APPLICATION OF TEMPERATURE-DEPENDENT THERMAL PROPERTIES IN FOOD THERMAL PROCESS SIMULATION AND SELECTION OF PRODUCT FORMULATION

by

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To my family, friends, and mentors who supported me through this journey

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ABSTRACT

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Mathematical modeling of heat transfer is a common method utilized in designing thermal processes for food, modeling degradation kinetics of microorganisms and nutrients, designing food processing equipment as well as for process optimization and for ensuring scale-up feasibility of a product. It is essential to have all the necessary components for modeling including the geometry, boundary conditions, initial temperature, and the temperature-dependent thermal properties. Getting temperature-dependent thermal properties of food product is difficult due to the lack of effective and efficient devices or techniques. To show the influence of temperature-dependent thermal properties, retort processing of potato soup was simulated using both temperature-dependent (dynamic) and fixed thermal properties. Three methods, TPCell, Choi-Okos predictive model and KD2 Pro, were used to determine the thermal conductivity at 25°C and 120°C for comparison. The proximate composition of the sample was determined for prediction of thermal properties with the Choi-Okos model. The accuracy of simulation was evaluated based on the temperature at the cold spot and corresponding sterilization value. Results suggested that using temperature-dependent thermal properties in heat transfer modeling increased the accuracy of the simulation. Simulation performed with temperature-dependent properties obtained from TPCell matched very closely with experimental heat penetration data. Additionally, the sensitivity of temperature-dependent thermal properties obtained from TPCell in detecting variation in product formulation was evaluated. Four variations of potato soup were prepared to compare their respective lethality value. Thermal conductivity, specific heat capacity and density of the potato soups were measured, and simulation was performed using the measured thermal properties and a scheduled process as boundary conditions. Thermal properties of food product changed with the formulation which affected the processing time to achieve minimum lethality value. A significant difference in thermal conductivities was seen for these potato soups causing the scheduled process

to be only suitable for thermal processing of some formulations while others would be undercooked that could lead to food safety risk. Since the thermal conductivity measurements were sensitive in detecting the difference in the formulation, it can be used as a tool to select a formulation that can best suit the processing conditions of the heat penetration tests. The technique described can be used for any thermal processes in the food industry including pasteurization, retort, and aseptic processing. This application will be beneficial for the industry to pre-screen the iterations and only select formulation that suits the scheduled process for successful heat penetration trials and reduce trial costs.

CHAPTER 1. INTRODUCTION

1.1 Introduction

1.1.1 Thermal Properties

Food thermal properties are important parameters in designing thermal processes which are aimed to ensure food safety. Reliable estimates of food thermal properties are crucial for modeling the kinetics of microbial destruction. Food thermal properties also play an important role in modeling degradation reactions which are intended to improve food quality. The thermal properties including thermal conductivity, specific heat capacity and thermal diffusivity, are temperature dependent. Hence, it is important to have effective and efficient determination of food thermal properties at multiple temperatures for accurate process simulation and modeling of heat transfer.

Thermal conductivity (k) is defined as the ability of a material to conduct heat which is a coefficient that quantifies the rate of heat transfer (dQ/dt) along the direction of a temperature gradient (dT/dx), governed by Fourier's law of heat conduction as shown in Eq 1.1. Specific heat (C_P) is the amount of heat required to raise the temperature of unit mass of the material by a unit degree. Thermal diffusivity (α) is the ability of a material to store thermal energy during heat transfer. All these thermal properties are related to each other and their relationship is shown in Eq. 1.2, where thermal diffusivity is the ratio of thermal conductivity to the volumetric heat capacity

$$\frac{dQ}{dt} = -kA\frac{dT}{dx} \tag{1.1}$$

$$\alpha = \frac{k}{\rho C_P} \tag{1.2}$$

1.1.1.1 Thermal Conductivity Measurement Methods and Challenges

Based on Eq. 1.2, it is clear that thermal diffusivity can be calculated as long as the thermal conductivity, specific heat and density values are obtained. Measurements of specific heat can be done easily. Specific heat is strongly dependent on the water content of food and a good estimation can be easily obtained based on the water content alone (E. Sweat & G. Haugh, 1974). A differential scanning calorimetry is typically used to determine the specific heat of a food material.

Estimating thermal conductivity is more difficult because it depends on the density, temperature and composition of food whereas specific heat is only affected by composition and temperature (Choi & Okos, 1986). Food has complex matrix that is not homogenous most of the time. A study reported correlation between the moisture content of food and their thermal conductivity, clearly elucidating the dependency of thermal conductivity on the composition of food (Sweat, 1974). Thermal conductivity of food materials varies between that of water (K_{water}=0.611 W/m°C at 25°C) and that of air (K_{air}0 0.026 W/m°C at 27°C) (Choi & Okos, 1986; Sahin & Sumnu, 2006). Some predictive models have been developed based on composition of food materials such as water, carbohydrates, proteins, fat, fiber, ash and ice (Choi & Okos, 1986). These models also included temperature (T) in calculating thermal conductivity (Eq. 1.3- 1.9) and is specific for each proximate composition. The thermal conductivity of a food product is then calculated based on the fractions of each proximate components as shown in Eq. 10

$$k_{water} = 5.7109 \times 10^{-1} + 1.7625 \times 10^{-3}T - 6.7036 \times 10^{-6}T^2 \quad (1.3)$$

$$k_{carbohydrate} = 2.0141 \times 10^{-1} + 1.3874 \times 10^{-3}T - 4.3312 \times 10^{-6}T^2 \quad (1.4)$$

$$k_{protein} = 1.7881 \times 10^{-1} + 1.1958 \times 10^{-3}T - 2.7178 \times 10^{-6}T^2 \quad (1.5)$$

$$k_{fat} = 1.8071 \times 10^{-1} - 2.7604 \times 10^{-4}T - 1.7749 \times 10^{-7}T^2 \quad (1.6)$$

$$k_{fiber} = 1.88331 \times 10^{-1} + 1.2497 \times 10^{-3}T - 3.1683 \times 10^{-6}T^2 \quad (1.7)$$

$$k_{ash} = 3.2962 \times 10^{-1} + 1.4011 \times 10^{-3}T - 2.9069 \times 10^{-6}T^2 \quad (1.8)$$

$$k_{ice} = 2.2196 - 6.2489 \times 10^{-3}T + 1.0154 \times 10^{-4}T^2 \quad (1.9)$$

$$k = \Sigma k_i X_{i,}. \quad (1.10)$$

Measurements of thermal conductivity can be done in steady-state or in transient-state. During steady-state measurements, food materials are let to equilibrate with desired temperature and the thermal conductivity is measured using a thermal conductivity probe. A steady-state condition is reached when the temperature at each point of the sample is constant and the temperature does not change with time. This method is easy when the measurements are done at room temperature. At elevated temperatures, the food materials take up to 12 h, depending on the samples, to equilibrate with the target temperature (Murakami & Okos, 1989). Since food matrix is complex, it is impossible to reach constant temperature at every point in the sample. Some spots in the food product will always be colder than the rest, depending on the composition of the sample, shape of the container, source of heat and the mode of heat transfer. At the same time, prolonged heating at elevated temperature causes many undesirable reactions including, Maillard browning, oxidation, color degradation, nutrient degradation, loss of moisture and loss of texture which results in complete destruction of sample by the time it reaches the target temperature. Any measurements taken on a severely decomposed sample may not be accurate since the composition of the food has changed.

Guarded hot plate (GHP) relies on a steady temperature difference over a known thickness of sample. Sample is placed between two plates at different temperatures. The steady temperature difference between these plates are achieved by controlling the heat flow through the material. As mentioned above, achieving steady-state in GHP is time consuming, just like any other steady-state techniques. The GHP measurements are analyzed based on the theory of heat transfer in the infinite slab geometry (Yuksel, 2016). Unidirectional heat flow is achieved through the use of guarded plates since the dimension of sample is finite. The temperature of the thermal guards is maintained until the steady-state is reached where the heating and cooling plates will have stable temperatures (Yuksel, 2016). The thermal conductivity of the sample is then determined based on the heat input (Q), the temperature difference through sample ΔT, the thickness of sample (l), and the size of metered area of heat transfer (A) based on Eq. 1.11. Though GHP is more suitable for dry homogenous products, it is known to be unsuitable for materials with potential moisture migration. Several studies were done to determine the thermal conductivity of food product using GHP, such as meat, offal and fat, fish fillets cheese, butter, apple and many more (Pham & Willix, 1989; Willix, Lovatt, & Amos, 1998). GHP method is only good for food material that can hold the shape and thickness since thickness is an important factor affecting the thermal conductivity which poses limitation for liquid samples.

$$k = \frac{l\dot{Q}}{A\Delta T} \tag{1.11}$$

The non-steady techniques, also known as the transient-state methods takes measurements during the heating process. Transient-state measurements can be done quickly because the sample does not need to equilibrate with the study temperature. This significantly reduces the thermal damage on the food product since prolonged heating is completely avoided. This method determines the value of thermal conductivity by a transient sensor utilizing the transient heat conduction equation.

Transient line-source (TLS) is one of the most commonly used transient-state method for measuring thermal conductivity of food materials (E. Sweat & G. Haugh, 1974; Sweat, 1974). This method has a small probe consisting of a hot-wire and a thermocouple that can be inserted into food. Thermal conductivity is estimated based on Eq 1.12, where Q (watts/m) is the heat supplied by the probe and M is the slope of ln time vs temperature (°C) curve. The slope is determined using the least square method (E. Sweat & G. Haugh, 1974). One major disadvantage of this method is that the probe has to be equilibrated to the experimental temperature before the measurements are taken which adds significant amount to the analysis time (Wang & Brennan, 1992). TLS method are not designed for measurements at high temperature as repeated use at this condition can cause failure of the sensors (Mishra, Dolan, Beck, & Ozadali, 2016). When measuring liquid samples, convection can be an issue and the thermal conductivity value can be inflated. For this reason, lower power input is recommended for samples with low viscosity (Murakami & Okos, 1989).

$$k = \frac{Q}{4\pi M}, \tag{1.12}$$

Transient plane-source (TPS) is another methodology that is developed for simultaneous measurement of thermal conductivity and diffusivity. The application has been focused more on solid materials, unlike TLS. The theory was developed in 1991 and it is commercially available. This technique is also commonly known as the "hot-square" or the "hot-disk" method (Gustafsson, 1991). When a thin layer of heat source is tightly sandwiched between two contact surfaces of the same material, the thermal energy generated is absorbed by the test material. The heating element in the TPS is constructed using a nickel foil resistance temperature detector (RTD) and is bound onto a stainless-steel sheet (Huang & Liu, 2009). The TPS element is used both as a heat source and a temperature sensor where temperature increase of the element is calculated based on the resistance (Gustafsson, 1991). The transient process is governed by the Eq. 1.13

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T + \frac{Q}{\rho C_P} \tag{1.13}$$

A new instrument, known as TPCell, is capable of measuring temperature-dependent thermal conductivity thermal conductivity of food materials in transient state in less than a minute (Mishra et al., 2016). It is also very much capable of measuring thermal conductivity values at elevated temperatures, up to 140°C (Mishra et al., 2016). In TPCell, the sample holder is pressurized to achieve elevated temperatures and minimize moisture loss. Thermal damage to the food sample is prevented due to shorter experimental time and prevention of moisture migration. The TLS and TPS methods are not capable of handling temperatures higher than 100°C which makes TPCell a better fit for application in the food industry, especially. The operating temperature range of TPCell covers the commercial processing conditions in the food industry making it a very useful tool. Based on the temperature profile from heating the sample gently, TPCell utilizes sequential parameter estimation based on Gauss minimization method (Beck & Arnold, 1977). Parameter estimation generally relies on scaled sensitivity coefficients that provides useful insight if a parameter in the model can be estimated with relative accuracy associated with it (Beck & Arnold, 1977). As a general rule in inverse problem approach, if the sum of scaled sensitivity coefficient is equal to zero, then all parameters in the model cannot be estimate uniquely and simultaneously (Beck & Arnold, 1977). This is the fundamental principle behind the design of TPCell where sum of all scaled sensitivity coefficients is equal to the negative temperature rise of the product that enables for simultaneous measurement of temperature-dependent thermal properties (Mishra et al., 2016).

1.1.2 Retort Processing

Retort processing or canning is an old technique but still a widely used thermal process to preserve food from being spoiled by microorganisms. The origin of canning dates back to eighteenth century when Nicholas Appert practiced preservation by heating food in sealed containers in boiling water. The relationship between temperature and microbial inactivation was later investigated by Louis Pasteur which serves as the foundation for development of commercial operation of retort processing.

Microorganisms are present in raw food ingredients, but thermal process inactivates them. With proper processing and packaging technology, their growth in processed food product can be inhibited. Retort processing is aimed to deliver commercial sterility to food products. According to the Food and Drug Administration's (FDA) Code of Federal Regulations title 21 (21 CFR 11.3), commercial sterility is defined as a condition achieved by application of heat alone or in combination with other treatments to render food that is free of pathogenic microorganisms that are capable of reproducing in the food under normal non-refrigerated condition during storage and distribution. Commercially sterile product is safe for consumption due to absence of viable foodborne-illness causing microorganisms, as long as the hermetic seal on the package is intact. Botulinum toxin from *Clostridium botulinum* is one of the deadliest concerns when it comes to low acid canned food product (Thompson & Tanner, 1925). C.*botulinum* is a spore-forming pathogenic microorganism that is capable of reproducing in anaerobic conditions of canned food product. The neurotoxin produced by this organism can cause severe health issues and can be fatal. C. *botulinum* can be inhibited by heating it above 121°C and the toxin can be destroyed by heating it at 85°C. However, inactivation of the spores is challenging because it is heat stable and can only be inactivated when heated at 121°C under pressure of 15-20 lb/in^2 for a certain period of time, depending on the product (Mishra & Sinha, 2011) .

In retort processing, raw ingredients or partially cooked food products are placed in a container and sealed hermetically before being subjected to thermal processing in a retort. Typically, steam is used as the means to deliver heat to the cans but other mediums such as steam-air and hot water or the combination of all of these can be used as well. Retorts can be classified as static retorts and rotary retorts. Retort processing can be done in batches or continuously. Static retorts are typically a batch process where cans are loaded into crates which will then be placed in the retort. The retort is then pressurized to achieve steam temperature of 250°F (121.1°C). Continuous supply of steam ensures the retort temperature is maintained. In rotary retorts, the cans are rotated to provide agitation with the aim to increase heat transfer. Rotary retorts are more efficient than static retorts due to significantly lower processing time. In continuous process, cans are carried from one end of the retort to the other end along the surface of the retort. Sometimes agitation is also provided to increase the heat transfer rate through forced convection.

Transient heat transfer is the fundamental mechanism during thermal processing of a can in a retort processing. There are two modes of heat transfer that occurs inside the can during heating: (1) conduction, and (2) convection. Conduction primarily drives the heat if the product is solid or semi-solid. When the sample is a mixture of solid and liquid, the heat transfer is governed by both conduction and convection. In still retort, the primary mode of heat transfer is conduction since there is no movement of liquid. In agitated retort, due to rotation of the can, both conduction and convection drives the heat transfer.

1.1.3 Heat Penetration and Sterilization Value

Heat penetration study is typically done to evaluate the thermal behavior of a food product during thermal processing. It is an important step in determining if a thermal process can provide sufficient heat to inactivate target organism to the desired level. During a heat penetration test, the product is processed using pre-determined processing conditions (i.e temperature, time, pressure). During this study, thermocouples are placed inside a sealed can, especially at the slowest heating spot or cold spot, without compromising the hermetic seal. For a cylindrical can, the cold spot is the geometric center for conduction-heated food. The temperature at the slowest heating point is monitored and used to determine if the process applied was sufficient to achieve commercial sterility. Two methods are commonly used to evaluate the minimum required thermal process to achieve commercial sterility; known as the general method and the formula method.

Adequacy of thermal processing is evaluated using the sterilization value. The sterilization value or lethality (F_o) of a given process is defined as the length in minutes of a thermal process at 250°F. The container contents, immediately upon the beginning of the process, are held at processing temperature for the length of the process. At the end of process, it is cooled down to sublethal temperature (Ball & Olsen, 1957).

The lethality is an important measure for designing thermal processing as it indicates if a thermal process has adequately inactivated the microorganisms present in the food product. This can be calculated using the general method which serves as the basis for all modern thermal process calculations (Bigelow, Bohart, Richardson, & Ball, 1920; Patashnik, 1953). The time-temperature data from the cold spot is used to calculate the lethality. The size of the container, initial temperature of the product, retort temperature profile, the thermal properties of the can and the product play important roles in heat transfer to the coldest point.

Lethal rate (L) is calculated using Eq. 1.14 for each temperature at the center of the can from the heat penetration data (Ball, 1923) where T is the temperature at the cold spot at time (t), T_r is the reference temperature (250°F), z refers to temperature change at which a tenfold reduction in the D -value which depends on the thermal resistance of the microorganism of interest and can vary from one microorganism to another.

$$L = 10^{(1/z)(T-T_r)} \tag{1.14}$$

The area under the lethal rate curve vs time can be calculated by integrating lethal rate over time and is referred to as lethality (F_0) as shown in Eq. 1.15 (Patashnik, 1953).

$$F_0 = \int_0^t 10^{(1/z)(T-T_r)}\, dt \tag{1.15}$$

General method is not capable of calculating the processing time directly. Hence the formula method was developed to address the deficiency of general method in determining the process time (Ball, 1923). The formula method also utilizes heat penetration data to determine process time. Eq.1.16 is derived from the heat penetration curve,

$$B = f_h \log(j_h I_h / g) \tag{1.16}$$

$$I_h = (T_r - T_{ih}) \tag{1.17}$$

$$g_c = (T_r - T) \tag{1.18}$$

$$j_h = (T_r - T_{pih})/(T_r - T_{ih}) \tag{1.19}$$

where B is the process time, f_h is the slope of heating line, j_h is the lag factor, I_h is the initial temperature difference (Eq.1.17), g_c is the difference between retort temperature and temperature of cold spot at the end of heating (Eq.1.18). Lag factor j_h is determined based in Eq. 1.19, where T_r is the retort temperature, T_{pih} is pseudo-initial product temperature and T_{ih} is the initial product temperature. g is determined on a relationship with f_h/U (Eq. 1.20), where $F_0F_{121.1}^{z}$ (Eq.1.21) is the number of min at the retort temperature and is equivalent to 1 min at 121.1° C

$$U = F_0F_{121.1}^{z} \tag{1.20}$$

$$F_0F_{121.1}^{z} = 10^{(121.1-T_r)/z} \tag{1.21}$$

1.1.4 Heat Transfer Simulation

Mathematical modeling of heat transfer during retort processing requires the initial temperature of the product inside the can, boundary condition of the outer surface and thermo-physical properties (i.e thermal conductivity, specific heat capacity and density) of the product along with the dimensions of the container. Since a can is symmetrical on both sides of the central axis, modeling of heat transfer can be done using a 2D axisymmetrical problem even though a can is a three-dimensional object. Using 2D axisymmetrical approach, the geometry can be simplified to a rectangular cross section with the sides representing the length (z) and the radius (r) of the can as shown in Figure 1.1.

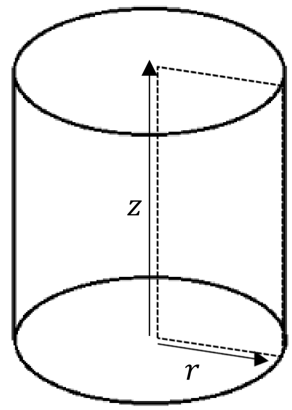


Figure 1.1 3D geometry of a cylinder with 2D axisymmetric rectangular cross section with sides represented with the length (z) and radius (r) of the can

Numerical methods such as finite difference or finite element, can be used to solve the transient heat conduction problems using software such as "COMSOL" (COMSOL Inc, Burlington, MA). The heat transfer equation (Eq. 1.22) for the axisymmetric case is written as:

$$\left[\frac{1}{r}\frac{\partial}{\partial r}\left(k(T)r\frac{\partial T}{\partial r}\right) + k(T)\frac{\partial^2 T}{\partial z^2}\right] = \rho C_p(T)\frac{\partial T}{\partial t} \qquad (1.22)$$

where $k(T)$ is the thermal conductivity of the product, ρ is the density, $C_p(T)$ is the specific heat capacity. Both thermal conductivity and specific heat capacity are modeled as functions of temperature. Temperature-dependent thermal properties (i.e thermal conductivity and specific heat capacity) is extremely important in modeling heat transfer and may influence the accuracy of simulation. Accurate modeling plays a crucial role in food thermal process design because any miscalculations can lead to either undercooking or overcooking of product which causes risk of an outbreak of foodborne illness or severe quality degradation, respectively.

Hence, the focus of this study is to show the importance of temperature-dependent thermal properties on heat transfer simulations and to evaluate thermal behavior of various iterations of a formulation during thermal processing. Retort processing was chosen to demonstrate these applications. Similar approach can be used for other thermal processes such as pasteurization and aseptic processing.

Typically in the food industry, many iterations of product formulations are made before commercialization of the final formulation. However, each iteration requires a time intensive and costly heat penetration study to examine the impact of thermal process on product safety and quality. We propose TPCell as a bench top alternative to evaluate the thermal behavior of all iterations or formulations without having to do expensive large-scale trials. It would be very useful for product developers to utilize the thermal properties, from the very beginning, in making decisions on finalizing the formulation.

1.1.5 Objectives of the Study

There were two objectives of the study;

1. Simulate retort processing using temperature-dependent thermal properties to improve the accuracy of simulation
2. Show influence of variation in product formulation in retort processing and detection of variation using thermal properties

1.2 Literature Review

1.2.1 Use of Temperature-Dependent Thermal Properties in Thermal Process Simulation

Food thermal properties play a crucial role in modeling of heat transfer for a thermal process. The accuracy of modeling relies heavily upon the geometry of the container, boundary conditions, initial temperature of the product and thermal properties (Mishra & Sinha, 2011). While obtaining other factors are fairly straightforward, acquiring accurate thermal properties can be challenging. Thermal properties such as thermal conductivity and specific heat capacity are temperature dependent. Their values change based on the temperature. It is important to include thermal properties of a food product at multiple temperatures when modeling the thermal processes. The model should at least involve the thermal conductivity and specific heat capacity measured at temperature range that the thermal process would be operating. Food is a complex product that undergoes various changes during cooking. Phase transition, glass transition, moisture migration are some phenomena that happen during thermal process which have significant impact on the thermal properties of the product. Continuous monitoring of specific heat, thermal conductivity and density during baking of cupcake revealed the thermal properties did not stay the same during baking (Baik, Sablani, Marcotte, & Castaigne, 2006). The accuracy of heat transfer simulation for a thermal process may decrease if only thermal properties at room temperature were used.

Simulation of heat transfer can be done numerically using finite element or finite difference methods. For simple problems with simple geometries and boundary conditions, the finite difference approach may be sufficient which uses temperature-independent thermal properties. The finite element method is more powerful than finite difference and is commonly used for more complicated problems. Finite element method requires temperature-dependent thermal properties (Rodríguez, Martínez, Rodrigo, & Safón, 1996). The use of finite element method in modeling thermal processing of food (Naveh, Kopelman, Zechman, & Pflug, 1983) and the advantages of finite element method to solve heat conduction problems related to food have been studied (De Bearemaeker, Singh, & Segerlind, 1977).

A heat penetration study done on retorting kimchi soup attempted to simulate the heat transfer using finite element method and compared the center temperature distribution and corresponding sterilization value (F_0) values over time. Poor correlation was reported between experimental and predicted F_0 value with deviation of 53.87% though a good correlation was seen with the experimental center temperature distribution itself (R^2=0.975) (Cho, Park, Cheon, & Chung, 2015). It is quite common to see large deviations in F_0 though the temperature distribution between experimental and predicted data are close to each other which emphasizes the importance of having accurate heat transfer simulation. The mathematical modeling for heat distribution prediction in the study was developed using thermal properties of kimchi soup measured at 63.52 °C while the retort was ran at as high as 120.7°C (Cho et al., 2015). The author concluded the discrepancy is most likely rooted from the headspace acting as barrier for heat transfer, preventing the cold spot from reaching the target temperature sooner. It is our hypothesis that if temperature-dependent thermal properties were to be included, an accurate simulation could have been created because the thermal properties change with temperature. Using thermal property values at only one temperature may lead to overestimation or underestimation of heat transfer, depending on the product, resulting in overcooking of the product and decrease in the quality, and undercooking with food safety issue, respectively. (Cho et al., 2015).

When prediction of center temperature of retorted product was carried out utilizing thermal properties that were determined at the room temperature, a slight deviation was seen between the experimented and predicted temperature (Bhowmik Santi & Tandon, 1987; Lebowitz Samuel & Bhowmik Santi, 2006). These studies utilized finite difference method which did not require temperature-dependent thermal properties. Good agreement between the experimental and predicted center temperature was reported for beef utilizing temperature-dependent thermal conductivity (McGinnis, 1986). The author stated, temperature-dependent thermal conductivity, specific heat, density and viscosity were incorporated in the model for improved accuracy. The study did not compare the lethality value of center point for experimental and predicted, though predicted center point lethality was reported.

Another study attempting to simulate heat transfer in retort processing of canned peas in water utilized thermal properties of water at multiple temperatures (Kızıltaş, Erdoğdu, & Koray Palazoğlu, 2010). The results obtained show overlap between simulated and experimental data indicating the importance of using temperature-dependent thermal properties in heat transfer simulation. The retort process, however, was carried out under pasteurization condition at about 98°C. Typical retort processing condition operates at temperatures above pasteurization conditions.

Modeling blanching of potato cubes was achieved by utilizing thermal diffusivity at multiple temperatures using finite difference method (Mauricio & Francisco, 2017). Thermal diffusivity of potato cubes was obtained at temperatures from 40-90°C and fitted those value in software to simulate the temperature of the center of cubes, the cold spot. The simulated temperature profiles fitted well with the experimental profile. However, the lethality achieved by both the simulated and experimental profile was not reported. The lethality plays a crucial role in ensuring the food safety. Hence, the lethality should be the primary way of checking the accuracy of simulation. This is because even when the simulated temperature profiles match closely with the experimental profiles, tremendous difference can still be seen when the temperature is converted to lethality values (Cho et al., 2015).

Thermal diffusivity is conventionally used in the simulation of heat penetration in canned food. There are two ways this value can be obtained: 1) by individually obtaining the thermal conductivity, specific heat capacity and density 2) from experimental heat penetration data and calculating apparent thermal diffusivity by taking the reciprocal of the slope of the heating curve. The second method is used to due to lack of tools to determine thermal conductivity at high temperatures, especially at temperatures above 100°C. Hence, there is a need for a device that could measure the thermal properties of food products at high temperatures.

1.2.2 Use of Temperature-Dependent Thermal Properties in Selection of Production Formulation

During product development in the food industry, modification to existing formulation is a common process to achieve different nutrient content (for instance, low calories) or when there is change in suppliers. Often times the decision on which modification to select as the final formulation is decided based on the sensory attributes. A similar approach is done during development of new products as well. These formulations will then be tested with a scheduled process with a heat penetration study. If the modification is drastic, the scheduled process may no longer be suitable to process the formulation as severe deviation may occur. The adequacy of thermal process is evaluated based on accumulated lethality (FDA, 2015).

A number of things affect the accumulated lethality that a food product receives during thermal processing such as consistency of the product, initial temperature, initial microbial load and thermal properties (i.e thermal conductivity, specific heat capacity, density) besides the processing conditions (Holdsworth & Simpson, 2016). FDA's guide to inspection of low acid canned food has stated that all formulation changes should be monitored carefully because it can have dramatic effects on the thermal heating characteristics of the product, especially for products containing starch. Even a change in suppliers or small changes in the amount of starch used (i.e 1% to 2%) can have a significant impact on the amount of time required to reach minimum lethality (FDA, 2015).

Heat penetration studies on various formulation of dairy-based dessert (kheer) revealed that not all formulations requires the same process time. The process time reported varied from 14.89 to 21.52 min, depending on the ratio of rice to milk solids, indicating the influence of variation in formulation in thermal process time (Jha, Patel, Gopal, & Ravishankar, 2014). Another study investigating the impact of addition of 1% xanthan or 1% avicel to cream style corn showed significantly different temperature profiles at the cold spot (Naveh et al., 1983).

Data from literature supports that significant changes to thermal behavior could happen to food product when a formulation is changed, or even when one ingredient is added or removed. Hence, it is important to make a well-thought decision when it comes to formulation selection and modification. While sensory attributes are used as primary tools for such selections, other parameters such as thermal properties could be considered for adequacy of thermal process. Since thermal properties of food product influence the heat transfer directly, it would be more reasonable to select the final formulation based on their thermal properties given the food product still has decent sensory attributes. No data from literature was found on using food thermal properties as a tool to select formulation that would fit the established thermal process so far.

1.3 Conclusion

Food thermal properties are extremely important for food processing. These properties determine the heat transfer to the product during the processing. While it is a common understanding that including temperature-dependent thermal properties is important for accurate process modeling, it is not well-practiced due to lack of devices in the market that is applicable to food products. Additionally, application of food thermal properties in the food industry can be extended to product development as well as a bench-top practice in selecting formulations for heat penetration studies and scale ups.

1.4 Reference

Baik, O. D., Sablani, S. S., Marcotte, M., & Castaigne, F. (2006). Modeling the Thermal Properties of a Cup Cake During Baking. *Journal of Food Science, 64*(2), 295-299. doi:10.1111/j.1365-2621.1999.tb15886.x

Ball, C. O. (1923). Thermal process time for canned foods. *Bull National Research Council 7, Part 7*(37).

Ball, C. O., & Olsen, F. C. W. (1957). General Method of Process Calculation. In *Sterilization in food technology; theory, practice, and calculations* (1st ed.). New York: McGraw-Hill Book Company, Inc.

Beck, J. V., & Arnold, K. J. (1977). *Parameter Estimation in Engineering and Science*. New York: John Wiley & Sons.

Bhowmik Santi, R., & Tandon, S. (1987). A Method for Thermal Process Evaluation of Conduction Heated Foods in Retortable Pouches. *Journal of Food Science, 52*(1), 202-209. doi:10.1111/j.1365-2621.1987.tb14005.x

Bigelow, W. D., Bohart, G. S., Richardson, A. C., & Ball, C. O. (1920). Heat penetration in processing canned foods. *Bull. Nr 16-L Res. Washington, D.C: Lab Natl. Canners Assn*.

Cho, W.-I., Park, E.-J., Cheon, H. S., & Chung, M.-S. (2015). The Study of Heat Penetration of Kimchi Soup on Stationary and Rotary Retorts. *Preventive Nutrition and Food Science, 20*(1), 60-66. doi:10.3746/pnf.2015.20.1.60

Choi, Y., & Okos, M. R. (1986). Effect of temperature and composition on the thermal properties of food. In M. L. Maguer & P. Jelen (Eds.), *Food Engineering and Process Applications 1* (Vol. 1, pp. 93-101). London and New York: Elsevier Applied Science.

De Bearemaeker, J., Singh, R. P., & Segerlind, L. J. (1977). Uses of finite element method in food processing. *Journal of Food Engineering, 1*, 37.

E. Sweat, V., & G. Haugh, C. (1974). A Thermal Conductivity Probe for Small Food Samples. *Transactions of the ASAE, 17*(1), 56. doi:https://doi.org/10.13031/2013.36786

FDA. (2015). Guide to Inspections of Low Acid Canned Food 6.

Gustafsson, S. E. (1991). Transient plane source techniques for thermal conductivity and thermal diffusivity measurements of solid materials. *Review of Scientific Instruments, 62*, 797.

Holdsworth, S. D., & Simpson, R. (2016). Heat Penetration in Packaged Foods. In S. D. Holdsworth & R. Simpson (Eds.), *Thermal Processing of Packaged Foods* (pp. 161-195). Cham: Springer International Publishing.

Huang, L., & Liu, L.-S. (2009). Simultaneous determination of thermal conductivity and thermal diffusivity of food and agricultural materials using a transient plane-source method. *Journal of Food Engineering, 95*(1), 179-185. doi:https://doi.org/10.1016/j.jfoodeng.2009.04.024

Jha, A., Patel, A. A., Gopal, T. K. S., & Ravishankar, C. N. (2014). Heat penetration characteristics and physico-chemical properties of in-pouch processed dairy dessert (kheer). *Journal of Food Science and Technology, 51*(10), 2560-2567. doi:10.1007/s13197-012-0750-8

Kızıltaş, S., Erdoğdu, F., & Koray Palazoğlu, T. (2010). Simulation of heat transfer for solid–liquid food mixtures in cans and model validation under pasteurization conditions. *Journal of Food Engineering, 97*(4), 449-456. doi:https://doi.org/10.1016/j.jfoodeng.2009.10.042

Lebowitz Samuel, F., & Bhowmik Santi, R. (2006). Determination of Retortable Pouch Heat Transfer Coefficients by Optimization Method. *Journal of Food Science, 54*(6), 1407-1412. doi:10.1111/j.1365-2621.1989.tb05122.x

Mauricio, V.-R. J., & Francisco, S.-V. W. (2017). Modeling Heat Transfer During Blanching of Cubic Particles of Loche (Cucurbita moschata Duch.) and Potato (Solanum tuberosum L.) Using Finite Difference Method. *40*(3), e12451. doi:doi:10.1111/jfpe.12451

McGinnis, D. S. (1986). Prediction of Transient Conduction Heat Transfer in Foods Packaged in Flexible Retort Pouches. *Canadian Institute of Food Science and Technology Journal, 19*(4), 148-157. doi:https://doi.org/10.1016/S0315-5463(86)71622-2

Mishra, D. K., Dolan, K. D., Beck, J. V., & Ozadali, F. (2016). A novel instrument for rapid measurement of temperature-dependent thermal properties of conduction-heated food up to 140 °C. *Journal of Food Engineering, 191*, 19-27. doi:10.1016/j.jfoodeng.2016.06.028

Mishra, D. K., & Sinha, N. K. (2011). Principles of Vegetable Canning. In N. K.Sinha (Ed.), *Handbook of Vegetables and Vegetables Processing* (pp. 243-257). Hoboken, NJ: Wiley-Blackwell.

Murakami, E. G., & Okos, M. R. (1989). Measurement and Prediction of Thermal Properties of Foods. In R. P. Singh & A. G. Medina (Eds.), *Food Properties and Computer-Aided Engineering of Food Processing Systems* (pp. 3-48). Dordrecht: Springer Netherlands.

Naveh, D., Kopelman, I. J., Zechman, L., & Pflug, I. J. (1983). TRANSIENT COOLING OF CONDUCTION HEATING PRODUCTS DURING STERILIZATION: TEMPERATURE HISTORIES. *Journal of Food Processing and Preservation, 7*(4), 259-274. doi:10.1111/j.1745-4549.1983.tb00827.x

Patashnik, M. (1953). A simplified procedure for thermal process evaluation. *Food Technology, 7*(1), 1-6.

Pham, Q. T., & Willix, J. (1989). Thermal Conductivity of Fresh Lamb Meat, Offals and Fat in the Range -40 to +30oC: Measurements and Correlations. *54*(3), 508-515. doi:doi:10.1111/j.1365-2621.1989.tb04639.x

Rodríguez, R. D. P., Martínez, A., Rodrigo, M., & Safón, J. (1996). Numerical method for prediction of final microbial load in inoculated cylindrical cans of tomato concentrate heated in a pilot plant. *31*(6), 489-496. doi:doi:10.1046/j.1365-2621.1996.00367.x

Sahin, S., & Sumnu, S. G. (2006). Thermal Properties of Foods. In *Physical Properties of Foods* (pp. 107-155). New York, NY: Springer New York.

Sweat, V. E. (1974). EXPERIMENTAL VALUES OF THERMAL CONDUCTIVITY OF SELECTED FRUITS AND VEGETABLES. *Journal of Food Science, 39*(6), 1080-1083. doi:10.1111/j.1365-2621.1974.tb07323.x

Thompson, L., & Tanner, F. W. (1925). Toxin Production by Clostridium botulinum in Canned Foods. *The Journal of Infectious Diseases, 37*(4), 344-352.

Wang, N., & Brennan, J. G. (1992). Thermal conductivity of potato as a function of moisture content. *Journal of Food Engineering, 17*(2), 153-160. doi:https://doi.org/10.1016/0260-8774(92)90058-E

Willix, J., Lovatt, S. J., & Amos, N. D. (1998). Additional thermal conductivity values of foods measured by a guarded hot plate. *Journal of Food Engineering, 37*(2), 159-174. doi:https://doi.org/10.1016/S0260-8774(98)00086-7

Yuksel, N. (2016). The Review of Some Commonly Used Methods and Techniques to Measure the Thermal Conductivity on Insulation Materials. In A. Almusaed & A. Almssad (Eds.), *Insulation Materials in Contest of Sustainability* (pp. 113-140): IntechOpen.

CHAPTER 2. TEMPERATURE-DEPENDENT THERMAL PROPERTIES FOR THERMAL PROCESS SIMULATION

2.1 Abstract

Mathematical modeling of heat transfer is a common method utilized in designing thermal processes for food, modeling degradation kinetics of microorganisms and nutrients, as well as for designing food processing equipment. Hence, it is essential to have all the necessary components including the geometry, boundary conditions, initial temperature and the temperature-dependent thermal properties. While other components can be obtained easily, getting temperature-dependent thermal properties of food product is often the restraining step due to lack of devices and time-consuming techniques. To show the influence of temperature-dependent thermal properties, retort processing of potato soup and 1.5% (w/w) CMC was simulated using both temperature-dependent (dynamic) and fixed thermal properties. Three methods were used to determine the thermal conductivity values; TPCell, Choi-Okos predictive model and KD2 Pro at 25°C and 120°C for comparison. The proximate composition of the sample was also determined for prediction of thermal properties with Choi-Okos model (Choi & Okos, 1986). The accuracy of simulation was evaluated based on the temperature at cold spot and corresponding lethality value. Overall, using temperature-dependent thermal properties in heat transfer models increased the accuracy of simulation. Though thermal properties obtained from all three methods were similar, simulation performed with temperature-dependent properties obtained from TPCell matched very closely with experimental data. Using lethality value as a benchmark for comparison provides more accuracy due to higher sensitivity than comparing the cold spot temperature alone. The

technique described can be used for any thermal processes in the food industry including pasteurization, retort and aseptic processing.

2.2 Introduction

Simulation of heat transfer plays a crucial role when it comes to designing thermal processes of food products and modelling of microbial and/or nutrient degradation kinetics. This requires inputs of the temperature-dependent thermal properties, besides the geometry, boundary conditions and initial temperature of the product (McGinnis, 1986; Mishra & Sinha, 2011). Thermal properties, such as thermal conductivity, specific heat capacity and density changes with temperature. Since thermal properties are temperature-dependent, it is important to include thermal properties at more than one temperature in the simulation. However, adding temperature-dependent thermal properties to simulation becomes the limiting step due to lack of devices in the market that is designed to measure thermal properties of food, especially at temperatures above 100 °C. Hence, it is important to have effective and efficient determination of food thermal properties at multiple temperatures for successful thermal process simulation and modeling of heat transfer.

Thermal conductivity (k) is defined as the ability of a material to conduct heat which is a coefficient that quantifies the rate of heat transfer (dQ/dt) along the direction of a temperature gradient (dT/dx), governed by Fourier's law of heat conduction as shown in Eq 2.1. Specific heat (C_P) is the amount of heat required to raise the temperature of unit mass of the material by a unit degree. Thermal diffusivity (α) is the ability of a material to store thermal energy during heat transfer. All these thermal properties are related to each other and their relationship is shown in

Eq. 2.2, where thermal diffusivity is the ratio of thermal conductivity to the volumetric heat capacity.

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

$$\alpha = \frac{k}{\rho C_P} \tag{2.2}$$

Determination of specific heat capacity can be done easily using a Differential Scanning Calorimetry (DSC) and it is only dependent on the composition and temperature of the food product (Sweat, 1974). Unlike specific heat capacity, estimating thermal conductivity is more difficult because it depends on a number of factors; density, temperature and composition of food. Predictive models based on the composition of food to estimate the temperature-dependent thermal properties up to 150 °C are available (Choi & Okos, 1986). Mass fraction of water, carbohydrates, proteins, fat, fiber and ash is needed to use the compositional model came up by Choi-Okos (Eq. 3-10).

Measurements of thermal conductivity can be done in steady-state or in transient-state. During steady-state measurements, food materials are let to equilibrate with desired temperature before thermal conductivity is measured using a thermal conductivity probe. A steady-state condition is reached when the temperature at each point of the sample is constant which is easy when the measurements are done at room temperature. At elevated temperatures, the food materials may take up to 12 h, depending on the samples, to equilibrate with the target temperature (Murakami & Okos, 1989). Since food matrix is complex, it is impossible to reach constant temperature at every point in the sample. Prolonged heating at elevated temperature causes significant thermal damages leading to destruction of the product. Some of the undesirable reactions include Maillard browning, oxidation, color degradation, nutrient degradation, loss of moisture and loss of texture. Since the composition of the food has changed, any measurements taken may not reflect the actual thermal properties. This makes the steady-state measurements are not suitable for food products, especially at high temperatures.

Transient techniques are preferred methodology for measurements of food thermal conductivity. The measurements can be done quickly without the need to equilibrate sample to target temperature which significantly reduces decomposition of sample matrix. Transient line-source (TLS) is one of the commonly used technique for measuring thermal conductivity of food materials (E. Sweat & G. Haugh, 1974). The commercial unit that utilizes TLS principles is KD2 Pro by Decagon, Inc. KD2 Pro is a handheld device that has a probe with sensor at the tip. After equilibrating the probe with the sample temperature, it raises the sample temperature slightly and estimates the thermal conductivity based on the time-temperature slope.

TPCell is a new device that is capable of measuring temperature-dependent thermal properties of food products using non-isothermal heating in less than a minute (Mishra, Dolan, Beck, & Ozadali, 2016). The operating range was reported as 20-140 °C which can be reached with the help of a resistance heater and pressure. In a cylindrical sample holder, the sample is heated with a cartridge heater in the middle where the temperature of the heater during the experiment is then used to determine the thermal conductivity using sequential parameter estimation based on 2D transient heat conduction.

While different methods of obtaining thermal properties may yield slightly different result with their respective margin of error, it is important to select techniques that can match closely with real values when it comes to predicting food product temperatures. Simulation of heat transfer to determine the thermal processing parameter conditions should be done accurately. We hypothesize that utilizing temperature-dependent thermal properties in simulation can improve the accuracy of simulation. Three different methods were used to obtain thermal conductivity and were compared to determine the best method that is able to provide values that enables the simulation to match closely with experimental data. Using the thermal properties, multiple values vs single values were fitted to prediction model to compare the accuracy of simulation. Retort processing was chosen to demonstrate the application, but any thermal process can be used to elucidate the importance of using temperature-dependent thermal properties.

2.3 Materials and Methods

2.3.1 Materials

Carboxymethyl cellulose (Pre-hydrated® Ticalose® CMC 2500) was obtained from TIC gums. 1.5% (w/w) carboxymethyl cellulose (CMC) was used for all the experiments. Potato soup was prepared using the ingredients and formulation shown in Table 2.1. The materials chosen for this study was based on their viscosity. Only food product with high viscosity was chosen so the heat conduction is primarily governed by conduction. When low viscosity food materials are used, increased in the heater temperature induces natural convection in samples which leads to unrealistically high values of thermal conductivities (Huang & Liu, 2009).

Table 2.1 Potato soup formulation

Ingredients	Percentage (%)
heavy cream	39.6
whole milk	0.0
potato flakes	9.3
chicken broth	40.3
butter	7.7
onion powder	1.1
pepper	0.4
salt	1.6
Total	100

2.3.2 Methods

2.3.2.1 Proximate Analysis

Moisture content of the samples was determined using air-drying method using a forced convection oven at 60°C for 72 hours. Samples were cooled in a desiccator before weighing. The moisture content was calculated based on weight loss of sample (Eq. 2.3)

$$\%\ Moisture = \frac{Wt\ of\ sample{+}pan_{before} - Wt\ of\ sample{+}pan_{after}}{Wt\ of\ sample{+}pan_{before} - Wt\ of\ pan} \times 100\% \qquad (2.3)$$

Ash analysis was performed according to AOAC 940.46(b). After samples were dehydrated in a forced convection oven at 100°C for 12 hours, about 5g of samples were transferred to crucibles.

They samples were incinerated in a muffle furnace at 550°C overnight. The ash remaining in the crucibles was measured and determined as the ash content according to Eq. 2.4.

$$\% \, Ash = \frac{Wt \; of \; sample + crucible_{before} - Wt \; of \; sample + crucible_{after}}{Wt \; of \; sample + crucible_{before} - Wt \; of \; crucible} \times 100\% \tag{2.4}$$

Protein analysis was performed using the Dumas method using LECO Trumac N (St. Joseph, MI) according to AOAC Official Method of Analysis 992.32 (AOAC International, 2007). About 1-2 g of potato soup sample was loaded onto the instrument and analyzed for nitrogen (%) content. The sample were combusted at 1100°C with a flow of pure oxygen. N_2 and nitrogen oxides were produced from nitrogen-containing compounds, where nitrogen oxide is then reduced to nitrogen using a copper column. The total nitrogen released is then carried by helium to be quantified by gas chromatography coupled with a thermal conductivity detector. A conversion factor of 6.25 was used to calculate protein content (%) (Eq. 2.5). Ethylenediamine tetraacetic acid (EDTA) was used as the standard to calibrate the instrument.

$$\% \, Protein = \% \, Nitrogen \times 6.25 \tag{2.5}$$

Total fat content was determined using Soxhlet semi-continuous extraction method according to AOCS Official Method Am 5-04. Samples were dried in a forced convection oven at 100°C for 12 hours. 5-6 g of dried samples were placed on thimble with glass wool. Soxhlet extraction was performed with petroleum ether for 6-8 h with a rate of 3-4 drops per second condensation. Total fat (%) was by quantifying weight loss of sample as shown in Eq. 2.6.

$$\% \, fat = \frac{Wt \; of \; sample + thimble + glass \; wool_{before} - Wt \; of \; sample + thimble + glass \; wool_{after}}{Wt \; of \; sample + thimble - Wt \; of \; thimble} \times 100\% \tag{2.6}$$

Carbohydrate content was calculated by subtracting percentage of moisture, ash, fat and protein from 100% as shown in Eq. 2.7.

$$\% \, Carbohydrate = 100 - (\% \, moisture + \% \, ash + \% \, fat + \% \, protein) \quad (2.7)$$

2.3.2.2 Thermal Conductivity

TPCell

Thermal conductivity of the samples was measured using TPCell as described previously with slight modification (Mishra et al., 2016). 275 mL sample was loaded into the sample holder. The sample holder was sealed and pressurized up to 60 psig. The cartridge heater was supplied with 20W power to start the experiment. Once the temperature of the heater reached 140°C, the relay system cut the power supply off to stop the experiment. The resistance of the heater was converted to temperature using a calibration equation, T= 25.381R-12295. Based on the temperature profile, the thermal conductivity was determined using sequential estimation. The sequential estimation procedure was developed in Matlab® using the matrix inversion lemma (Beck & Arnold, 1977) based on the Gauss minimization method and requires prior information. The initial k_1 and k_2, values used are 0.52 and 0.62, respectively. The specific heat (C_p) and density (ρ) values used were obtained experimentally as described below. The sequential parameter estimation for k_1 and k_2 keeps changing as each datum is added and ends when the value becomes constant. k_1 and k_2 are thermal conductivities at 25°C and 120°C, respectively. Triplicate analysis was done for each sample.

KD2 Pro

KD2 Pro was used to determine the thermal conductivity at 20, 40, 60 and 80°C. This unit utilizes TLS method for thermal conductivity determination. Samples were placed in a cylindrical samples holder that was submerged in a water bath set at the temperatures mentioned above. Once the center of sample achieved equilibrium with the bath temperature, KS-1 sensor was used to determine the thermal conductivity. Triplicate analysis was done for each sample at each temperature.

Choi-Okos Predictive Model

Thermal conductivity was estimated based on the proximate composition of the food samples. Once the proximate composition is determined, the fraction was fitted into Eq. 2.8 to 14 and the thermal conductivity of each component is added to get the thermal conductivity of the food product.

$$k_{water} = 5.7109 \times 10^{-1} + 1.7625 \times 10^{-3}T - 6.7036 \times 10^{-6}T^2 \quad (2.8)$$

$$k_{carbohydrate} = 2.0141 \times 10^{-1} + 1.3874 \times 10^{-3}T - 4.3312 \times 10^{-6}T^2 \quad (2.9)$$

$$k_{protein} = 1.7881 \times 10^{-1} + 1.1958 \times 10^{-3}T - 2.7178 \times 10^{-6}T^2 \quad (2.10)$$

$$k_{fat} = 1.8071 \times 10^{-1} - 2.7604 \times 10^{-4}T - 1.7749 \times 10^{-7}T^2 \quad (2.11)$$

$$k_{fiber} = 1.88331 \times 10^{-1} + 1.2497 \times 10^{-3}T - 3.1683 \times 10^{-6}T^2 \quad (2.12)$$

$$k_{ash} = 3.2962 \times 10^{-1} + 1.4011 \times 10^{-3}T - 2.9069 \times 10^{-6}T^2 \quad (2.12)$$

$$k_{ice} = 2.2196 - 6.2489 \times 10^{-3}T + 1.0154 \times 10^{-4}T^2 \quad (2.13)$$

$$k = \Sigma k_i X_{i,}. \quad (2.14)$$

2.3.2.3 Specific Heat Capacity

Specific heat capacity of the sample at 25°C and 120°C are obtained using Differential Scanning Calorimetry (DSC Discovery Series, TA instruments) as described previously (ASTM E 1269-11, 2011) and reported as C_{p1} and C_{p2}, respectively. Sample weight of 9-10 mg was loaded into Tzero pan that was sealed with hermetic lid and measured against an empty reference pan made of the same pan material. The heat capacity was measuring during non-isothermal heating from 5°C to 150°C with an increment of 10°C. The DSC was calibrated with a Sapphire standard. Triplicate measurements were taken for each sample. The specific heat obtained from DSC was used with thermal conductivity from TPCell and KD2 Pro for simulation of heat transfer.

Specific heat capacity was also calculated from Choi-Okos predictive model as listed below. Similar to thermal conductivity, this proximate composition was fitted into Eq. 2.15 to 2.20 to estimate the specific heat capacity of each component. Then the values of individual components were multiplied by their respective fraction and their sum was reported as the specific heat capacity of the sample (Eq.2.21). These values were used in simulation with thermal conductivity calculated from Choi-Okos prediction model above.

$$C_{p\,water} = 4.1762 - 9.0864 \times 10^{-5}T + 5.4731 \times 10^{-6}T^2 \quad (2.15)$$

$$C_{p\,carbohydrate} = 1.5488 + 1.9625 \times 10^{-3}T - 5.9399 \times 10^{-6}T^2 \quad (2.16)$$

$$C_{p\,protein} = 2.0082 + 1.2089 \times 10^{-3}T - 1.3129 \times 10^{-6}T^2 \quad (2.17)$$

$$C_{p\,fat} = 1.9842 + 1.4733 \times 10^{-3}T - 4.8008 \times 10^{-7}T^2 \quad (2.18)$$

$$C_{p\,fiber} = 1.8459 + 1.8306 \times 10^{-3}T - 4.6509 \times 10^{-6}T^2 \quad (2.19)$$

$$C_{p\,ash} = 1.0926 + 1.8896 \times 10^{-3}T - 3.7817 \times 10^{-6}T^2 \quad (2.20)$$

$$C_p = \Sigma C_{pi} X_{i,}. \quad (2.21)$$

2.3.2.4 Density

Density was determined by measuring the weight and volume of the samples in a graduated cylinder at room temperature and reported as g/m^3.

2.3.2.5 Heat Penetration Study for Retort Processing

Retort processing was accomplished by placing the sample in a sample holder that contained a thermocouple probe in the center. A surface thermocouple was also placed on the surface of the sample holder. The sample holder was pressurized to 30 psig and placed in silicone oil bath. Silicon oil bath was used as a means to provide high heat. The bath was set at 121.1 °C (250°F). The center and surface thermocouples were used to monitor temperature at the center and at the surface, respectively, using LabView (National Instruments, Austin, TX) as the data acquisition software. The software was programmed to simultaneously calculate the lethality as temperature was being recorded. Once the sample was placed in the oil bath, the experiment was performed until the center of the container achieved lethality of 6 min. The experiment was then terminated by removing the sample holder from the oil bath and cooling it below 100°C before releasing the pressure.

2.3.2.6 Simulation of Retort Processing

COMSOL, a finite element software, was used to simulate the heat distribution inside sample holder during retort processing. Simulations were performed using temperature-dependent thermal conductivity (k_1 and k_2) and specific heat (C_{p1} and C_{p2}) using Eq. (2.22) and (2.23), respectively. For simulations with fixed thermal properties only k_1 and C_{p1} were used. Simulations were performed using thermal properties obtained using different methods and were compared. Thermal conductivity values from TPCell and KD2 Pro were used with specific heat capacity obtained from DSC during simulation. For Choi-Okos method, both the thermal conductivity and specific heat capacity were estimated from predictive Eq. 2.8 through 2.14 and Eq. 2.15 through 2.21, respectively. The density values used in the simulation were experimentally determined as mentioned above.

$$k(T) = k_1\left(\frac{T2-T}{T2-T1}\right) + k_2\left(\frac{T-T1}{T2-T1}\right) \quad (2.22)$$

$$C_p(T) = C_{p1}\left(\frac{T2-T}{T2-T1}\right) + C_{p2}\left(\frac{T-T1}{T2-T1}\right) \quad (2.23)$$

2.3.2.7 Sterilization Values (Lethality)

The temperature profile at the center of the can from retorting experiment and simulation were used to calculate lethal rate, L (Ball, 1923) and lethality, F_0 (Patashnik, 1953) using the General method as shown in the Eq. (2.24) and (2.25), respectively. The simulation data were compared with the experimented data.

$$L = 10^{\left(1/z\right)(T-T_r)} \quad (2.24)$$

where L is the lethal rate, z is the temperature change required to reduce microbial by 1D where D-value is the time to reduce the microorganisms by tenfold and T_r is the reference temperature (121.1°C).

$$F_0 = \int_0^t 10^{\left(1/z\right)(T-T_r)} \quad (2.25)$$

2.3.2.8 Statistical Analysis

Statistical analysis was performed using SAS 9.4. Means were analyzed using ANOVA and significant difference between the means were determined using Tukey's test at α=0.05.

2.4 Results

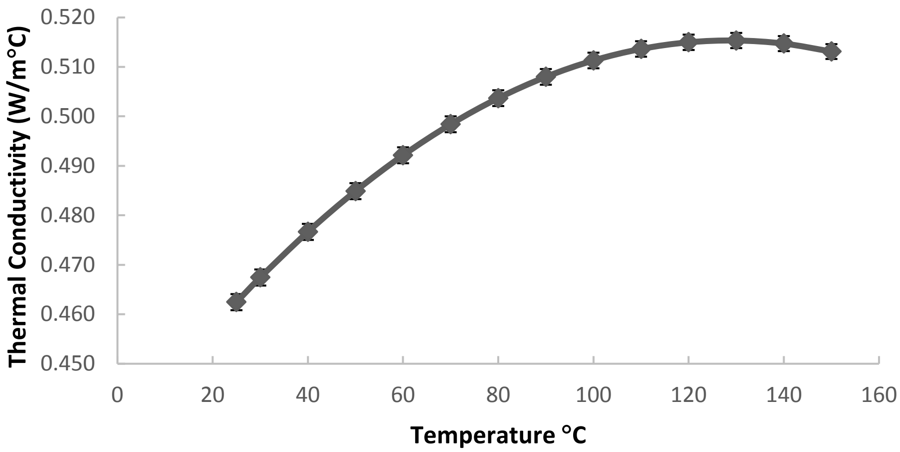
Table 2.2 Proximate composition and density of 1.5% (w/w) carboxymethyl cellulose (CMC) and potato soup

	1.5% (w/w) CMC	**Potato soup**
Moisture (%)	98.52 ± 0.01	63.84 ± 0.46
Protein (%)	0.00 ± 0.00	1.14 ± 0.04
Carbohydrate (%)	0.00 ± 0.00	12.58 ± 0.55
Fat (%)	0.00 ± 0.00	21.53 ± 0.12
Ash (%)	1.00 ± 0.00	0.90 ± 0.12
Fiber (%)	0.48 ± 0.01	ND
Density (g/cm^3)	1019 ± 10	1096 ± 25

Footnote: Values represents average of triplicate analysis ± standard deviation. ND= not determined.

Table 2.2 shows the proximate composition of 1.5% (w/w) CMC solution and potato soup. The CMC solution contains water and fiber. The major component of the potato soup is water, followed by fat and carbohydrates. The proximate compositions presented in Table 2.2 were used in estimating both thermal conductivities and specific heat capacity using Choi-Okos predictive equations. The density of 1.5% (w/w) CMC solution and potato soup is 1019 ± 10 and 1096 ± 25 g/cm^3 respectively as shown in Table 2.2.

a)



b)

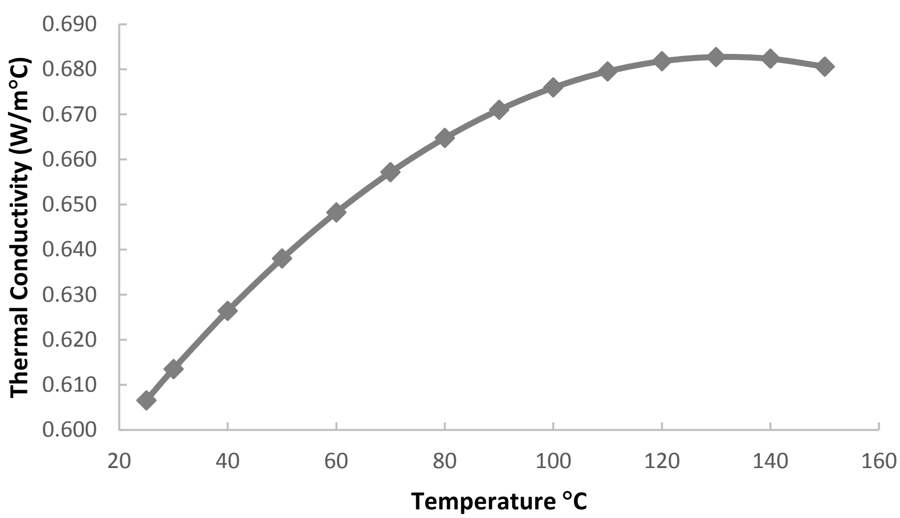


Figure 2.2 Thermal conductivity estimated based on Choi-Okos predictive model. a) Potato soup b) 1.5% (w/w) carboxymethyl cellulose (CMC).

Figure 2.1 shows the thermal conductivity of potato soup and 1.5% (w/w) CMC, estimated using Choi-Okos predictive model based on fractions of water, carbohydrate, protein, fat and ash. The estimation was done from 25°C to 150°C. These predictive models are good for estimation for temperatures from -40°C to 150°C, as claimed by the author (Choi & Okos, 1986). The thermal conductivity at 25°C and 120°C is estimated to be 0.462 ± 0.002 and 0.515 ± 0.001(W/m°C), respectively. These values are statistically different from each other. 1.5% (w/w) CMC has thermal conductivity values of 0.607 ± 0.000 and 0.682 ± 0.000 at 25°C and 120°C, respectively and found to be significantly different from each other. For CMC, Eq. 10 was used to quantify the proportion of CMC powder since CMC is considered as fiber instead of carbohydrate. As the temperature increases, the thermal conductivity of the potato soup and 1.5% (w/w) CMC seems to be increasing with a quadratic trend. It is important to note, CMC is homogenous product while potato soup has a very complex matrix. High fat content of the potato soup, about 22% (Table 2.1) caused lower thermal conductivity value, compared to 1.5%(w/w) CMC. From Figure 2.2 it is clear that fat decreases the thermal conductivity values. Negative impact of fat content on thermal conductivity was also seen in another study that investigated meat and poultry products (Marcotte, Taherian, & Karimi, 2008). Figure 2.2 also reveals that presence of water is a significant factor and is the main factor influencing the thermal conductivity of a sample. The potato soup and 1.5% (w/w) CMC has 63.84% and 98.52% of water, respectively and water is the major composition in both these samples. Similar observation was reported previously (E. Sweat & G. Haugh, 1974; Marcotte et al., 2008). Positive trend with increasing water but negative trend with increasing fat content was reported as well (Tavman & Tavman, 1999).

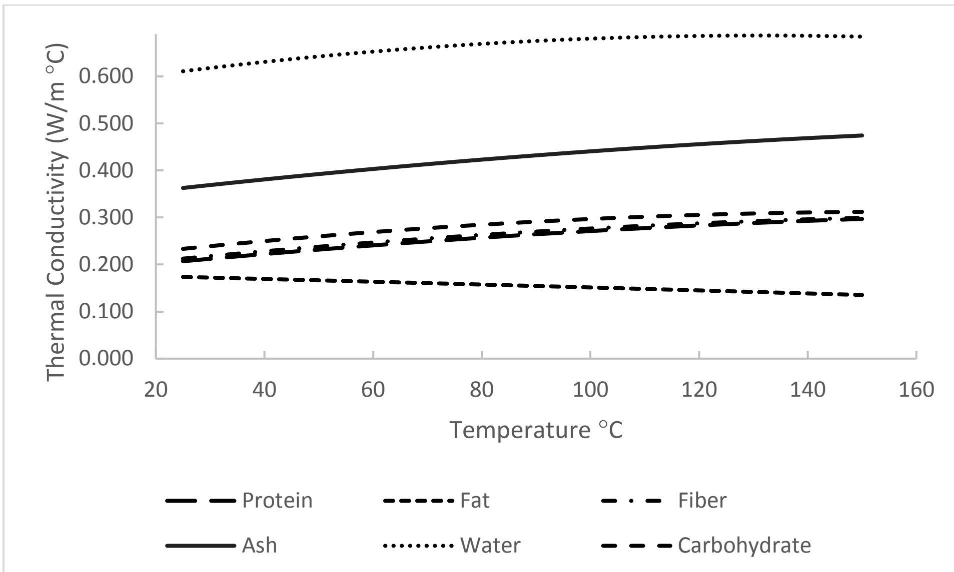


Figure 2.3 Thermal conductivity of each proximate composition calculated based on Choi-Okos predictive model (Eq. 2.8-2.14).

Table 2.3 Thermal conductivity of potato soup and 1.5% (w/w) carboxymethyl cellulose (CMC) determined by KD2 Pro

Temperature (°C)	Potato Soup	1.5% CMC
25	0.422[a] ± 0.002	0.575[a] ± 0.001
40	0.250[b] ± 0.009	0.596[ab] ± 0.019
60	0.248[b] ± 0.000	0.635[ab] ± 0.019
80	0.249[b] ± 0.001	0.611[b] ± 0.024

Footnote: Values represents average of triplicate analysis ± standard deviation. Values with same letter in the same columns are not significantly different at α=0.05.

Table 2.4 Thermal conductivity of potato soup and 1.5% (w/w) carboxymethyl cellulose (CMC) determined using TPCell

Temperature (°C)	Potato Soup	1.5% CMC
25	0.467[a] ± 0.014	0.627[a] ± 0.012
120	0.456[a] ± 0.012	0.666[b] ± 0.004

Footnote: Values represents average of triplicate analysis ± standard deviation. Values with same letter in the same columns are not significantly different at α=0.05.

Table 2.3 shows the thermal conductivity of potato soup and 1.5% (w/w) CMC determined using KD2 Pro. The measurements were only taken up to 80°C because it was quite difficult to keep the temperature of the sample equilibrated at high temperatures. A previous study has reported failure of sensors when used at high temperatures (Mishra et al., 2016). Literature value of thermal conductivity at 20°C for mashed potato is 0.59 W/m°C and is measured with KD2-Pro device using TR-1 sensor (Chen et al., 2013). This value is slightly higher than that potato soup value reported here probably due to presence of high fat content. It is well known that presence of fat decreases thermal conductivity (Choi & Okos, 1986; Marcotte et al., 2008). The thermal conductivity values obtained for potato soup at high temperatures (40, 60, 80°C) show significantly low values around 0.25 W/m°C. At high temperatures, the lipids in the soup were separated from the matrix and the sensor may have measured the separated components instead of the product as a whole. As mentioned above, potato soup has complex matrix due to the number and the kind of ingredients used in the recipe. In addition, the sample had to equilibrate with the bath temperature before the measurement could be taken. Though the actual measurement may only takes less than 2 min, the time to increase the temperature of the sample for each temperature takes about 2 h per every step change. This could have caused severe destruction of the sample, including separation issues.

Thermal conductivity value of potato soup measured with TPCell at 25°C and 120°C was 0.456 and 0.466 W/m°C. These values are not statistically different from each other as expected. As explained above, as temperature increases, the thermal conductivity of high fat containing food products starts to decrease at some point (Figure 2.2), which is why no statistically significance was found between thermal conductivity of potato soup at different temperatures. Separation issue seen with KD2 Pro method did not happen in TPCell since the measurements were taken much faster without having to equilibrate the sample to target temperature.

Table 2.5 Specific heat capacity of potato soup determined using differential scanning calorimetry (DSC) and Choi-Okos predictive model

Temperature (°C)	Specific Heat Capacity (J/g°C)	
	Differential Scanning Calorimetry (DSC)	Choi-Okos
25	3.307[a] ± 0.262	3.336[a] ± 0.013
120	3.758[a]± 0.486	3.410[a] ± 0.013

Footnote: Values represents average of triplicate analysis ± standard deviation. Values with same letter in the same rows are not significantly different at α=0.05.

Table 2.5 shows the specific heat capacity of potato soups measured using differential scanning calorimetry (DSC) and Choi-Okos predictive model at 25°C and 120°C. No significant difference was found between either method at both temperatures (*p-value* < 0.05). Similarly, Table 2.6 shows the specific heat capacity of 1.5% (w/w) CMC measured with DSC and predicted with Choi-Okos compositional based model at both 25°C and 120°C. Just like potato soup, specific heat capacity of 1.5% (w/w) CMC from both methods are not significantly different at both temperatures. Literature value of specific heat capacity of 1.5% (w/w) CMC is 4.21 (J/g°C) at 20°C (Semmar, Tanguier, & Rigo, 2004), which is very close to the values reported here. These values are also very close to the specific heat capacity of water (4.186 J/g°C) since the major composition of 1.5% (w/w) CMC is water (Choi & Okos, 1986).

Table 2.6 Specific heat capacity of 1.5% (w/w) carboxymethyl cellulose determined using differential scanning calorimetry (DSC) and Choi-Okos predictive model

Temperature (°C)	Specific Heat Capacity (J/g°C)	
	Differential Scanning Calorimetry (DSC)	Choi-Okos
25	$4.051^{a} \pm 0.059$	$4.136^{a} \pm 0.011$
120	$4.154^{a} \pm 0.183$	$4.204^{a} \pm 0.011$

Footnote: Values represents average of triplicate analysis ± standard deviation. Values with same letter in the same rows are not significantly different at α=0.05.

Both the potato soup and 1.5% (w/w) CMC were subjected to a heat penetration test using retort processing conditions. The heat penetration data was compared to simulated temperature profiles. The simulation was performed using thermal properties of the sample, boundary conditions and initial temperature from the heat penetration study. The simulation was performed to compare the accuracy of different methods of measuring thermal properties, specifically thermal conductivity. For simulations of temperature-time profiles, specific heat capacity values obtained from DSC were used with thermal conductivities from TPCell and KD2 Pro whereas specific heat capacity and thermal conductivity obtained from Choi-Okos predictive models were used together. Density of the potato soup, 1096 g/cm^3 was used for all three simulations. The accuracy of simulation was evaluated for comparison of temperature-dependent thermal properties (dynamic) and fixed properties (static). Since the thermal conductivity value at 120°C was not obtained with KD2 Pro, the simulation was performed using thermal properties at room temperature only. The simulated profile of center temperatures of potato soup using three different methods are presented in Figure 2.3, Figure 2.4 and Figure 2.5. The simulated profile was compared with the heat penetration data. For both TPCell (Figure 2.3) and Choi-Okos (Figure 2.4), the simulated temperature matched closely to heat penetration data for both dynamic and fixed thermal properties. For KD2 Pro (Figure 2.5), only the temperature profile simulated from static thermal properties matched closely. Visually, all simulated profile, regardless of the techniques or the type (static vs dynamic) of thermal conductivity, matched closely with the heat penetration data with no obvious concerns.

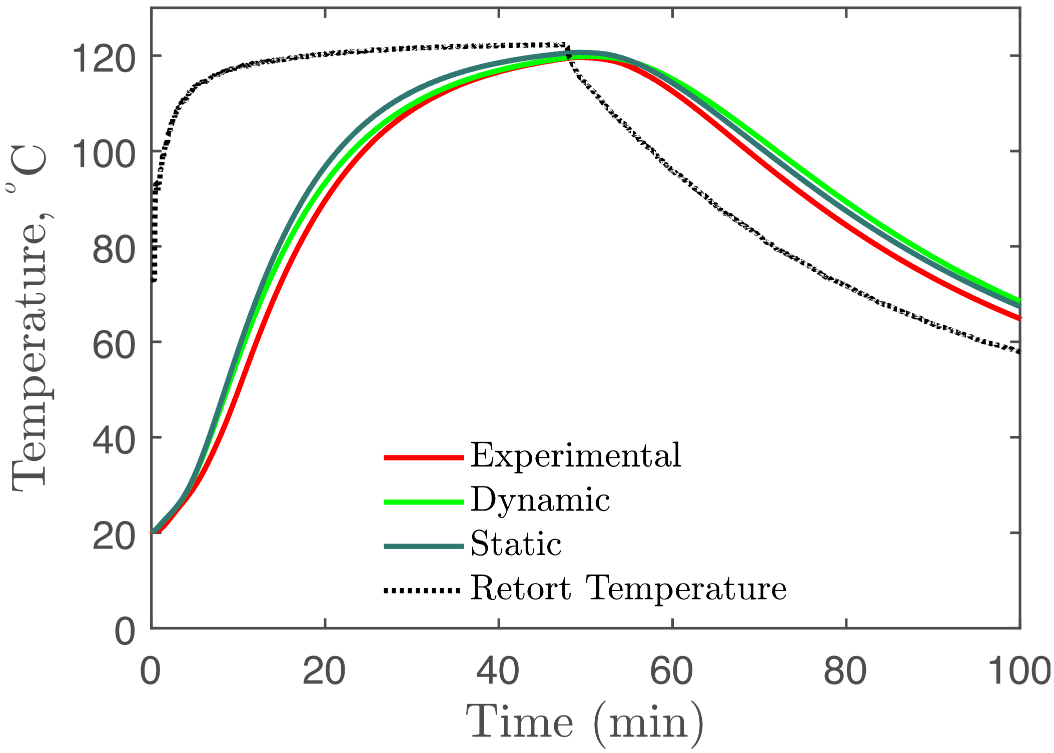


Figure 2.4 Experimental and predicted cold spot temperature of potato soup using thermal properties estimated using TPCell.

Footnote: Dynamic indicates use of temperature-dependent thermal properties and static represents use of fixed thermal properties at room temperature.

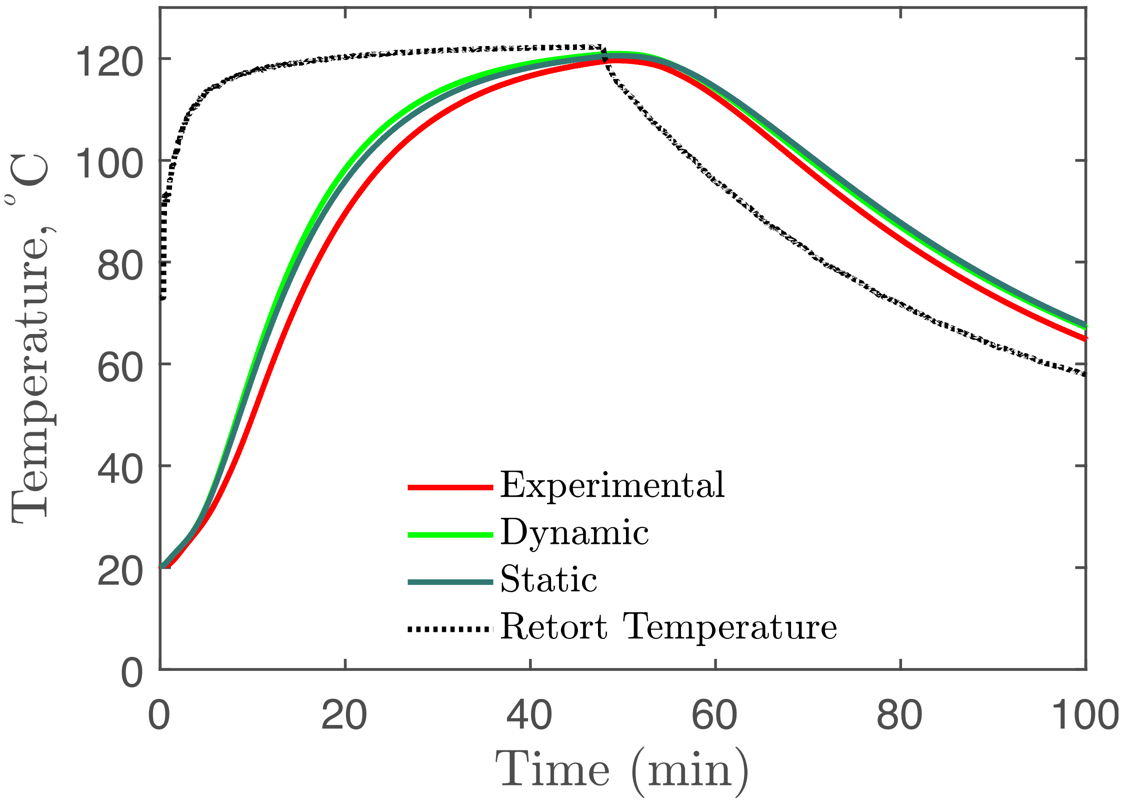


Figure 2.5 Experimental and predicted cold spot temperature of potato soup using thermal properties estimated using Choi-Okos predictive model.

Footnote: Dynamic indicates use of temperature-dependent thermal properties and static represents use of fixed thermal properties at room temperature.

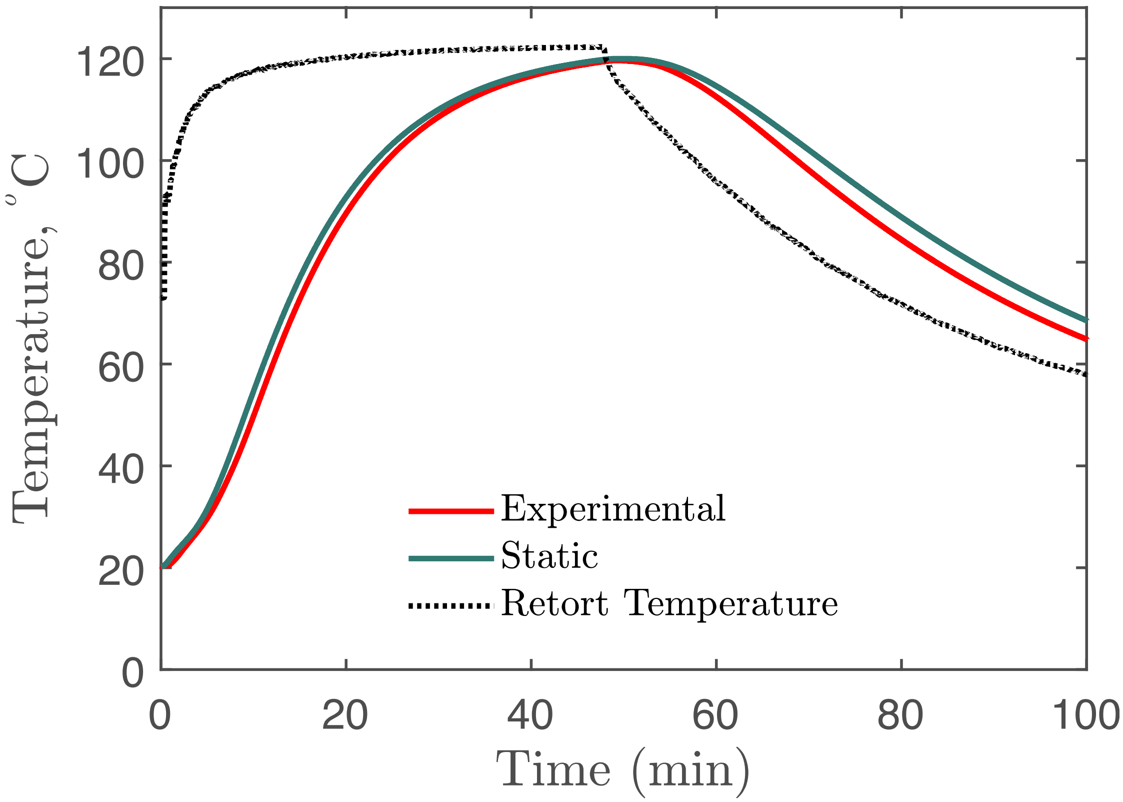


Figure 2.6 Experimental and predicted cold spot temperature of potato soup using thermal properties estimated using KD2 Pro.

Footnote: Static represents use of fixed thermal properties at room temperature. Temperature-dependent thermal properties were not used in simulation due to inaccurate thermal conductivity value at high temperatures.

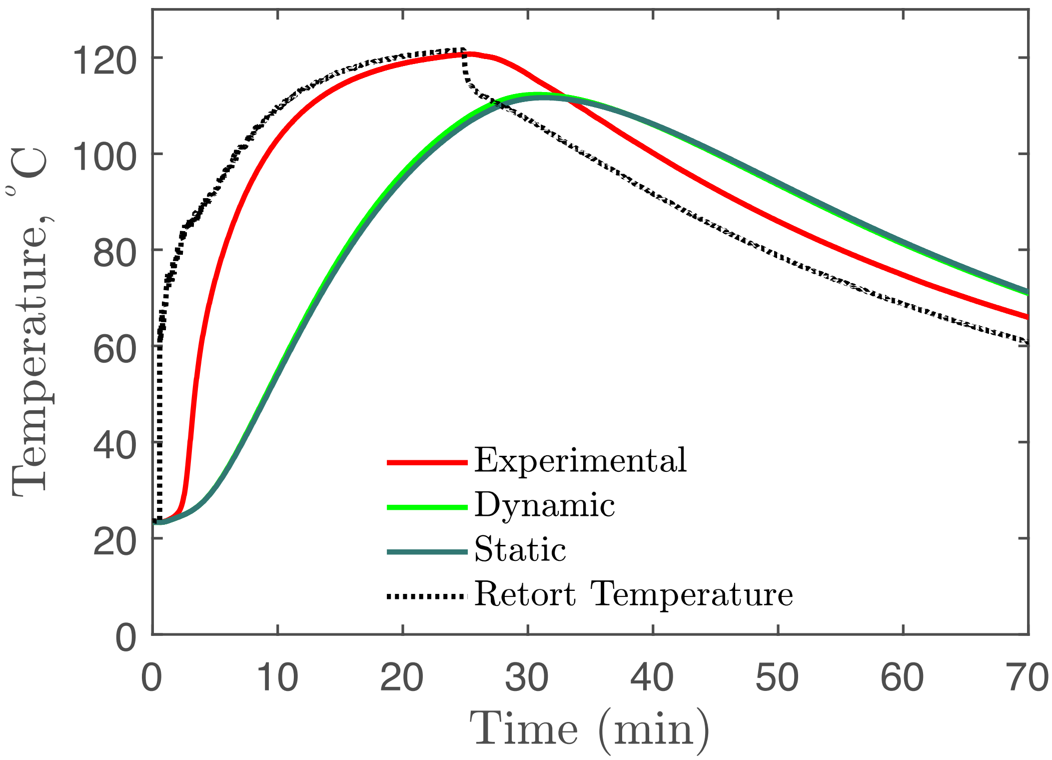


Figure 2.7 Experimental and predicted cold spot temperature of 1.5% (w/w) CMC using thermal properties estimated using TPCell.
Footnote: Dynamic indicates use of temperature-dependent thermal properties and static represents use of fixed thermal properties at room temperature.

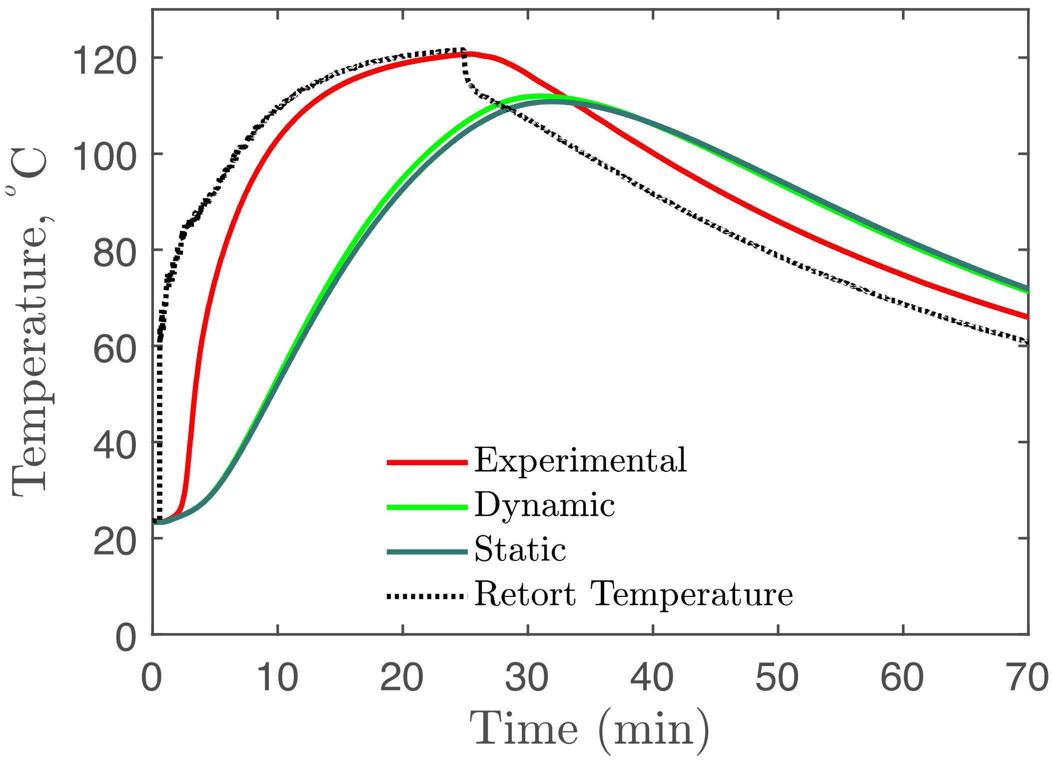


Figure 2.8 Experimental and predicted cold spot temperature of 1.5% (w/w) CMC using thermal properties estimated using Choi-Okos predictive model.

Footnote: Dynamic indicates use of temperature-dependent thermal properties and static represents use of fixed thermal properties at room temperature.

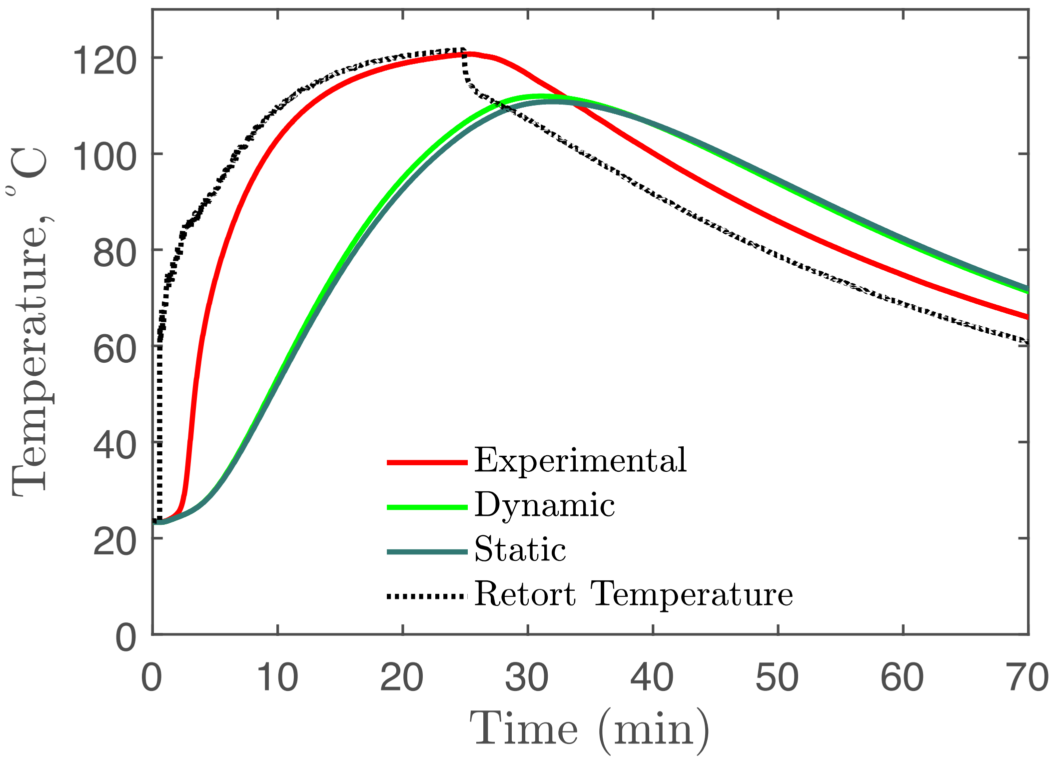


Figure 2.9 Experimental and predicted cold spot temperature of 1.5% (w/w) CMC using thermal properties estimated using KD2 Pro.

Footnote: Static represents use of fixed thermal properties at room temperature. Temperature-dependent thermal properties were not used in simulation due to inaccurate thermal conductivity value at high temperatures.

For 1.5% (w/w) CMC, simulation of heat transfer did not match the experimental data for all three methods as shown in Figure 2.6, Figure 2.7 and Figure 2.8 for TPCell, Choi-Okos model and KD2 Pro, respectively. The degree of deviation was large and that this is not a result of inaccurate thermal properties. It is possible for natural convection to happen in CMC sample, especially at high temperatures. Such convection typically changes the location of cold spot from center of the cylindrical sample holder to the bottom (Mishra & Sinha, 2011). The experiment was only set to investigate conductive heat transfer using modeling. With the conduction model it was not possible to get estimation that matches closely with heat penetration data. Since, there was a possibility for the change of cold spot location, the heat penetration data for 1.5% (w/w) was not reliable as well. Further analysis on CMC samples was discontinued for these reasons.

Based on the simulated temperature profile of the cold spot, time to reach minimum lethality of 6 min for potato soup was calculated and the results were summarized in Table 2.7. The predicted and simulated lethality plot for potato soup is shown in Figure 2.9, Figure 2.10 and Figure 2.11 for estimation using thermal properties from TPCell, Choi-Okos and KD2 Pro, respectively. Time taken to reach minimum lethality is a critical cut-off point that decides if a thermal process is sufficient. Based on information presented on Table 2.7, the order of estimation that is close to the experimental value was TPCell dynamic > KD2 Pro > Choi-Okos static > TPCell static > Choi-Okos dynamic. For TPCell, the results suggest that using temperature-dependent properties resulted in more accurate simulation, judging from the time taken to reach minimum lethality. However, such trend was not seen with simulation obtained for thermal properties estimated with Choi-Okos predictive models. It is important to note that different sets of specific heat capacity were used to estimate the time to reach minimum lethality for Choi-Okos methodology.

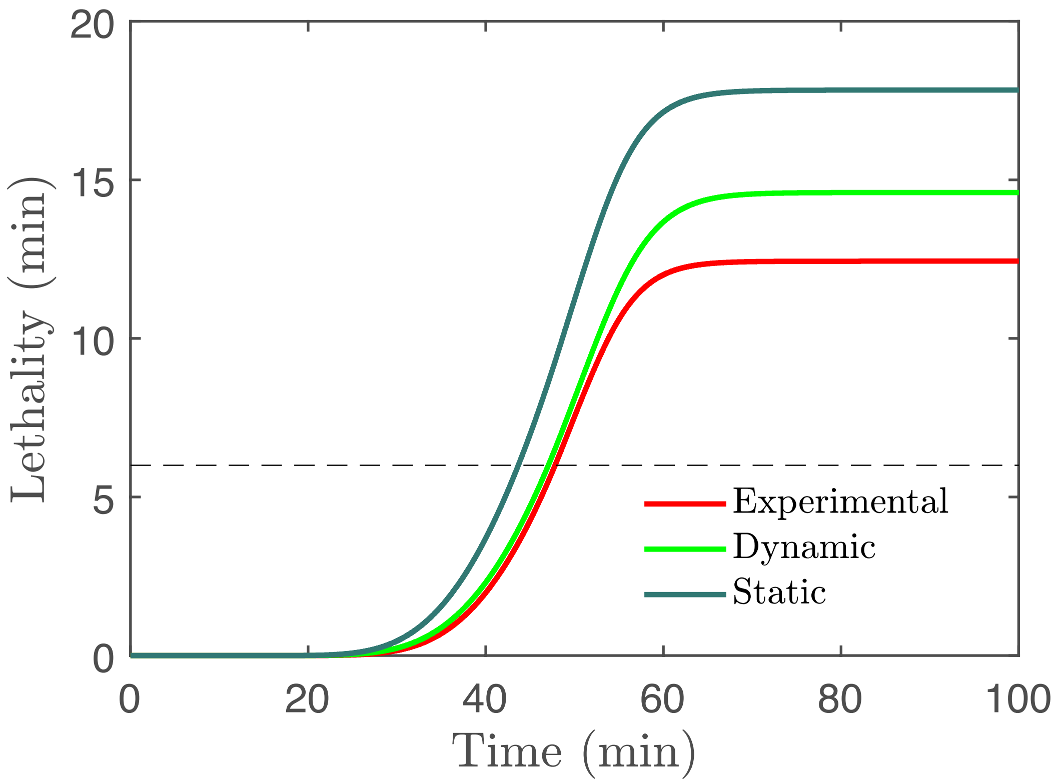


Figure 2.10 Experimental and predicted lethality of potato soup using thermal properties estimated using TPCell.

Footnote: Dynamic indicates use of temperature-dependent thermal properties and static represents use of fixed thermal properties at room temperature

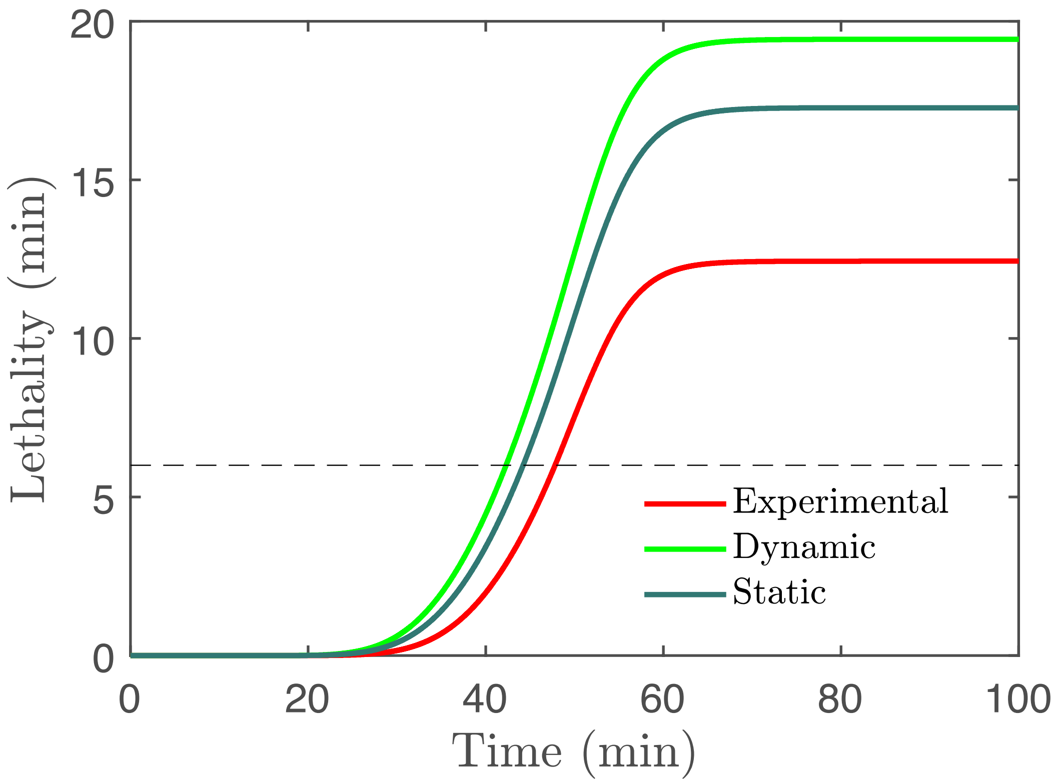


Figure 2.11 Experimental and predicted lethality of potato soup using thermal properties estimated using Choi-Okos predictive model.

Footnote: Dynamic indicates use of temperature-dependent thermal properties and static represents use of fixed thermal properties at room temperature.

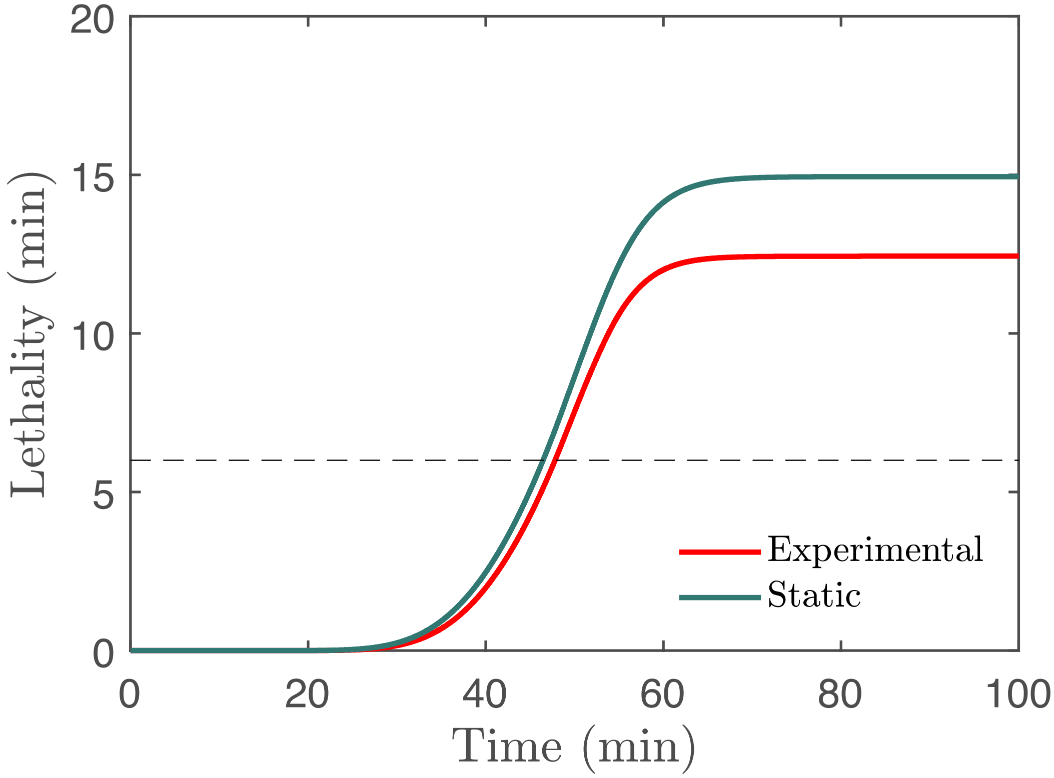


Figure 2.12 Experimental and predicted lethality of potato soup using thermal properties estimated with KD2 Pro.

Footnote: Static represents use of fixed thermal properties at room temperature. Temperature-dependent thermal properties were not used in simulation due to inaccurate thermal conductivity value at high temperatures.

From the heat penetration test, it is clear that processing time needed for potato soup heated at 121.12°C with 30 psig is 48.46 min to achieve a minimum lethality of 6 min. If a process is designed to take time less than 48.46 min, it will undercook the product which can lead to risk of foodborne illness. Even the smallest deviation from established process can result in severe consequences. Based on the results presented in Table 2.1, it is obvious that the simulation that matches the experimental heat penetration data came from thermal properties determined from TPCell and DSC. The accuracy of simulation was significantly improved when temperature-dependent (dynamic) thermal properties were used instead of fixed values.

Table 2.7 Time to reach minimum lethality (F_0=6 min) for experimental and simulated center temperature using fixed and dynamic thermal properties

Method		Time to reach lethality (min)
Experimental		$48.46^{a} \pm 1.26$
TP Cell	Dynamic	$47.19^{a} \pm 0.57$
	Static	$43.75^{bc} \pm 0.48$
Choi-Okos	Dynamic	$42.32^{c} \pm 0.44$
	Static	$44.31^{b} \pm 0.50$
KD2 Pro		$46.61^{a} \pm 0.58$

Footnote: Values represents average of triplicate analysis ± standard deviation. Values with same letter in the same columns are not significantly different at α=0.05.

2.5 Discussions

Current study focused on evaluating three different methods of obtaining thermal properties, thermal conductivity to be specific. Compared to specific heat capacity and density, changes in thermal conductivity and diffusivity are much sensitive to changes in the temperature (Marcotte et al., 2008). The thermal properties of food changes with temperature. KD2 Pro device which utilizes “Transient Line Source” principle was not able to provide reliable thermal conductivity values of potato soup at high temperatures. Though the measurements were done non-isothermally based on TLS principles, the samples still needed to be equilibrated at test temperature prior to measurement which was not only time consuming but severely degraded the samples. Many adverse reactions happen at this condition including moisture loss, separation of lipid and moisture, formation of unwanted compounds and degradation of nutrient and sensory quality attributes. Many studies have reported the accuracy of KD2 Pro device and TLS method for thermal conductivity determination (Kou et al., 2018; Zielinska, Ropelewska, & Markowski, 2017). These studies were mostly done at room temperature. KD2 Pro device is very reliable for measurements done at room temperature since the temperature equilibration time is very minimal. Multiple measurements are needed if thermal properties at more than one temperature is needed which further increases the analysis time.

TPCell and Choi-Okos predictive models were able to provide necessary thermal property values at high temperatures. The working range of TPCell and Choi-Okos were reported as up to 140 °C and 150°C, respectively (Choi & Okos, 1986; Mishra et al., 2016). Since the retort processing in this study was done 121.12 °C, only thermal properties up to 120°C were considered. Choi-Okos predictive model is very well-known and is a widely used method for estimates of thermal conductivity and specific heat capacity of food products. One of the major drawbacks this method has is that it requires information about the composition of the sample. The mass fraction of carbohydrate, protein, fat, ash, fiber and moisture content of the samples must be determined prior to calculation. These analyses are often cumbersome and time consuming. It is also reported that composition-based model are not very reliable and should only be used for initial assessment (Paluri, Phinney, & Heldman, 2018).

TPCell is a recent invention that is capable of measuring thermal conductivity of liquid product using non-isothermal method. The first report about this device was not published until 2016 (Mishra et al., 2016). However, the device has a lot of potential to compete with existing techniques such as TLS and Choi-Okos predictive model. In the first published article, thermal conductivities of sweet potato purees reported at room temperature were in agreement with thermal conductivity values obtained from KD2 Pro and Choi-Okos predictive model (Mishra et al., 2016). With a single experiment, TPCell is capable of measuring temperature-dependent thermal conductivities up to 140 °C in less than a minute. The heat transfer in this device is primarily governed by transient heat conduction which limits the application on low viscosity food products. Generally, natural convection in sample could lead to unrealistic thermal conductivity values (Huang & Liu, 2009) but can be mitigated by using lower power input (Murakami & Okos, 1989). Further investigation is needed to evaluate if TPCell can be used to measure thermal conductivity of low viscous product with lower power input.

The thermal conductivity values at room temperature of TPCell, KD2 Pro and Choi-Okos predictive model for potato soups are 0.456, 0.422 and 0.462 W/m°C, respectively. These values are very close to each other in the order of Choi-Okos> TPCell > KD2 Pro. Thermal conductivity obtained from KD2 Pro is significantly lower than the other two methods. Values obtained from TPCell and Choi-Okos do not differ significantly at 25°C. Large discrepancy was seen with these values at 120°C. Thermal conductivity of TPCell and Choi-Okos at 120°C are 0.456 and 0.515

W/m°C, respectively. Overall, the thermal conductivity values obtained from three different methods agree with each other at room temperature. No dramatic difference in thermal conductivity values was seen for potato soup, except at 120°C.

For 1.5% (w/w) CMC, the values reported using the three methods differ slightly from each other. At 25°C, the thermal conductivity is 0.627, 0.607 and 0.575 W/m°C for TPCell, Choi-Okos models and KD2 Pro, respectively. The first two values are closer to each other compared to the value obtained using KD2 Pro. Similar observation was also seen at 120 °C where the values obtained were 0.666 and 0.682 TPCell and Choi-Okos models, respectively. Literature value thermal conductivity of 1% (w/w) and 3% (w/w) CMC is reported as 0.582 (Lee, Cho, & Hartnett, 1981) and 0.560 W/m°C (Tian, He, Xu, Fang, & Zhang, 2016), respectively at room temperatures which matches closely with the thermal conductivity obtained using KD2 Pro device.

Thermal properties are also strongly dependent on the composition of the sample and estimation of thermal conductivity and specific heat capacity can be done based on the proportion of proximate composition in a food product using Choi-Okos predictive model, as shown above (Choi & Okos, 1986). Presence of water as major composition can influence the thermal conductivity of food positively, while presence of fat can decrease the values of thermal conductivity, especially at elevated temperatures. It is also shown that relationship of temperature and thermal conductivity is not linear. This should be an important factor to be considered when designing a device that measures thermal properties of food products. Porosity is another factor that may significantly influence the thermal conductivity of food products (Choi & Okos, 1986). The food products chosen for the study is not porous, hence it was not a concern here. However, for dry food products, such as breads, cakes, muffins, that contains air pocket, porosity must be factored into the estimation (Baik, Sablani, Marcotte, & Castaigne, 2006).

Heat transfer simulations are extremely important in designing thermal processes for food product. In order to have high accuracy, all the necessary components for simulations must be incorporated including temperature-dependent thermal properties. Often time, thermal-properties included in simulation are determined at room temperature only. Though some techniques can be time consuming to determine thermal conductivity at multiple temperature but at least the thermal properties of food product at the minimum and the maximum processing temperature should be determined. For instance, a product that is subject to retorting temperature should have its thermal property determined at both room temperature and at retort temperature. It is important to cover the thermal properties within the operating range of the thermal process. Current study revealed the accuracy of simulation improved significantly when temperature-dependent thermal properties was fitted in the simulation.

Studies reported in the past often compared the simulated temperature with temperature of the cold spot from the heat penetration study. Comparing the cold spot temperature alone does not show the accuracy of simulated profile. As presented in current study, though the center temperature matched closely between experimental and simulated data, significant difference was only seen when lethality was compared. While it is well established that temperature-time relationship is an important factor in ensuring food safety, the food processing guidelines uses sterilization values (lethality) as a strong support. Hence, when it comes to food thermal processing, it makes more sense to use lethality as a basis of comparison, besides the temperature at cold spot. Even a smallest deviation in the temperature can cause significant deviation in the sterilization value, as shown in Table 2.7. Similar observation was also reported in retort simulation study on kimchi soup (Cho, Park, Cheon, & Chung, 2015) where about 2.38% deviation from experimental temperature results in 58% deviation from actual sterilization value.

2.6 Conclusions

Three methods were compared in determining the thermal properties of potato soup at multiple temperatures. The thermal conductivity values agreed with each other for TPCell and Choi-Okos predictive model for both at 25°C and 120°C. Thermal conductivity values from KD2 Pro agreed with the rest of the methods at room temperature but was not capable to provide measurements at high temperature. The importance of including temperature-dependent thermal properties in thermal process simulated was elucidated. The accuracy of conductive heat transfer significantly improved when temperature-dependent thermal properties were used as opposed to fixed values. TPCell provided values that enabled simulation of retort process that matched very closely with heat penetration data. Choi-Okos predictive models gave similar thermal conductivity values but the proximate composition of the food product must be determined prior to estimation. For TPCell, the proximate composition is irrelevant, and measurements can be done in less than a minute for any temperature up to 140°C in a single run on liquid products. Accuracy of thermal process simulations should be evaluated using sterilization value besides the temperature of cold spot. It is shown even a slight deviation in temperature can results in huge deviation for lethality value proving the sensitivity of sterilization calculation in detecting changes. These observations were demonstrated using retort processing. The techniques presented in this study applies to a wide variety of thermal processes used in the food industry including pasteurization and aseptic processing. Results from the study will help in designing thermal processes, modeling degradation of microorganism and nutrients, as well as designing food processing equipment.

2.7 Reference

AOAC International. (2007). *Official Method of Analysis Method 992.23 (Generic combustion method)* (18th edn, 2005; Current through revision 2, 2007 (On-line). ed.). Gaithersburg, MD: AOAC International.

ASTM E 1269-11. (2011). Standard Test Method for Determining for Specific Heat Capacity by Differential Scanning Calorimetry. *ASTM International*.

Baik, O. D., Sablani, S. S., Marcotte, M., & Castaigne, F. (2006). Modeling the Thermal Properties of a Cup Cake During Baking. *Journal of Food Science, 64*(2), 295-299. doi:10.1111/j.1365-2621.1999.tb15886.x

Ball, C. O. (1923). Thermal process time for canned foods. *Bull National Research Council 7, Part 7*(37).

Beck, J. V., & Arnold, K. J. (1977). *Parameter Estimation in Engineering and Science*. New York: John Wiley & Sons.

Chen, J., Pitchai, K., Birla, S., Gonzalez, R., Jones, D., & Subbiah, J. (2013). Temperature-Dependent Dielectric and Thermal Properties of Whey Protein Gel and Mashed Potato. *Transactions of the ASABE, 56*(6), 1457-1467. doi:https://doi.org/10.13031/trans.56.10314

Cho, W.-I., Park, E.-J., Cheon, H. S., & Chung, M.-S. (2015). The Study of Heat Penetration of Kimchi Soup on Stationary and Rotary Retorts. *Preventive Nutrition and Food Science, 20*(1), 60-66. doi:10.3746/pnf.2015.20.1.60

Choi, Y., & Okos, M. R. (1986). Effect of temperature and composition on the thermal properties of food. In M. L. Maguer & P. Jelen (Eds.), *Food Engineering and Process Applications 1* (Vol. 1, pp. 93-101). London and New York: Elsevier Applied Science.

E. Sweat, V., & G. Haugh, C. (1974). A Thermal Conductivity Probe for Small Food Samples. *Transactions of the ASAE, 17*(1), 56. doi:https://doi.org/10.13031/2013.36786

Huang, L., & Liu, L.-S. (2009). Simultaneous determination of thermal conductivity and thermal diffusivity of food and agricultural materials using a transient plane-source method. *Journal of Food Engineering, 95*(1), 179-185. doi:https://doi.org/10.1016/j.jfoodeng.2009.04.024

Kou, X., Li, R., Hou, L., Cheng, T., Zhou, X., & Wang, S. (2018). Evaluation of a heating block system for accurate temperature-time controlled pasteurization treatments on various foods. *International Journal of Agricultural and Biological Engineering, 11*(3), 220-228. doi:http://dx.doi.org/10.25165/j.ijabe.20181103.3734

Lee, W. Y., Cho, Y. I., & Hartnett, J. P. (1981). Thermal conductivity measurements of non-Newtonian fluids. *Letters in Heat and Mass Transfer, 8*(4), 255-259. doi:https://doi.org/10.1016/0094-4548(81)90039-4

Marcotte, M., Taherian, A. R., & Karimi, Y. (2008). Thermophysical properties of processed meat and poultry products. *Journal of Food Engineering, 88*(3), 315-322. doi:https://doi.org/10.1016/j.jfoodeng.2008.02.016

McGinnis, D. S. (1986). Prediction of Transient Conduction Heat Transfer in Foods Packaged in Flexible Retort Pouches. *Canadian Institute of Food Science and Technology Journal, 19*(4), 148-157. doi:https://doi.org/10.1016/S0315-5463(86)71622-2

Mishra, D. K., Dolan, K. D., Beck, J. V., & Ozadali, F. (2016). A novel instrument for rapid measurement of temperature-dependent thermal properties of conduction-heated food up to 140 °C. *Journal of Food Engineering, 191*, 19-27. doi:10.1016/j.jfoodeng.2016.06.028

Mishra, D. K., & Sinha, N. K. (2011). Principles of Vegetable Canning. In N. K.Sinha (Ed.), *Handbook of Vegetables and Vegetables Processing* (pp. 243-257). Hoboken, NJ: Wiley-Blackwell.

Murakami, E. G., & Okos, M. R. (1989). Measurement and Prediction of Thermal Properties of Foods. In R. P. Singh & A. G. Medina (Eds.), *Food Properties and Computer-Aided Engineering of Food Processing Systems* (pp. 3-48). Dordrecht: Springer Netherlands.

Paluri, S., Phinney, D. M., & Heldman, D. R. (2018). Recent Advances in Thermophysical Properties — Measurements, Prediction, and Importance. *Current Opinion in Food Science*. doi:https://doi.org/10.1016/j.cofs.2018.10.005

Patashnik, M. (1953). A simplified procedure for thermal process evaluation. *Food Technology, 7*(1), 1-6.

Semmar, N., Tanguier, J. L., & Rigo, M. O. (2004). Analytical expressions of specific heat capacities for aqueous solutions of CMC and CPE. *Thermochimica Acta, 419*(1), 51-58. doi:https://doi.org/10.1016/j.tca.2004.01.030

Sweat, V. E. (1974). EXPERIMENTAL VALUES OF THERMAL CONDUCTIVITY OF SELECTED FRUITS AND VEGETABLES. *Journal of Food Science, 39*(6), 1080-1083. doi:10.1111/j.1365-2621.1974.tb07323.x

Tavman, I. H., & Tavman, S. (1999). Measurement of thermal conductivity of dairy products. *Journal of Food Engineering, 41*(2), 109-114. doi:https://doi.org/10.1016/S0260-8774(99)00079-5

Tian, J., He, Z., Xu, T., Fang, X., & Zhang, Z. (2016). Rheological Property and Thermal Conductivity of Multi-walled Carbon Nano-tubes-dispersed Non-Newtonian Nano-fluids

Based on an Aqueous Solution of Carboxymethyl Cellulose. *Experimental Heat Transfer, 29*(3), 378-391. doi:10.1080/08916152.2014.1001919

Zielinska, M., Ropelewska, E., & Markowski, M. (2017). Thermophysical properties of raw, hot-air and microwave-vacuum dried cranberry fruits (Vaccinium macrocarpon). *LWT - Food Science and Technology, 85*, 204-211. doi:https://doi.org/10.1016/j.lwt.2017.07.016

2.8 Appendix

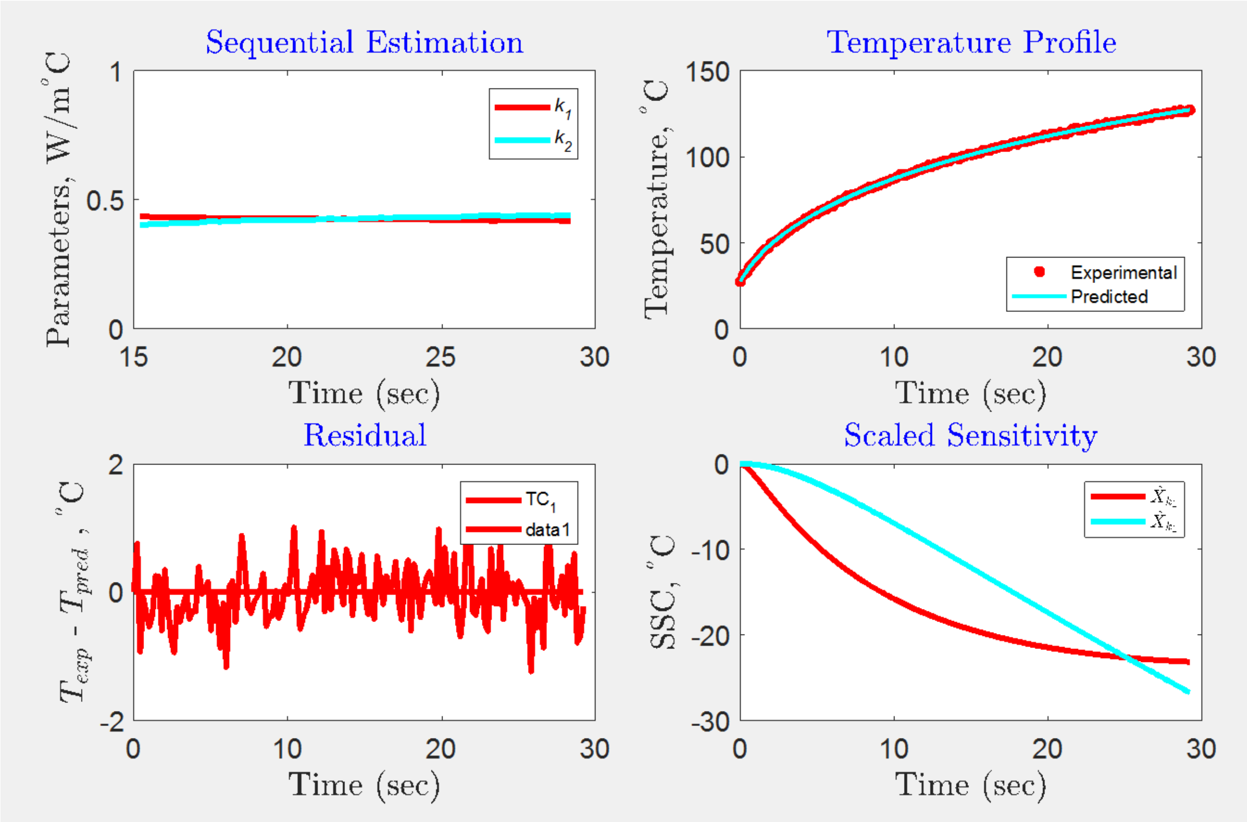


Figure 2.13. Sequential estimation of thermal conductivity of potato soup using TPCell.

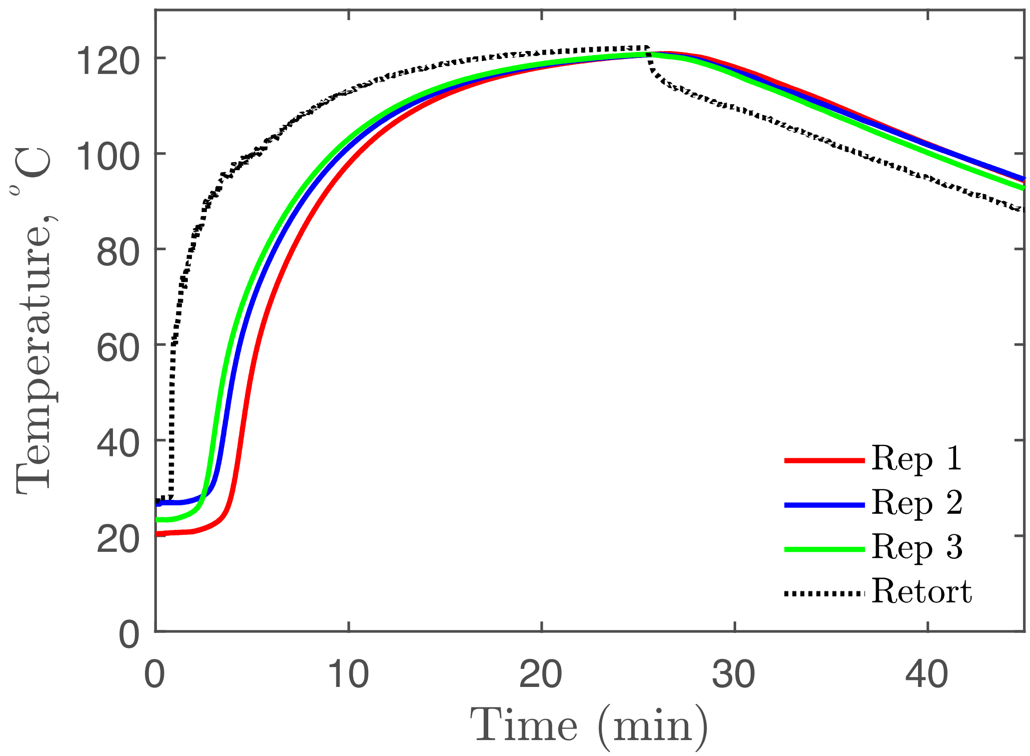


Figure 2.14. Experimental temperature profile of 1.5% (w/w) carboxymethyl cellulose (CMC) at the cold spot

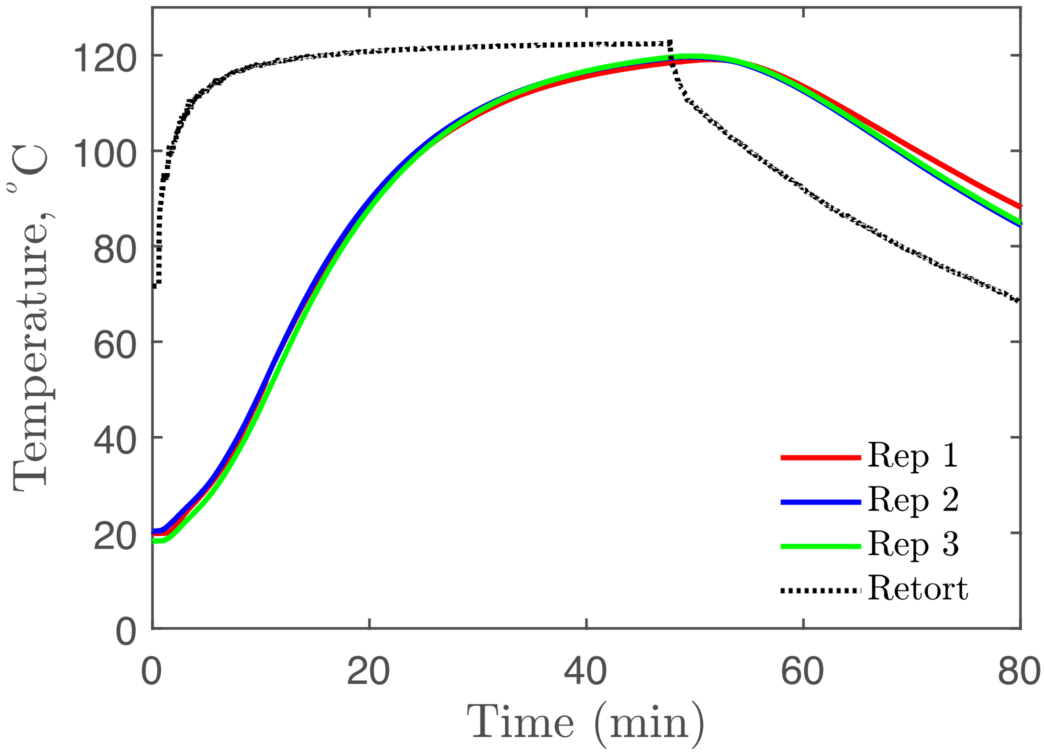


Figure 2.15. Experimental temperature profile of potato soup at the cold spot

CHAPTER 3. USE OF TEMPERATURE-DEPENDENT THERMAL PROPERTIES FOR FOOD PRODUCT DEVELOPMENT IN THE FOOD INDUSTRY

3.1 Abstract

Retorting, a conventional thermal processing method, is still a widely used technology in the food industry for various food production. Prior to commercial production, a heat penetration study is performed to evaluate feasibility of scale up to ensure that the scheduled process is sufficient to deliver commercial sterility to the product. However, depending on the scale and operational cost, heat penetration study can be very expensive which limits the number of iterations that can be studied. The aim of the study is to evaluate the thermal process adequacy based on temperature-dependent thermal properties of various iteration of potato soup. Thermal properties, i.e. thermal conductivity, specific heat capacity and density of four potato soup recipes were measured. These samples were also subjected to heat penetration study to evaluate the required process time to reach minimum sterilization value at process temperature. A scheduled thermal process was used to simulate the retort processing on all four potato soups using their temperature-dependent thermal properties. Results from the study suggest that thermal properties of food product changed with the formulation which affected the processing time to achieve minimum lethality value. Significant difference in thermal conductivities was seen for different recipes of potato soups while the specific heat and density was not significantly different. The established scheduled process was shown to be suitable for thermal treatment of some formulations only. Since the thermal conductivity measurements were sensitive to detect the difference in the formulation, it can be used as a tool to select formulation for heat penetration tests. This application will be beneficial for the industry to pre-screen the iteration and only select formulations that suit the scheduled process for successful heat penetration trials and reduce cost and labor-intensive trials.

3.2 Introduction

Thermal process is used by the food industry for food preservation. While many advances have been made with heating technology, retort is still most commonly used thermal process. In retorting, food products are packaged in a hermetically sealed container before being subjected to thermal treatment. Retort processing is designed to deliver commercial sterility to food products. According to the Food and Drug Administration's (FDA) Code of Federal Regulations title 21 (21 CFR 113.3), commercial sterility is defined as a condition achieved by application of heat alone or in combination with means to render food that is free of pathogenic microorganisms that are capable of reproducing in the food under normal non-refrigerated condition during storage and distribution. Due to absence of pathogenic microorganisms, any product with commercial sterility will be safe for consumption, as long as the hermetic seal is intact prior to consumption. The main food safety concern with low acid canned product is Botulinum toxin, a neurotoxin produced by *Clostridium botulinum* that can be fatal. C. *botulinum* is a spore-forming microorganism that is capable of reproducing in low acid anaerobic conditions. The vegetative form of C. *botulinum* can be deactivated by heating it beyond 121°C and the toxin can be destroyed with heat at 85°C. Inactivation of spores is challenging due to high heat stability which can only be inactivated when heated at 121°C under pressure of 15-20 lb/in^2 for a certain period of time, depending on the product (Mishra & Sinha, 2011).

Transient heat transfer is the fundamental mechanism behind the thermal processing of canned food in retort processing. There are two modes of heat transfer that occurs inside the can during heating: (1) conduction, and (2) convection. Conduction governs the heat transfer primarily if the product is solid or semi-solid. If the product is a mixture is solid and liquid, then the heat transfer is governed by both conduction and convection. In static retort, the primary mode of heat transfer is conduction since there is no movement of liquid inside the can. In agitated retort, due to rotation of can, both conduction and convection drives the heat, resulting in efficient process.

Prior to commercial production, a heat penetration study is typically done in the food industry to evaluate the thermal behavior of a food product during thermal processing. This is performed to determine if a thermal process is capable of providing sufficient heat to inactivate all target organisms to the desired level. During this study, thermocouples are placed inside the can, especially at the slowest heating spot of the container without compromising the hermetic seal. For a cylindrical can, the slowest heating spot is the center during conduction heating. The temperature at the slowest heating point is monitored and used to determine process parameters that will be sufficient to achieve commercial sterility. The adequacy of the thermal process is determined by calculating sterilization value. The sterilization or lethality (F_0) of a given process is defined as "the length in minutes of a process at 250°F where the container contents, immediately upon the beginning of the process, attain retort temperature, are held at that temperature for the length of the process, and at the end of process, immediately drop to sublethal temperature" (Ball & Olsen, 1957).

Mathematical modeling of heat transfer is used in designing appropriate thermal processing for a food product. This simulation requires the initial temperature of the product inside the can, boundary condition of the outer surface and thermo-physical properties (i.e thermal conductivity, specific heat capacity and density) as well as the dimensions of the container. Numerical method such as finite difference or finite element, can be used to solve the transient heat conduction problems. Software such as "COMSOL" are available to provide numerical solution for transient heat conductions problems. The heat transfer equation (Eq. 3.1) for axisymmetric case in written as:

$$\left[\frac{1}{r}\frac{\partial}{\partial r}\left(k(T)r\frac{\partial T}{\partial r}\right) + k(T)\frac{\partial^2 T}{\partial z^2}\right] = \rho C_p(T)\frac{\partial T}{\partial t} \tag{3.1}$$

where k is the thermal conductivity of the product, ρ is the density, C_p is the specific heat capacity where both thermal conductivity and specific heat capacity are modeled as functions of temperature.

In the food industry, many iterations of product formulations are typically made before selecting a final formulation for commercialization. However, each formulation requires a time intensive and costly heat penetration study to examine the impact of thermal process on product safety and quality. The aim of the study is to show influence of variation in formulation in retort processing and detection of the variation using thermal properties. We propose TPCell as a bench top alternative to access the feasibility of scale up prior to expensive large-scale trials. It would be very useful for product developers to utilize the thermal properties, from the very beginning, in making decisions on finalizing the formulation as well as selecting formulations for successful heat penetration studies.

3.3 Materials and Methods

3.3.1 Materials

Potato soups were prepared using the ingredients and formulation shown in Table 3.1. All ingredients were purchased at a local grocery store.

Table 3.8 Formulation of four different potato soups

Ingredients	**F1**	**F2**	**F3**	**F4**
Heavy cream (%)	39.6	18.2	0.0	0.0
Whole milk (%)	0.0	22.0	38.7	36.7
Potato flakes (%)	9.3	9.2	9.4	13.5
Chicken broth (%)	40.3	39.9	40.8	39.3
Butter (%)	7.7	7.7	7.9	7.5
Onion powder (%)	1.1	1.1	1.1	1.0
Pepper (%)	0.4	0.4	0.4	0.4
Salt (%)	1.6	1.6	1.6	1.6
Total (%)	100	100	100	100

Footnote: Values were determined by taking the ratio of weight of the ingredient to the total weight and were presented in percentages (%).

3.3.2 Methods

3.3.2.1 Proximate Analysis

A forced convection oven was used to determine the moisture content of the samples with the air-drying method 60°C for 72 hours. Samples weights were measured before and after the drying process. Samples were cooled in desiccator before weighing after the drying process. The moisture content was calculated based on weight loss of sample (Eq. 3.2)

$$\%\,Moisture = \frac{Wt\ of\ sample{+}pan_{before} - Wt\ of\ sample{+}pan_{after}}{Wt\ of\ sample{+}pan_{before} - Wt\ of\ pan} \times 100\% \qquad (3.2)$$

Ash analysis was performed according to AOAC 940.46(b). Samples were first dehydrated in a forced convection oven at 100°C for 12 hours. About 5g of samples were transferred to crucible to be incinerated in a muffle furnace at 550°C overnight. The determination of ash content was done according to Eq. 3.3 by measuring the weight of remaining ash in the crucibles.

$$\% \, Ash = \frac{Wt\ of\ sample+crucible_{before} - Wt\ of\ sample+crucible_{after}}{Wt\ of\ sample+crucible_{before} - Wt\ of\ crucible} \times 100\% \quad (3.3)$$

Dumas method using LECO Trumac N (St. Joseph, MI) was utilized to determine the protein content of the sample. This procedure was done according to AOAC Official Method of Analysis 992.32 (AOAC International, 2007). About 1-2 g of potato soup sample was loaded onto the instrument and analyzed for nitrogen (%) content. The sample was combusted with a flow of pure oxygen at 1100°C. Nitrogen oxides produced from nitrogen-containing compounds is reduced to nitrogen using a copper column. The total nitrogen released carried by helium gas was quantified by a gas chromatography that was coupled with a thermal conductivity detector. A conversion factor of 6.25 was used to calculate protein content (%) (Eq. 3.4). Ethylenediamine tetraacetic acid (EDTA) was used as the standard to calibrate the instrument.

$$\% \, Protein = \% \, Nitrogen \times 6.25 \quad (3.4)$$

Soxhlet semi-continuous extraction method was used to determine the fat content which followed the AOCS Official Method Am 5-04. Prior to the extraction with petroleum ether, samples were dried in a forced convection oven at 100°C for 12 hours. 5-6 g of dried samples were placed on thimble with glass wool. Extraction was performed for 6-8 h with a rate of 3-4 drops per second condensation. Weight loss of sample was quantified to determine the total fat (%) as shown in Eq. 3.5.

$$\% fat = \frac{Wt\ of\ sample+thimble+glass\ wool_{before} - Wt\ of\ sample+thimble+glass\ wool_{after}}{Wt\ of\ sample+thimble - Wt\ of\ thimble} \times 100\% \quad (3.5)$$

Carbohydrate content was calculated by subtracting percentage of moisture, ash, fat and protein from 100% as shown in Eq. 3.6.

$$\% Carbohydrate = 100 - (\% moisture + \% ash + \% fat + \% protein) \quad (3.6)$$

3.3.2.2 Thermal Conductivity, TPCell

Thermal conductivity of the samples was measured using TPCell as described previously with slight modification (Mishra, Dolan, Beck, & Ozadali, 2016). The sample holder was loaded with 275 mL sample, sealed and pressurized up to 60 psig. The cartridge heater in the center was supplied with 20W power to the experiment. Once the temperature of the heater reached 140°C, the relay system cuts the power supply off to stop the experiment to avoid overheating. a calibration equation, T= 25.381R-12295, was used to convert the resistance of the heater to temperature. The thermal conductivity was determined based on the experimental temperature profile, the using sequential estimation which was developed in Matlab®. The sequential estimation utilizes the matrix inversion lemma (Beck & Arnold, 1977) based on the Gauss minimization method and requires prior information. The initial $k_1$and k_2, values used are 0.52 and 0.62, respectively. $k_1$and k_2, are thermal conductivities at 25°C and 140°C, respectively. The specific heat (C_p) and density (ρ) values used were obtained experimentally as described below.

The sequential parameter estimation for $k_1$and k_2,continuous as each datum is added and ends when the value becomes constant. Triplicate analysis was done for each sample.

3.3.2.3 Specific Heat Capacity

Specific heat capacity of the sample were obtained using Differential Scanning Calorimetry (DSC Discovery Series, TA instruments) as described previously (ASTM E 1269-11, 2011). These values were reported as C_{p1} and C_{p2} which indicates values at 25°C and 140°C, respectively. The DSC was calibrated with a Sapphire standard. 9-10 mg sample was loaded into a Tzero pan which was sealed with a hermatic lid. The sample was measured against an empty reference pan made of the same material. The heat capacity was measuring during non-isothermal heating from 5°C to 150°C with an increment of 10°C. Triplicate measurements were taken for each sample.

3.3.2.4 Density

Density was determined by measuring the weight and volume of the samples in a graduated cylinder at room temperature and reported as g/m^3. Triplicate measurements were taken for each sample.

3.3.2.5 Heat Penetration Study for Retort Processing

Sample was placed in a cylindrical sample holder containing a thermocouple at the center for the retort processing A surface thermocouple was also placed on the outer surface of the sample holder to monitor the surface temperature. The sample holder was sealed, pressurized to 30 psig and placed in silicone oil bath. Silicon oil bath was set at 121.67 °C (252°F) which was used as the means to provide heat. The temperature of the thermocouples was monitored using LabView (National Instruments, Austin, TX) as the data acquisition software. The software was programmed to simultaneously calculate the lethality as center temperature was being recorded.

The experiment was performed until the center of the container has shown lethality of 6 min. Termination of the experiment was done by removing the sample holder from the oil bath and let it air-cooled to at least below 100°C before releasing the pressure.

3.3.2.6 Simulation of Retort Processing

Simulate the heat distribution inside sample holder during retort processing was simulated using COMSOL (COMSOL Inc, Burlington, MA). Simulations were performed using temperature-dependent thermal conductivity (k_1 and k_2) and specific heat (C_{p1} and C_{p2} using formulas (3.7) and (3.8), respectively. For simulations with fixed thermal properties, only $k_1$and C_{p1} were used.

$$k(T) = k_1\left(\frac{T2-T}{T2-T1}\right) + k_2\left(\frac{T-T1}{T2-T1}\right) \tag{3.7}$$

$$C_p(T) = C_{p1}\left(\frac{T2-T}{T2-T1}\right) + C_{p2}\left(\frac{T-T1}{T2-T1}\right) \tag{3.8}$$

3.3.2.7 Sterilization Values (Lethality)

Lethal rates (L) were calculated from the center temperature profile from the retorting experiment and simulation using the General method as shown in Eq (3.9) (Ball, 1923). Lethality (F_0) is then calculated by integrating L with time as shown in Eq (3.10) (Patashnik, 1953). F_0 from simulated data were compared with the experimented data.

$$L = 10^{(1/z)(T-T_r)} \tag{3.9}$$

where L is the lethal rate, z is the temperature change required to reduce microbial by 1D where D-value is the time to reduce the microorganisms by tenfold and T_r is the reference temperature (121.1°C).

$$F_0 = \int_0^t 10^{(1/z)(T-T_r)} \tag{3.10}$$

3.3.2.8 Statistical Analysis

Means were analyzed using ANOVA and significant difference between the means were determined using Tukey's pairwise comparison at α=0.05. Statistical analysis was performed using SAS 9.4.

3.4 Results

The formulation of potato soup was determined based on commonly used potato soup recipes. The major component of the soup is chicken broth followed by either the heavy cream or whole milk or the combination of both the heavy cream and the whole milk and then potato flakes. The remaining ingredients were kept the same. For F1, F2 and F3 the ratio of heavy cream to whole milk was varied to elucidate the influence of fat content on the thermal properties, whereas formulation 4 has higher amount of potato flake to show the influence of carbohydrate. The ratios of heavy cream to whole milk for F1, F2 and F3 are 100:0, 50:50, 0:100, respectively. For F4, only whole milk was used to maintain the viscosity since the viscosity of the soup will increase with added potato flakes. The formulation was designed to show major changes in proximate values as presented in Table 3.2.

Table 3.9 Proximate composition of four different potato soups

	Protein (%)	**Ash (%)**	**Fat (%)**	**Moisture (%)**	**Carbohydrate (%)**
F1	1.14 ± 0.04^{a}	0.90 ± 0.12^{a}	21.53 ± 0.12^{a}	63.84 ± 0.46^{a}	12.58 ± 0.55^{a}
F2	1.79 ± 0.60^{a}	0.97 ± 0.00^{a}	17.65 ± 0.37^{b}	68.56± 0.43^{b}	11.02 ± 0.50^{b}
F3	1.65 ± 0.20^{a}	0.97 ± 0.00^{a}	11.93 ± 0.30^{c}	74.70 ± 0.63^{c}	10.75 ± 0.14^{b}
F4	1.73 ± 0.11^{a}	0.97 ± 0.00^{a}	9.74 ± 0.79^{d}	71.67 ± 0.80^{d}	15.89 ± 0.15^{c}

Footnote: Values are average of triplicate measurements ± standard deviations. Carbohydrate content was calculated using the following formula, Carbohydrate = 100-protein-ash-fat-moisture.
Values with same letter in the same columns are not significantly different at α=0.05.

Based on the proximate composition in Table 3.2, the major composition of the potato soup is moisture, followed by fat and then carbohydrate. Ash and protein content are the least and their values are not significantly different for any formulation.

The moisture content in these soups are significantly different from each other with F3 being the highest, followed by F4, F2, and F1. This is due to highest amount of whole milk content in the F3 compared to F2 and F1. Whole milk and chicken broth are the major sources for moisture in these formulations. Though F4 and F3 have the same amounts of chicken broth and whole milk, addition of extra potato flakes in F4 may have reduced the amount of moisture due to interaction between starch and water. When starch swells and gelatinizes, it forms hydrogen bonding with water, which reduces the amount of moisture that can be removed during moisture analysis.

The order of fat composition from highest to lowest is F1 > F2 > F3 > F4. This is consistent with the ratio of heavy cream to whole milk mentioned above. F1 has the highest amount of heavy cream, followed by F2. F3 and F4 do not contain any heavy cream. The source of fat in F3 and F4 is mainly due to the fat that is naturally present in the whole milk. However, the fat content reported for F4 is slightly lower than F3. This could be due to interaction of fat with starch. Amylose molecules have helical conformation which creates a hydrophobic region in the center that enables interaction with lipids (Kaur & Singh, 2000). In the presence of water and heat and with subsequent cooling, amylose molecules form a helical complex with lipid by an exothermic reaction (Kugimiya & Donovan, 1981). It is important to note that F4 has more potato flakes compared to F3.

Highest carbohydrate content is seen with F4, followed by F1. F2 and F3 have similar amounts but significantly lower than F1. It was not a surprise to see F4 to be highest given that the formulation contained more potato flakes.

Table 3.10 Thermal conductivity, specific heat capacity and density of four different potato soups.

	Thermal Conductivity (W/m°C)		Specific Heat Capacity (J/g°C)		Density (g/cm^3)
	25°C	120°C	25°C	120°C	25°C
F1	0.466 ± 0.014^a	0.456 ± 0.012^a	3.307 ± 0.262^a	3.758 ± 0.486^a	1096 ± 25^a
F2	0.496 ± 0.014^a	0.494 ± 0.008^b	3.415 ± 0.108^a	3.734 ± 0.151^a	1074 ± 35^a
F3	0.535 ± 0.016^b	0.523 ± 0.010^c	3.456 ± 0.055^a	3.849 ± 0.205^a	1142 ± 20^a
F4	0.551 ± 0.014^b	0.531 ± 0.004^c	3.416 ± 0.072^a	3.637 ± 0.069^a	1114 ± 37^a

Footnote: Values are average of triplicate measurements ± standard deviations. Values with same letter in the same columns are not significantly different at α=0.05.

The density of the potato soups is quite similar in the range of 1074 to 1142 g/cm^3 and no significant difference was seen among their means. This would indicate that any difference seen in the thermal processing would not be caused by the difference in the density. The thermal conductivity of the soups at both temperatures are significantly different from each other in the order of F4 > F3 > F2 > F1. At 25°C, thermal conductivity values of F1 and F2 are not significantly different from each other, just like F3 and F4 (Table 3.3). At higher temperature, F1 and F2 have distinct specific heat capacity while F3 and F4 still remain insignificantly different from each other. The order of specific heat capacity is slightly different than thermal conductivity, with F3 having the highest value, followed by F4, F2 and F1 though no statistically significant difference was seen among the specific heat capacity at both temperatures. These trends align with the moisture content of the samples. Studies have reported that the specific heat and thermal conductivity are strongly dependent on the water content, especially when the major composition of food is water (E. Sweat & G. Haugh, 1974). While the thermal conductivity and specific heat are affected by their composition, detailed study has shown how the composition changes the thermal properties of food (Choi & Okos, 1986). The specific heat capacity of pure carbohydrate, protein, fat, moisture and ash were reported to be in the order of water > protein > fat > carbohydrate > ash (Choi & Okos, 1986). This explains why the trend of specific heat capacity follows the trends of moisture content. Similarly, for thermal conductivity, the order of pure components would be water > ash > carbohydrate > protein > fat explaining why the thermal conductivity of the potato soups were in agreement with the moisture content of the soups (Choi & Okos, 1986).

Generally, thermal property values increase with increasing temperatures. Both thermal conductivity and specific heat capacity reported show higher values at higher temperatures. However, the thermal conductivity of pure fat decreases with increasing temperature (Choi & Okos, 1986; Marcotte, Taherian, & Karimi, 2008). The change in thermal properties with temperature is quadratic, not linear (Choi & Okos, 1986), and this is probably why the values decreased slightly at higher temperature for all soups. This also clearly emphasizes the importance of measuring the thermal properties at high temperatures for modeling of heat transfer and designing food processing.

Table 3.3 also clearly elucidates the influence of formulation on the thermal properties of potato soups. The variations in the formulation were mainly the ratio of heavy cream to whole milk and the ratio of potato flakes. The variation in the formulation not only caused difference in the proximate composition but also impacted the thermal properties significantly, especially for thermal conductivity. Each food ingredient has different thermal properties and these properties change when they are combined together. Different combination as well as different amounts of ingredient change the thermal properties which results in different behavior during thermal processing (Table 3.3 and Table 3.4). For example, replacing the heavy cream with whole milk in potato soup (F1 vs F3) can considerably change the thermal conductivity as shown in Table 3.3. Subsequently, it affects the time to reach lethality (F_0) (Table 3.4).

Lethality (F_0) indicates the adequacy of thermal processing to ensure the product is free from any disease-causing foodborne pathogen. The lethality is determined at the coldest spot, the center for a cylindrical can, by monitoring the temperature over time. The current study utilized a custom-made program that simultaneously calculated the lethality during data acquisition. In retort processing, the cans filled with food products are placed in a pressurized retort. The temperature of the retort is raised to 121.11°C (250°F) and held for a pre-determined time. At this condition, the center of the cans is heated and reaches a lethality of at least 6 min before the retort is cooled.

The process time required to reach the minimum lethality of 6 min is presented in Table 3.4. Experimental data in Table 3.4 shows that F1 takes significantly longer time to reach minimum lethality than the rest of the soups. The remaining potato soups took similar time to reach minimum lethality and their times are not statistically different from each other. F1 has higher amount of fat compared to the rest of formulation. As mentioned before, high fat containing food tends to have lower thermal conductivity at high temperature which could slow down the heat transfer. The remaining recipes have fairly higher water content and the heat transfer could be driven by the thermal properties of water predominantly than fat. Similar observation was seen in dairy-based dessert (kheer) where different rice to milk ratio influence the total required process time (Jha, Patel, Gopal, & Ravishankar, 2014).

Table 3.11 Time (min) to reach minimum lethality (F_0) of 6 min for four different potato soups

	Experimental	Simulated
F1	48.46 ± 1.13^a	47.28 ± 0.55^a
F2	46.23 ± 0.55^b	44.80 ± 0.56^b
F3	45.97 ± 0.53^b	44.65 ± 0.56^b
F4	46.08 ± 0.12^b	43.28 ± 0.57^c

Footnote: Values are average of triplicate measurements ± standard deviations. Values with same letter in the same columns are not significantly different at α=0.05.

Figure 3.1 shows simulated center temperature of all four potato soups. The surface temperature obtained from heat penetration study for F3 was used as the established process to predict the temperature of cold spot for all formulations. The goal was to evaluate if all four formulations can be processed using the scheduled process. From Figure 3.1, there was no obvious deviation seen with any soup's heating profile. The temperature of slowest heating point for all formulation is very close to each other.

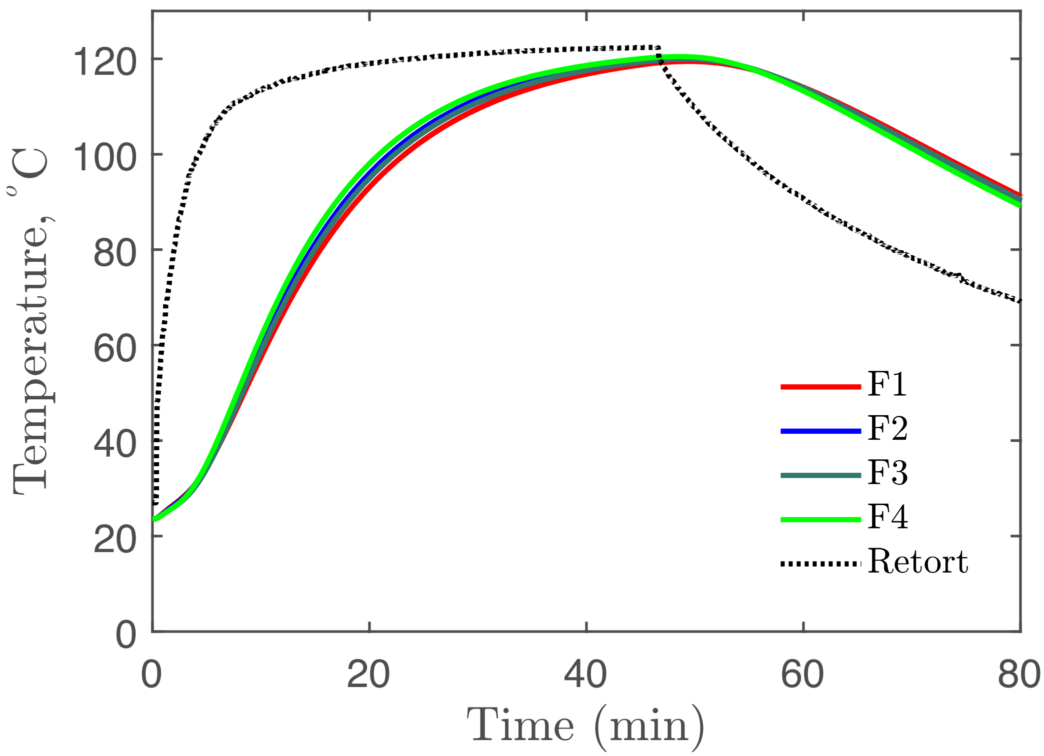


Figure 3.16 Simulated temperature profile of potato soups at the cold spot

Figure 3.2 shows the accumulated lethality calculated from the predicted cold spot temperature to understand the impact of formulation variety in achieving required lethality. While no obvious difference in center-temperature was seen among the soups, distinct difference is seen with their lethality. The horizontal line in Figure 3.2 represents the mark for minimum required lethality (F_0=6 min). Comparing the time taken for each soup to get to minimum lethality, looks like F4 was heated the fastest, followed by F2, F3 and F1.

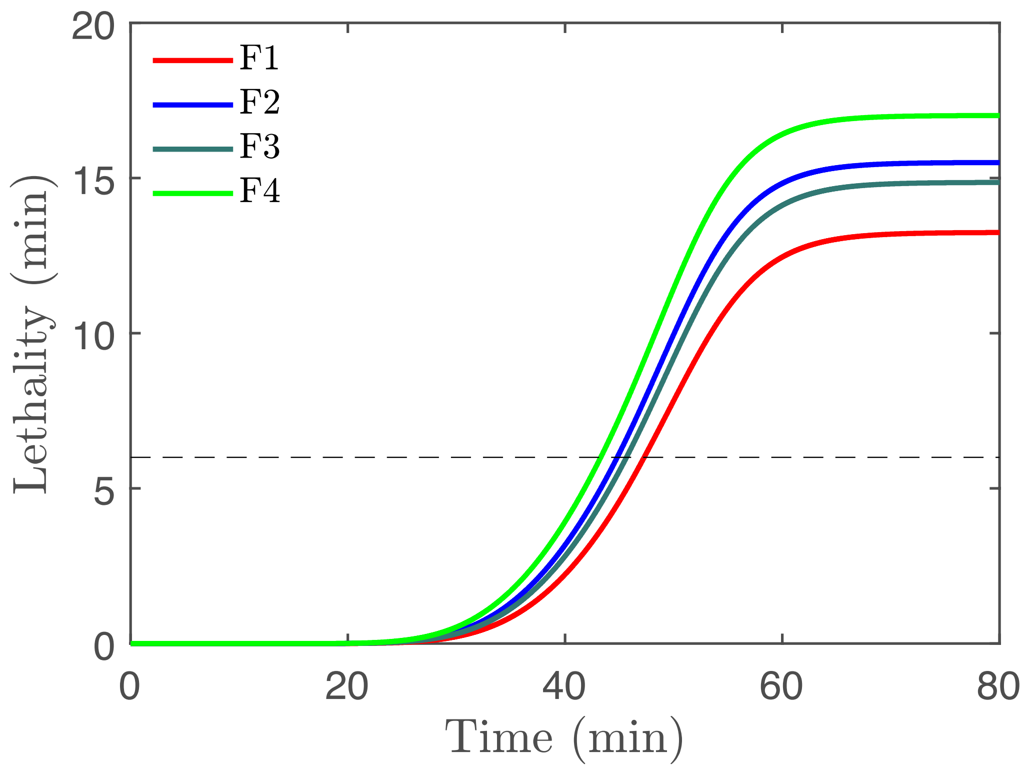


Figure 3.17 Accumulated lethality of potato soup based on simulated temperature profile at cold spot

The boundary condition from F3 was assigned as the scheduled thermal process. The thermal behaviors of all four soups were estimated using their respective temperature-dependent thermal properties and the scheduled thermal process. The time taken for each sample to reach the minimum lethality (F_0=6 min) was calculated and reported as simulated data in Table 3.4. F1 took significantly longer time to reach adequate sterilization values than the rest of the formulation. This is in agreement with experimental data. On the other hand, F4 look the shortest time to achieve similar sterilization condition and the time is significantly lower than the rest of the formulation. F2 and F3 took similar time (about 45 min) to reach the minimum lethality. The order of formulation in undergoing heat transfer from the slowest to fastest is F1 > F3 > F2 >F4.

3.5 Discussions

Food processing companies take a very conservative approach generally. It is safer to overcook the food product rather than undercooking to avoid any potential recall due to foodborne pathogen. Overcooking may severely degrade the sensory qualities as well as the nutrient content. From the experimental data (Table 3.4), the difference in processing time to reach minimum lethality of 6 min for F1 and F3 is 2.49 min. When the same retort processing conditions (i.e time and temperature) were used for both F1 and F3 potato soups as presented in Table 3.4 with simulated data, it is clear that F3 was overcooking for another 2.63 min which can degrade the quality of the product. The sample may be slightly browner and may even have burned notes. It is important to note that the lethality will keep accumulating during cooling process until the temperature of the product is significantly low. This further adds to nutrient and sensory degradation. Hence, overcooking for even a few more second could cause significant damage to the product. At the same time, at the industrial scale it could be expensive to run the retort for additional minutes when it is not needed. A study performed on fish stew reported significant difference in sensory quality when different processing temperatures were using though all samples received lethality of 6 min (Ohlsson, 1980). This study shows the importance of controlling the processing time and temperature to produce food products with good sensory quality without compromising the safety. Similar observation was also seen with fish curry where another minute of lethality significantly affected the sensory attribute of the product (Majumdar, Dhar, Roy, & Saha, 2014).

Alternatively, when the retort processing was designed to cook F3 but F1 was being processed instead, the process would lead to undercooking. This mean when the cooling process is started, F1 would still not have reached the minimum lethality of 6 min, which can cause severe consequence due to food safety concerns. When a food product is processed below the minimum lethality requirement, the food processors would risk an outbreak of foodborne illness which can affect the health of consumers as well as product recalls, huge lawsuit or maybe even the closure of business. Hence, getting the right processing conditions for each food product is crucial.

In the food industry, a heat penetration test is conducted to evaluate if a formulation or the processing conditions are suitable for each other. It is quite evident from Table 3.4 that one processing condition may not work for all recipes. However, it is more expensive to conduct heat penetration test for every formulation that was created. Generally, only one or a few recipes are selected for heat penetration test due to high cost to run pilot experiments. Accurate heat transfer simulation becomes crucial to understand the thermal behavior of food product under given retort conditions. Based on the simulation, the processing conditions or the formulation can be modified to meet the desired requirements.

The key component of a successful thermal process simulation strongly depends on the accuracy of temperature-dependent thermal properties for the modeling. Specific heat capacity and density are relatively easy to measure. Density of food product do not change significantly at high temperature and their changes can be neglected (Choi & Okos, 1986). Specific heat capacity measurement can be easily done using DSC to desired temperatures, even at temperatures higher than 100°C using non-isothermal heating. However, it is not the same for thermal conductivity of food, especially at higher temperatures. Commercial devices, such as KD2 Pro (Decagon Inc, Pullman WA), that are available to measure thermal conductivity of food are not equipped to be used at high temperatures because the sample need to be equilibrated at the desired temperatures before the measurements can be taken. If the temperature of the sample changes too much during measurement, the sensor will not be able to measure the thermal conductivity successfully. Measurements taken at this condition will have high error values (Mishra et al., 2016).

Besides being time consuming, equilibrating food samples at high temperature for a long time causes severe moisture loss and degradation which completely alters the composition of the samples. Any thermal conductivity measurement taken at this condition will not reflect the actual condition of the sample. It may take about 2 h to increase the temperature of the sample but the heat distribution inside the product may not be even. During food processing, product is heated for only a short period of time, for instance, about 45 min for potato soup in this study, which may not cause severe degradation as compared for being heated for 2 h. Hence, there is a huge limitation in determining the thermal conductivity at high temperatures using commercial devices, especially for food products.

TPCell used in this experiment uses non-isothermal heating to determine the thermal conductivity of food (Mishra et al., 2016). This device is capable of measuring the thermal conductivity within a minute. The unit is also pressurized to prevent moisture loss and to increase the temperature of the food product to above 100°C. The operating range of this device covers the processing temperatures utilized in the food industry. This device is also sensitive in detecting even the small changes in the thermal conductivity of the food products. The thermal conductivity values of potato soup presented in Table 3.3 shows significant difference across the four formulation at high temperatures. At 25°C, the results show that F1 and F2 are significantly different in thermal conductivity than F3 and F4 which proves the sensitivity of TPCell to changes in formulation. Though the time to reach lethality obtained experimentally was only significantly different for F1 (Table 3.4), it was surprising that TPCell was still able to detect the difference among the formulation.

The results suggest that thermal properties obtained from TPCell can be used for accurate prediction of heat transfer simulation prior to expensive heat penetration tests. Alternatively, the thermal properties can be used during bench top product development to select the formulation than suits a pre-determined retort processing scheduled process. As mentioned before, not all formulation are typically chosen for heat penetration tests. By utilizing the information gathered from thermal properties, a well-thought decision can be made on the formulation that will be tested in the pilot scale to establish the processing parameters for scheduled process. Some formulations may not perform as expected during a pilot run which causes delay in product development, as well as large material and operation cost. A pilot run the food industry can easily cost about $10,000, depending on the scale and the type of product being processed.

We suggest developing a range of thermal properties where outside this range, the scheduled process will no longer be able to provide adequate sterility to the food product. This can help in avoiding unexpected errors in heat penetration tests. This range of workable thermal properties should be determined for each food category or food product. For example, if the product developers decided to cut down the heavy cream in the potato soup formulation and replace it with whole milk to reduce total calories from fat, a quick determination of thermal conductivity should be carried using TPCell. These values should be compared with the range of workable thermal properties that has been developed for the potato soup processing conditions. Results from this study suggest that, partial replacement of heavy cream with milk is not going to affect the time to reach minimum lethality significantly. Hence, it is safe to make such replacement if the thermal properties fall in the designed range of the scheduled process. However, a complete replacement affected the processing time to reach minimum lethality. This can be predicted by just evaluating the thermal properties. This example clearly illustrates how thermal properties can be used as a tool to pre-screen workable formulation for a scheduled thermal processing condition. Similar approach can also be utilized in other thermal processes such as aseptic processing and pasteurization.

3.6 Conclusions

The influence of variation of formulation on their thermal properties was investigated. TPCell was able to detect the difference in thermal conductivity values as influenced by the composition of the food product. The impact of formulation on heat transfer during thermal processing was also examined. Not all food products can be treated by the same scheduled process. A quick study on thermal properties can be used to evaluate if a formulation fits a thermal process that was filed with FDA. A workable range of thermal properties for a scheduled process should be established prior to using this application. This can help the food industry access the feasibility of scale up quickly and cut down on the cost of unsuccessful heat penetration studies. The demonstration provided in this study is applicable to any thermal processes including pasteurization, retort and aseptic processing.

3.7 References

AOAC International. (2007). *Official Method of Analysis Method 992.23 (Generic combustion method)* (18th edn, 2005; Current through revision 2, 2007 (On-line). ed.). Gaithersburg, MD: AOAC International.

ASTM E 1269-11. (2011). Standard Test Method for Determining for Specific Heat Capacity by Differential Scanning Calorimetry. *ASTM International*.

Ball, C. O. (1923). Thermal process time for canned foods. *Bull National Research Council 7, Part 7*(37).

Ball, C. O., & Olsen, F. C. W. (1957). General Method of Process Calculation. In *Sterilization in food technology; theory, practice, and calculations* (1st ed.). New York: McGraw-Hill Book Company, Inc.

Beck, J. V., & Arnold, K. J. (1977). *Parameter Estimation in Engineering and Science*. New York: John Wiley & Sons.

Choi, Y., & Okos, M. R. (1986). Effect of temperature and composition on the thermal properties of food. In M. L. Maguer & P. Jelen (Eds.), *Food Engineering and Process Applications 1* (Vol. 1, pp. 93-101). London and New York: Elsevier Applied Science.

E. Sweat, V., & G. Haugh, C. (1974). A Thermal Conductivity Probe for Small Food Samples. *Transactions of the ASAE, 17*(1), 56. doi:https://doi.org/10.13031/2013.36786

Jha, A., Patel, A. A., Gopal, T. K. S., & Ravishankar, C. N. (2014). Heat penetration characteristics and physico-chemical properties of in-pouch processed dairy dessert (kheer). *Journal of Food Science and Technology, 51*(10), 2560-2567. doi:10.1007/s13197-012-0750-8

Kaur, K., & Singh, N. (2000). Amylose-lipid complex formation during cooking of rice flour. *Food Chemistry, 71*(4), 511-517. doi:http://dx.doi.org/10.1016/S0308-8146(00)00202-8

Kugimiya, M., & Donovan, J. W. (1981). Calorimetric Determination of the Amylose Content of Starches Based on Formation and Melting of the Amylose-Lysolecithin Complex. *Journal of Food Science, 46*(3), 765-770. doi:10.1111/j.1365-2621.1981.tb15344.x

Majumdar, R. K., Dhar, B., Roy, D., & Saha, S. (2014). Study of Instrumental and Sensory Characteristics of Catla in Curry Medium during Retort Pouch Processing to Optimize F0 Value. *Journal of Food Processing and Preservation, 39*(6), 1595-1604. doi:10.1111/jfpp.12388

Marcotte, M., Taherian, A. R., & Karimi, Y. (2008). Thermophysical properties of processed meat and poultry products. *Journal of Food Engineering, 88*(3), 315-322. doi:https://doi.org/10.1016/j.jfoodeng.2008.02.016

Mishra, D. K., Dolan, K. D., Beck, J. V., & Ozadali, F. (2016). A novel instrument for rapid measurement of temperature-dependent thermal properties of conduction-heated food up to 140 °C. *Journal of Food Engineering, 191*, 19-27. doi:10.1016/j.jfoodeng.2016.06.028

Mishra, D. K., & Sinha, N. K. (2011). Principles of Vegetable Canning. In N. K.Sinha (Ed.), *Handbook of Vegetables and Vegetables Processing* (pp. 243-257). Hoboken, NJ: Wiley-Blackwell.

Ohlsson, T. (1980). OPTIMAL STERILIZATION TEMPERATURES FOR SENSORY QUALITY IN CYLINDRICAL CONTAINERS. *Journal of Food Science, 45*(6), 1517-1521. doi:10.1111/j.1365-2621.1980.tb07553.x

Patashnik, M. (1953). A simplified procedure for thermal process evaluation. *Food Technology, 7*(1), 1-6.

CHAPTER 4. OVERALL CONCLUSIONS

4.1 Conclusions

Comparison between three methods of determination the thermal properties of potato soup at multiple temperatures reveals that TPCell is most suited for determination of temperature-dependent thermal properties. Thermal conductivity values determined by TPCell were in agreement with other common methods. Choi-Okos predictive model was equally good for determining temperature-dependent thermal properties. Thermal conductivity values from KD2 Pro agreed with the rest of the methods at room temperature but is not suitable for measurements at high temperature. Improved accuracy in thermal process simulation was seen when temperature-dependent thermal properties was included in the model as compared to only using fixed values measured at room temperature. TPCell provided thermal conductivity values that enabled simulated profile of retort processing that matched very closely with experimental heat penetration data. Simulation using predicted thermal properties values using Choi-Okos model came close but proximate composition of the sample must be determined prior to application. TPCell does not require information on composition which saves more time. Measurements with TPCell is done in less than a minute for any temperatures up to 140°C in a single run on liquid products. The study also revealed the importance of using sterilization value as a basis for comparison besides the temperature of cold spot. A slight deviation in temperature resulted in huge deviation in sterilization value indicating that lethality calculation is more sensitive in detecting changes.

The influence of variation of ingredients in potato soup formulation was studied. TPCell was sensitive to detect the difference between these samples and was able to provide distinct thermal conductivity values for each formulation. The impact of variation in formulation during thermal process was also investigated. It was revealed that not all iterations of potato soups were able to be processed using the same scheduled process. Thermal properties can be used as a quick tool to evaluate feasibility of scale up for a food product. Establishing a workable thermal conductivity range using TPCell based on a scheduled process can help with pre-screening the iterations prior to expensive and time-consuming heat penetration study. This helps the food industry to access the possibility of scale up faster without having to face unsuccessful heat penetration study.

Retort processing was used to demonstrate the application of temperature-dependent thermal properties in food thermal process simulation and selection of product formulations. These applications are not limited to only retort processing. Other thermal processes such as pasteurization and aseptic processing can utilize the technique to achieve similar results. Results from this study will benefit food industry in designing thermal processes, modeling degradation kinetics of microorganisms and nutrients, as well as designing food processing equipment.

4.2 Recommendations for future work

Future work related to current research should include but not limited to;

1. Studying the impact of batch variation in thermal processing and process time required to achieve minimum sterility.
2. Investigating the tolerance of TPCell in detecting variability between batches of a food product.
3. Developing optimal experimental design to evaluate if TPCell can simultaneously estimate $C_p(T)$.
4. Developing model food product that is sensitive in detecting changes due to thermal treatment.