected liquids.



Figure 5.1. Sample pressure-temperature curves of selected liquids of different polarity index



Figure 5.2. Heat of compression of selected liquids of varying polarity index at process temperatures of 25 and 50  $^{\circ}$  [Dotted lines represent 25  $^{\circ}$  C and continuous lines represent 50  $^{\circ}$ ].



Figure 5.3. Effect of pressure on the heat of compression of short chain fatty acids at  $25 \,^{\circ}$ C.



Figure 5.4. Effect of pressure on the heat of compression behaviour of long chain fatty acids with varying degree of unsaturation at  $25 \,^{\circ}$ C.

# **CHAPTER 6**

# EFFECT OF HIGH PRESSURE AND IRRADIATION TREATMENTS ON HYDRATION CHARACTERISTICS OF NAVY BEANS

## ABSTRACT

The effects of high-pressure (33, 400 and 700 MPa for 3 min at 24 and 55°C) and irradiation (2 and 5 kGy) pre-treatments on hydration behavior of navy beans were studied by soaking the treated beans in water (1:2, w/w) at 24 and 55°C. Beans hydrated at 55°C and allowed to cool by natural convection served as the control. Treating beans under moderate pressure (33 MPa) resulted in high initial moisture uptake (0.59 to 1.02 kg/kg dry mass) and reduced loss of soluble materials. The final moisture content after three hours of soaking was the highest in irradiated beans (5 kGy) followed by HPP (33 MPa; 3 min; 55°C). Within the experimental range of the study, Peleg's model was found to satisfactorily describe the rate of water absorption of navy beans. Peleg's constant K<sub>1</sub> had an inverse correlation with soaking temperature whereas K<sub>2</sub> increased with increases in temperature and pressure.

#### **6.1.** Introduction

Legumes are a good source of protein (20-40%), carbohydrates (50-60%) and a reasonably good source of thiamin, niacin, calcium, and iron (Aykroyd & Doughty, 1977). Soaking is an important pre-treatment in the processing of legumes, particularly beans such as soybeans, red kidney beans and navy beans. The treatment achieves a number of objectives that include improving heat transfer, chemical transformation (e.g., protein denaturation and starch gelatinization), reducing firmness (Bilanski, 1966; Paulsen, 1978; Gandhi & Bourne, 1991), improving digestibility and removing antinutritional factors (El-Adawy, Rahma, El-Bedawy, & Sobihah, 2000; Morris, Olson, & Bean, 1950). One of the bottlenecks of bean processing is the long soaking time (12-48 h) at room temperature and the concern that this may result in bacterial growth (Silva, Bates, & Deng, 1981). Many researchers have attempted to shorten the soaking time of a number of bean varieties using different techniques. These techniques include the hydravac process for lima beans (Rockland & Metzler, 1967), the peeling process for Sanilac and pinto beans (Kon, Brown, Ohanneson, & Booth, 1973) and the blanching process for red kidney beans (Abu-Ghannam & McKenna, 1997). Other techniques used are an enzyme method (Chukwu, 2000), chemical methods for soybean, lupin and bean seeds (El-Adawy et al., 2000) and high-pressure treatment for soybeans (Zhang, Ishida, & Isobe, 2004).

Hydration is the process of water uptake by beans during soaking and is reported to be a diffusion-controlled phenomenon (Deshpande, Bal, & Ojha, 1994). Hydration is a function of soaking time, soaking temperature and solute concentration (Wang, Swain, Hesseltine, & Heath, 1979; Hsu, Kim, & Wilson, 1983; Sopade & Obekpa, 1990; Chopra & Prasad, 1994). The amount of water absorbed increased with increases in soaking time and temperature. Nevertheless, soaking at temperatures greater than 60°C resulted in loss of total solids, nitrogenous compounds, sugars, oligosaccharides, minerals and vitamins (Kon, 1979; Pan & Tangratanavalee, 2003).

Irradiation, like heating, subjects food materials to electromagnetic energy (Lacroix & Quattara, 2000) and was found to have similar effects on food components (Urbain, 1986). Irradiation results in the production of short, straight-chain molecules. Starch digestibility of raw and cooked beans was found to be increased by irradiation at 2.5 kGy with a reduction in digestibility at doses above 2.5 kGy (Rombo, Taylor, & Minnaar, 2004). Very little information is available on the effect of irradiation on hydration behavior of navy beans. Application of high pressure processing (HPP) to improve the rate of hydration and reduce soaking time has been reported for rice (Luh & Mickus, 1980; Velupillai & Verma, 1982), corn kernels (Gunasekaran & Farkas, 1988), black beans (Sangronis, Swanson, & Barbosa-Canovas, 1997) and soybeans (Zhang et al., 2004). High-pressure hydration reportedly reduces cooking time and decreases flatulence problems. However, hydration of beans under elevated pressures (>400MPa) for an extended holding time (>10 min) may not be a commercially viable process. Very little information is available on hydration of navy beans at lower pressures and shorter pressure holding times.

The aim of this study was to obtain quantitative information on the effect of alternative processing technologies like high pressure and irradiation on the hydration behavior of navy beans. The specific objectives of the study were: (1) To study the hydration characteristics of navy beans at 24 and 55°C, (2) To study the effect of HPP

(33, 400 and 700 MPa for 3 min) and irradiation (2 and 5 kGy) pretreatments on the hydration behavior of navy beans at 24 and 55°C, and (3) To examine the applicability of Peleg's equation to model hydration behavior of navy beans under various treatment conditions.

# 6.2. Materials and methods

Dry navy beans (*Phaseolus nanus* L.) obtained from an industrial source were used for all the hydration experiments.

# 6.2.1. Moisture determination

Dry navy beans were cleaned and whole beans were separated manually from small and split beans. Samples of dry beans were ground into flour, using a food processor, to pass through a No. 140 USA standard mesh (1 mm) screen (M.S.Tyler, Mentor, OH). Three samples, each with three grams of bean flour, were dried to a constant weight in a thermostatic oven at 103±1°C (AOAC, 1995) and the average initial moisture content was calculated as percentage dry weight basis (kg/kg dry mass).

#### 6.2.2. Water absorption of thermally treated samples

Sorted whole navy beans (20 g samples) were packed in high barrier polyethylene bags with distilled water (1:2, w/w) at room temperature ( $24\pm1^{\circ}C$ ) (referred to as 'THER24' hereafter). A second set of 20 g samples were packed with distilled water at 55°C and the entire set placed in a water bath (Fisher Scientific International Inc.) maintained at 55±1°C (referred to as 'THER55' hereafter). A third set of 20 g samples of whole navy beans were added with distilled water at 55°C which were then allowed to cool by natural convection to 24°C (referred to as 'THER55CONV' hereafter). The THER55CONV treatment was used as the control as it is a representative common industrial practice.

Samples from each of the sets were cut open after every 15 min of soaking time, the free water drained (approximately 50 per cent of original volume), and the weight of beans recorded after blotting them with tissue paper to remove adhering moisture. Observations were continued for a total soaking period of three hours. The drained water from soaking was discarded and there was no correction for lost solids. All soaking tests were triplicated and the average quantity of water absorbed (g) per 100 g of dry beans and moisture content (kg/kg dry mass) was calculated.

#### 6.2.3. Water absorption of high pressure processed beans

Sorted whole navy beans of 20 g samples were packed in high barrier polyethylene bags with distilled water (1:2, w/w) and preheated for 5 min to desired initial temperature. The samples were then high pressure processed (QFP6, Flow Autoclave Systems, Columbus, OH) for 3 min at different pressure levels of 33 MPa (HPP33), 400 MPa (HPP400) and 700 MPa (HPP700) and at two different process temperatures (24 and 55°C) taking the compression heating factor into account (Rasanayagam et al., 2003). The pressure transmitting fluid used was food grade glycol i.e. Houghto Safe 620TY (HS) (Houghton International Inc., Valley Forge, PA) mixed with water (1:1). Thirteen samples were HPP treated at each of the temperature and pressure combinations; the water absorption was recorded at 15 min intervals for 3 hours. The hydration study was then carried out immediately as per the procedure outlined for thermally treated beans. Bean hydration time did not include HPP treatment time.

## **6.2.4.** Water absorption of irradiated beans

Sorted whole navy beans of 20g samples (dry) were packed in high barrier polyethylene bags and irradiated at 2 kGy (IRR2) and 5 kGy (IRR5) levels at ambient temperature using a  $^{60}$ Co  $\gamma$ -ray source available at The Ohio State University Nuclear Reactor Laboratory. Hydration studies of irradiated beans were then carried out immediately as per the procedure outlined for thermally treated beans. The steps followed in conducting the hydration study are illustrated in the flow diagram (Fig. 6.1).

To minimize biological variability in the bean samples, bean samples were obtained from the same lot of an industrial source and base line moisture content was determined. During the experimentation, attention was paid to minimize possible experimental errors in calculation of final bean moisture content.

## 6.2.5. Volume change

The volume of dry navy beans was recorded using the simple water displacement method with a graduated cylinder. The volume of soaked navy beans was measured by the same method at 15 min time intervals for HPP, irradiation, and control samples. The volume change was then calculated as the ratio of volume of soaked navy beans divided by the original volume.

# 6.2.6. Application of Peleg's equation

Peleg's equation (Peleg, 1988) has been widely used for predicting water absorption behavior of foods (Sopade, Ajisegiri, & Badau, 1992; Abu-Ghannam & McKenna, 1997; Pan & Tangratanavalee, 2003) during soaking at constant temperature. It is expressed as:

$$\mathbf{M}_{(t)} = \mathbf{M}_0 + t/(\mathbf{K}_1 + \mathbf{K}_2 t) \tag{6.1}$$

where M(t) is the moisture content (g/g dry mass) at a given soaking time (t h),  $M_0$  is the initial moisture content (g/g dry mass),  $K_1$  is the temperature dependent constant and  $K_2$  is the constant that defines the equilibrium/saturation moisture content. Rearranging equation (6.1) gives:

$$t/(\mathbf{M}_{(t)} - \mathbf{M}_0) = \mathbf{K}_1 + \mathbf{K}_2 t \tag{6.2}$$

Values of  $t/(M_{(t)}-M_0)$  were plotted against *t* and the Peleg's constants K<sub>1</sub> and K<sub>2</sub> were determined from the ordinate-intercept and the slope of the resultant straight line, respectively. Applicability of Peleg's equation to model hydration behavior of navy beans treated with HPP and irradiation was examined by analyzing Peleg's constants K<sub>1</sub> and K<sub>2</sub>. The relationship between equilibrium/saturation moisture content (EMC, kg/kg dry mass) and K<sub>2</sub> was given by Pan and Tangratanavalee (2003) by considering  $t \rightarrow \infty$ , as:

$$EMC = M_0 + 1/K_2$$
 (6.3)

#### 6.3. Results and discussion

#### **6.3.1.** Water absorption of thermally treated samples

Dry navy beans used in the study had an initial moisture content of 0.136 kg/kgdry mass. The water absorption curves of thermally treated beans exhibited the characteristic moisture sorption behavior with an initial faster rate of water absorption followed by slower absorption rate in the later stages (Fig. 6.2). This effect is more pronounced with an increase in soaking water temperature (24 to 55°C). Similar observations were made by earlier researchers (Ituen, Mittal, & Adeoti, 1985; Abu-Ghannam & McKenna, 1997). Beans soaked with water at 55°C (THER55) had the highest absorption rate initially and remained almost constant after 60 min of soaking. This was possibly due to the lower saturation moisture content of the heated samples, which was attained by the rapid initial uptake of water at a higher temperature. The initial rapid water uptake was reportedly due to the filling of capillaries on the surface of seed coats and at the hilum (Hsu et al., 1983). Whereas the slower absorption rate in the later stages was reported to be due to the effect of increased extraction and replacement of soluble materials from the beans by the imbibed water (Phlak, Caldwell, & Stanley, 1989). The maximum water holding capacity of navy beans was a function not only of the soaking temperature, but also whether or not isothermal conditions were maintained during the soaking period. Elevated temperature  $(55^{\circ}C)$  decreased the time required to attain the maximum water absorption capacity but resulted in lower equilibrium moisture content due to the increased extraction rate of soluble material. Allowing the soaking water temperature to cool down to 24°C under natural convection from 55°C

(THER55CONV), resulted in maximum water absorption and reduced loss of soluble materials at the end of three hours.

#### 6.3.2. Water absorption of high pressure processed beans

The synergistic effect of process temperature with pressure on the initial rapid uptake of water is clear by comparison of the plots in Fig. 6.3. Unlike conventional thermal treatment, HPP beans had significantly (p<0.05) higher (45.1 $\pm$ 1.7 to 89.4  $\pm$ 0.2 g/100g of dry beans) water absorption (Fig. 6.3) and moisture content (Table 6.1) at zero soaking time. The rapid water uptake was followed by slower absorption rates during extended atmospheric soaking. This was possibly due to the disruption of the microstructure of the beans during HPP. High pressure caused the cracking of seed coats, breaking of 'spongy' network structure, disruption of protein body structures in the cell (Kajiyama, Isobe, Uemura, & Noguchi, 1995) and increased extraction of soluble material thereby resulting in more infusion of water (Zhang et al., 2004). The initial rapid uptake of water increased with increase in pressure and process temperature (Table 6.1).

Because of the rapid infusion of water during HPP, the beans almost reached their saturation moisture levels in 60 min soaking time (Figure 6.3). It is evident from Table 5.1 that elevated pressures resulted in higher water uptake for both process temperatures (24 and 55°C) but the difference between 400 and 700 MPa is not significant at 60 min soaking time. This confirmed the results reported by Zhang et al. (2004) that the water uptake was nearly identical at pressures of 300 to 500 MPa during the first 30 min and elevated pressures did not influence water uptake any further. Elevated pressures (400

and 700 MPa) completely damaged the inner microstructures resulting in lower saturation moisture contents and loss of soluble solids (Zhang et al. 2004). The lipids were found to have higher mobility than water at higher pressures. Scanning electron microscopy analysis and electrophoresis analysis indicated that partial proteins were denatured and some high-molecular-weight protein fractions were dissociated during high-pressure soaking (Kajiyama et al. 1995; Zhang et al. 2004). These may be the reasons for the lower water holding capacity of navy beans treated at elevated pressures. On the other hand, treating beans at moderate pressures (33 MPa for 3 min) may help in high moisture uptake within a short soaking time and with reduced loss of soluble material. Treatment of beans at lower pressure (HPP33-THER55CONV) had the highest water absorption at the end of a 3 h soaking period; this curve did not reach the steady state indicating a further chance for water absorption. This may be attributed to the restricted disruption of bean microstructure by the lower pressure enabling it to absorb more water over an extended period of soaking.

#### **6.3.3.** Water absorption of irradiated beans

The water absorption curves of navy beans irradiated at 2 and 5 kGy levels of  $\gamma$ -radiation are shown in Fig. 6.4. These curves also follow the characteristic trends observed during thermal hydration studies and IRR5-THER55CONV resulting in maximum water absorption at the end of the 3 h soaking period. The irradiated beans showed the highest water absorption per 100 g of dry beans (107.3±0.1 g for 2 kGy and 108.9±0.1 g for 5 kGy) compared with the control (102.4±0.2 g). The irradiation curves were not stabilized at the end of the 3 h soaking period indicating possible further water

absorption with extended soaking. Though the difference between 2 and 5 kGy treatments was significant (P<0.05), it was not appreciable from the point of treatment time and energy. The increase in water absorption may be attributed to the opening up of starch molecules at doses up to 2 kGy (McArthur and D'Appolonia, 1984). At doses beyond 2 kGy, depolymerization of amylopectin and  $\beta$ -bonding of starch contributed to increased starch crystallization (Rombo et al., 2004). Irradiation treatment helps improve hydration over extended periods (>60 min) of soaking.

## **6.3.4.** Volume Change

The volume change of HPP and irradiated beans soaked in 55°C water and convection cooled is presented in Fig. 6.5. HPP treated beans resulted in greater swelling at zero soaking time. Regardless of the treatment, all the samples attained their maximum volume (127%) at the end of 120 minutes. This may be due to the lack of solids-free water available for uptake or due to the navy beans reaching its maximum seed coat plasticity (Abu-Ghannam & McKenna, 1997).

# **6.3.5.** Peleg's Equation Constants

Peleg's constants, obtained by fitting Peleg's equation into the experimental data, are summarized in Table 6.2. The inverse relationship between K<sub>1</sub> and soaking temperature as reported by Van Buren, Bourne, Downing, Queale, Chase, & Comstock, (1986) and Abu-Ghannam & McKenna (1997) is evident in all the treatments. A similar effect was observed in the HPP beans (33, 400 and 700 MPa) soaked under different thermal conditions. Increase in pressure from 33 MPa to 400 MPa also showed an inverse relationship with  $K_1$  (slightly pronounced) but the trend reversed as pressure was increased from 400 MPa to 700 MPa. This may be attributed to the complete damage of the beans' microstructure and reduced hydration rates at elevated pressures (Zhang et al., 2004).

Further, maintaining the elevated temperature (55°C) constant throughout the hydration process was found to have a pronounced effect on  $K_1$ . Hence, Peleg's constant  $K_1$  decreased not only with increasing temperature but also with maintaining the elevated temperature constant. The experimental results indicated that Peleg's constant  $K_1$  is dependent on not only temperature and pressure, but also any property affecting the condition of the seed coat, e.g., plasticity.

It can be seen from Table 6.2 that Peleg's constant  $K_2$  is similar for thermal and irradiation treated beans. Whereas  $K_2$  for the HPP beans are higher, indicating that HPP decreased the EMC of beans (Equation 6.3) thereby decreasing the time required to attain maximum water absorption capacity and the dry basis moisture content at which it was achieved. It is also evident that increase in pressure resulted in higher  $K_2$  values and lower saturation moisture levels of HPP beans. HPP33-THER24 has a closer  $K_2$  value than that of thermal and irradiated beans, as they were not influenced by elevated pressure and/or temperature. Though temperature does not influence  $K_2$  in thermal and irradiation treated beans, it seemed to have considerable effect in pressure treated beans. Comparison of  $K_2$  values at the same pressure but different soaking conditions revealed the effect of temperature with pressure. However, the near constant value of  $K_2$  for thermally treated and irradiated beans indicated that the equilibrium moisture content did not change with temperature. Elevated soaking temperatures can cut down the overall

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soaking time, but results in loss of bean material (Kon 1979; Pan & Tangratanavalee 2003). In the present study, similar observations were made at elevated pressures as well. This loss of soluble solids may change the equilibrium/saturation moisture content (Pan & Tangratanavalee 2003) and this may be the reason for the pressure dependency of Peleg's constant  $K_2$  at elevated pressures (400 and 700 MPa). Treating the beans at moderate pressure (33 MPa) limited the loss of bean materials but still lowered the EMC when compared to thermal and irradiation treated beans thereby enabling higher hydration rates during soaking. The linear regression values ( $R^2$ ) show the good fit between the data and the Peleg's model.

# 6.4. Conclusions

Treating navy beans at moderate pressure (33 MPa) may help achieve high initial moisture pick up over shorter soaking time (< 1 h). Irradiation may improve the hydration behavior of beans over extended soaking time (> 3 h). Soaking at an elevated temperature (55°C) followed by convection cooling resulted in better water absorption than maintaining elevated soaking temperatures for periods of more than 1.5 hours. Peleg's model can be used to describe the rate of water absorption of navy beans under various soaking temperatures (24 and 55°C) and under various pretreatment conditions like high pressure and irradiation. Loss of bean material at elevated pressures and/or higher soaking temperatures should be considered when applying alternative processing technologies to bean hydration.

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Figure 6.1. Navy beans hydration process flow diagram



Figure 6.2. Water absorption behavior of navy beans under different thermal soaking conditions.



Figure 6.3. Water absorption curves of pressure (33, 400 and 700 MPa) treated beans at process temperatures of  $23^{\circ}C$  (a) and  $55^{\circ}C$  (b, c and d)

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Figure 6.4. Water absorption curves of navy beans irradiated at 2 kGy (a) and 5 kGy (b) and soaked at different thermal conditions



Figure 6.5. Volume change of navy beans subjected to various pretreatments followed by soaking at 55°C and convection cooled. Values shown are the average of three measurements. Error bars indicate the maximum and minimum values.

Process temperature (°C)	Pressure (MPa)	Moisture content (X 10 <sup>-2</sup> kg/kg dry mass) <sup>a</sup>		
		Immediately after high pressure processing	At the end of 60 min soaking <sup>b</sup>	
24	33	58.8±0.2	82.2±0.5	
	400	68.7±0.1	93.9±0.3	
	700	70.8±0.2	95.2±0.3	
55	33	86.9±0.1	100.7±2.9	
	400	95.2±0.8	108.9±1.8	
	700	102.1±0.1	111.0±1.9	

<sup>a</sup> calculated with no correction for lost material <sup>b</sup> soaked at elevated temperature (55°C) water and cooled under natural convection

Table 6.1. Moisture content of pressure treated navy beans under different process conditions.

	Hydration			
Pretreatment	temperature (°C)	$\mathbf{K}_1$	<b>K</b> <sub>2</sub>	$\mathbf{R}^2$
Thermal				
THER24	24	4.5 x 10 <sup>-3</sup>	9.2 x 10 <sup>-3</sup>	0.96
THER55CONV	55 & conv. cool	2.1 x 10 <sup>-3</sup>	9.3 x 10 <sup>-3</sup>	0.99
THER55	55	5.0 x 10 <sup>-4</sup>	1.0 x 10 <sup>-2</sup>	0.99
High Pressure Processing				
HPP (3 min @24°C)				
33 MPa (HPP33-THER24)	24	1.9 x 10 <sup>-2</sup>	1.5 x 10 <sup>-2</sup>	0.82
400 MPa (HPP400-THER24)	24	1.8 x 10 <sup>-2</sup>	1.9 x 10 <sup>-2</sup>	0.90
700 MPa (HPP700-THER24)	24	2.5 x 10 <sup>-2</sup>	1.8 x 10 <sup>-2</sup>	0.78
HPP (3 min @ 55°C)				
33 MPa (HPP33-THER55CONV)	55 & conv. cool	1.4 x 10 <sup>-2</sup>	2.8 x 10 <sup>-2</sup>	0.93
400 MPa (HPP400-THER55CONV)	55 & conv. cool	6.4 x 10 <sup>-3</sup>	5.3 x 10 <sup>-2</sup>	0.99
700 MPa (HPP700-THER55CONV)	55 & conv. cool	1.2 x 10 <sup>-2</sup>	6.6 x 10 <sup>-2</sup>	0.99
HPP (3 min @ 55°C)				
33 MPa (HPP33-THER55)	55	1.4 x 10 <sup>-3</sup>	4.1 x 10 <sup>-2</sup>	0.99
400 MPa (HPP400-THER55)	55	1.3 x 10 <sup>-3</sup>	6.4 x 10 <sup>-2</sup>	0.99
700 MPa (HPP700-THER55)	55	1.1 x 10 <sup>-2</sup>	8.2 x 10 <sup>-2</sup>	0.99
Irradiation				
2 kGy (IRR2-THER24)	24	3.1 x 10 <sup>-3</sup>	9.2 x 10 <sup>-3</sup>	0.98
5 kGy (IRR5-THER24)	24	3.4 x 10 <sup>-3</sup>	9.1 x 10 <sup>-3</sup>	0.98
2 kGy (IRR2-THER55CONV)	55 & conv. cool	2.1 x 10 <sup>-3</sup>	9.0 x 10 <sup>-3</sup>	0.99
5 kGy (IRR5-THER55CONV)	55 & conv. cool	2.1 x 10 <sup>-3</sup>	8.7 x 10 <sup>-3</sup>	0.99
2 kGy (IRR2-THER55)	55	6.0 x 10 <sup>-4</sup>	1.0 x 10 <sup>-2</sup>	0.99
5 kGy (IRR5-THER55)	55	9.0 x 10 <sup>-4</sup>	9.5 x 10 <sup>-3</sup>	0.99

Table 6.2. Values of Peleg's hydration constants for navy beans subjected to various treatments.

# CHAPTER 7

# CONCLUSIONS

## Thermal conductivity of food materials under pressure

- The line heat source probe method was found to be a suitable method for measuring *k* of various liquid and solid foods under pressure. Using this method, *k* of selected liquid and solid foods was successfully measured at pressures up to 700 MPa and at various process temperatures.
- Thermal conductivity of all the tested foods increased linearly with increased pressures up to 700 MPa. Process temperature was found to have weaker but positive influence on *k* values.
- Depending on the pressure, temperature, moisture content and food composition, *k* varied between 0.21 and 0.90 W/m°C.
- Composition and compressibility characteristics of the foods were found to significantly influence *k* values. Among the constituents of food, water being the predominant component and having the highest k was found to have the largest influence on k values. Within range of experimental conditions tested, k decreased with increase in fat content of the foods studied. All other foods tested have intermediate k values between water and fat.

- Differences in the structural characteristics as influenced by the process pressure and temperature were found to play a major role in *k* of solid foods.
- The uncertainty associated with the *k* measurement varied between 0.6% (canola oil) and 3.8% (HFCS) for the liquid foods and between 1.7% (carrot) and 4.2% (chicken fat) for the solid foods.

#### Thermal effects of polar and non-polar substances under pressure

- Among the polar and non-polar materials tested, non-polar materials were found to show a non-linear behavior in their heat of compression (δ). Polar materials exhibited linear heat of compression values with increasing pressure.
- Among the substances tested, heat of compression values decreased with increasing polarity index (8.8°C per 100 MPa for chloroform to 3°C per 100 MPa for water).
- Change in carbon chain length (C<sub>2</sub> to C<sub>4</sub>) and degree of unsaturation (C<sub>18:1</sub> to C<sub>18:3</sub>) of selected fatty acids were found to have an effect on the δ only at elevated pressures.
  This was found to be due to the modified molecular interactions and associated bonds at high pressures.

## **Pressure blanching of navy beans**

- Application of moderate pressure (33 MPa) was found to improve the hydration behavior of navy beans over shorter soaking time (<1 h).
- Soaking at an elevated temperature (55°C) followed by convection cooling resulted in better water absorption than maintaining elevated soaking temperatures for longer periods. However, loss of bean material at elevated pressure and/or soaking temperatures should be considered in applying HPP to improve hydration.

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