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Yaser AbuDagga for the degree of Master of Science in Mechanical Engineering presented December 13, 1995.

Title: Finite Element Simulation of Heat Transfer in Pacific Whiting Surimi Paste During Ohmic and Conventional Heating

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The viability of using ohmic "resistance" heating as a process alternative to inactivating the heat-stable softening enzyme in Pacific whiting surimi was investigated. A fast heating rate through the enzyme-active temperature range would reduce the damage to the gelling network in surimi-based products. Simulating the ohmic heating process in surimi would help in designing industrial size equipment. Such simulation requires knowledge of thermal and electrical properties. Thermal conductivity, specific heat and density of Pacific whiting surimi with 74, 78, 80 and 84% moisture content were measured and modeled over the cooking temperature range. Thermal conductivity and specific heat were measured using a linear heat source probe and differential scanning calorimetry

(DSC) respectively. Both thermal conductivity and specific heat were found to increase with increasing moisture content and temperature. Surimi density was found to decrease with increasing moisture content and temperature. Empirical models for each property, as a function of temperature and moisture content, were fitted based on the experimental data. Those correlations were used to simulate the heat transfer in surimi using water bath "conventional" and ohmic "resistance" heating with the aid of commercial finite element partial differential equation software (PDEase). The heat transfer simulation was used to evaluate the heating rate, heat distribution in surimi and the parameters affecting the heating process. Ohmic heating was found to have higher heating rate with higher moisture content in surimi and higher voltage gradient across the sample. The electrode design for the ohmic heater is critical and has a significant effect on the heating rate. Ohmic heating was also compared to the conventional case (heating by convection through the boundaries) and was found to have a higher rate. Ohmic heated surimi paste was found to have better gel quality than that heated conventionally.

FINITE ELEMENT SIMULATION OF HEAT TRANSFER IN PACIFIC WHITING SURIMI PASTE DURING OHMIC AND CONVENTIONAL HEATING

by

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Yaser AbuDagga, Author

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Chapter 1

Introduction

BACKGROUND

Pacific whiting (*Merluccius productus*) represents one of the largest commercial source of biomass on the west coast of the United States, but it has limited usage due to the presence of a protease softening enzyme throughout its tissue. This enzyme can cause rapid softening of the flesh when heated. Due to this softening problem Pacific whiting has been used in surimi, a commercially valuable washed minced product into which various enzyme inhibitors can be easily mixed. Surimi is valued for its ability to form an elastic gel during cooking. A food grade enzyme inhibitor is typically added to surimi made from Pacific whiting to control the effect of the enzyme during heat-setting of surimi-based product such as imitation crabmeat and shrimp.

Several inhibitors such as beef plasma protein (BPP), dried egg white and potato extract were tested and proven to control the softening effect of the protease enzyme and to increase gel quality (Morrissey et al., 1993, Lee et al. , 1990). These inhibitors, however, have some usage limitations. For example, BPP carries

some labeling concern within the seafood industry. Dried egg white is expensive and contributes added cost to the final product. A high concentration of potato extract is needed, which limits its usage in some products. When it is infeasible to use enzyme inhibitors, a rapid heating through the temperature range at which the protease enzyme is most active (40-60°C, Wasson, 1992) would be an alternative. Rapid and controlled heating will inactivate the softening enzyme before it affects the gel network in surimi as shown in the work of Yongsawatdigul et al. (1995a) included as Appendix B. One way of effecting rapid heating is by using microwave heating. Although microwave heating is more rapid than conventional heating, it has limitations due to non-uniformity of the heating through the material (Singh and Heldman 1993), including surface over- heating in thick material due to limited microwave penetration. Another method of applying rapid heating would be ohmic "resistance" heating, in which an alternating current passes through the food medium between electrodes (Parrott 1992). Since heat is internally generated, ohmic heating is more rapid than "conventional heating" in which heat is conducted from the outer boundaries. Ohmic heating has been proven to control the softening enzyme effect and to give a better surimi gel quality than that cooked conventionally (Shiba 1992, Yongsawatdigul et al. 1995a).

Most of the recent applications of ohmic heating have been in sterilizing liquid-particle food mixtures (de Alwis and Fryer 1990a, Sastry and Palaniappan 1992a). Conventional heating in jacketed steam or hot water heat exchangers cause over-

processing of the liquid phase while ensuring that the center of each food particle is sterilized (Parrott 1992). In ohmic heating, liquid and solid particles are internally heated simultaneously, and over-processing of the liquid phase is avoided. In the seafood analogs industries, ohmic heating has not been used until very recently, when the Japanese used ohmic heating in processing seafood analogs from Pollock surimi. Shiba (1992), using an alternating current of 50 Hz achieved a very rapid heating rate: 47°C/min., compared to 0.9°C/min. using a water bath.

Utilization of ohmic heating in the industry calls for a full understanding of the process. Simulating the heat transfer process during ohmic heating of surimi will give valuable information on parameters influencing the heating rate and temperature distribution in the heated material. The simulation can be carried out using a finite-element PC-based partial differential equation package. However for accurate results we need an accurate prediction of temperature-dependent thermal conductivity, specific heat, density and electrical conductivity for surimi in the cooking temperature range.

The main objective of this study is to simulate the heating rate in surimi using ohmic heating under different conditions of voltage gradient, moisture content, geometry, and boundary conditions. Using the simulation results and analyzing the critical parameters that affect the ohmic heating process, a design recommendation is concluded. To obtain this objective we need to understand the following:

1- The ohmic heating process and its mathematical model

2- Thermal conductivity of surimi

3- Specific heat of surimi

4- Electrical conductivity of surimi

5- The critical parameters affecting the heating process.

OHMIC HEATING MODELING

Ohmic Heating is a method in which an alternating current is passed through an electrically conducting material resulting in an internal heat generation due to the electrical resistance of the material (Shiba 1992, de Alwis and Fryer 1990b, Sastry and Palaniappan 1992b). The rate of heat generation per unit volume "Q" (W/m^3) can be found according to

$$Q = \sigma V^2 \qquad (1.1)$$

where σ: the electrical conductivity of the sample (S/m), and

V: the voltage gradient in the sample (V/m).

Assuming isotropic electrical conductivity for surimi (σ is constant with position), then

$$V = \frac{E}{L} \qquad (1.2)$$

where E is the voltage across the sample, and

L: is the length of the sample.

The temperature distribution throughout the sample at any time can be found by solving the transient heat transfer equation with an internal heat source and appropriate boundary conditions

$$\nabla(k\nabla T) + Q = \rho C_p \frac{\partial T}{\partial t} \tag{1.3}$$

where T: temperature,

k: thermal conductivity,

Q: internal heat generation rate per unit volume,

ρ: density,

C_p: specific heat, and

t: time.

This equation is hard to solve analytically since k, Q, ρ and C_p are all functions of temperature. However this equation can be solved numerically using finite difference or finite element techniques. The formulation of the governing equations and the boundary conditions depends on the sample geometry. In the seafood analog industry most of the product has a cylindrical or rectangular slab geometries. So, In this study two different sample geometries similar to those found in the industry are investigated: a cylinder in one dimension and a rectangle in two dimensions.

Cylindrical Coordinates

This case describes a sample heated in a CPVC cylindrical tube using ohmic heater having an internal radius of R_i and outer radius of R_o as shown in Figure 1.1a.

Electrodes are placed at each end of the cylinder. (Note that description and construction of the ohmic apparatus used in this study is described briefly in the ohmic heating section of this chapter and in details in chapter 3 and appendices A and B). Assuming no heat loss to the electrodes and no heat resistance between the sample and the tube (perfect contact), the boundary conditions are (Ozisik 1992):

$$\frac{\partial T}{\partial r} = 0 \qquad \text{at } r=0 \text{ (symmetry)}$$

$$k_t \frac{\partial T_t}{\partial r} = k \frac{\partial T}{\partial r} \qquad \text{at } r=R_i \text{ (contact between surimi and tube)}$$

$$k_t \frac{\partial T_t}{\partial r} = h(T_\infty - T_t) \qquad \text{at } r=R_o \text{ (convection to the surrounding)}$$

$$T = T_t \qquad \text{at } r=R_i \text{ (contact between surimi and tube)}$$

and a uniform temperature initial condition

$$T = T_o \qquad \text{at } t=0$$

where R_i : sample tube inner radius,

R_i : sample tube outer radius,

k_t : sample tube thermal conductivity,

T_t : sample tube temperature

k : sample thermal conductivity,

h : convection coefficient between the tube and the surrounding, and

T_∞ : surrounding temperature.

Due to heat leakage to surroundings in the radial direction, a temperature gradient is presented in that direction. This temperature gradient causes a variable thermal

conductivity in the radial direction because it has temperature dependency. Constant thermal conductivity in θ and z direction is still valid. The governing Eq. (1.3) in cylindrical coordinates and under the above assumptions reduces to

$$\frac{1}{r}\frac{\partial}{\partial r}\left(k\frac{r\partial T}{\partial r}\right)+Q=\rho C_p\frac{\partial T}{\partial t} \qquad \text{for } 0\le x < R_i \qquad (1.4)$$

$$\left(\frac{1}{r}\frac{\partial T}{\partial r}+\frac{\partial^2 T}{\partial r^2}\right)=\frac{1}{\alpha_t}\frac{\partial T}{\partial t} \qquad \text{for } R_i \le x \le R_o \qquad (1.5)$$

Cartesian Coordinates

For a sample heated in a rectangular cross-sectional container as shown in Figure 1.1b, and considering the effect of the thermal mass of the electrodes on the heating process, the boundary conditions can be written as

$$\frac{\partial T}{\partial x}=0 \qquad \text{at x=0, (symmetry boundary)}$$

$$\frac{\partial T}{\partial y}=0 \qquad \text{at y=0, (symmetry boundary)}$$

$$k_t\frac{\partial T}{\partial x}=k\frac{\partial T}{\partial x} \qquad \text{at } x=L_s\text{, (contact between surimi and electrode)}$$

$$k_e\frac{\partial T}{\partial x}=k_c\frac{\partial T}{\partial x} \qquad \text{at } x=L_i\text{, (contact between electrode and container)}$$

$$k_c\frac{\partial T}{\partial y}=k\frac{\partial T}{\partial y} \qquad \text{at } y=L_i\text{, (contact between surimi and container)}$$

$$k_c\frac{\partial T}{\partial x}=h(T_\infty-T) \qquad \text{at } x=L_o\text{, (convection to the surrounding)}$$

$$k_c \frac{\partial T}{\partial y} = h(T_\infty - T)$$ at y= L_o, (convection to the surrounding)

$T = T_o$ at t=0 (initial condition)

and Eq. (1.3) can be written as follows:

For the surimi region

$$\frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left(k\frac{\partial T}{\partial y}\right) + Q = \rho C_p \frac{\partial T}{\partial t}$$ at $0<x< L_s$ and $0<y< L_i$ (1.6)

for the electrodes

$$\frac{\partial^2 T}{\partial x^2} + \frac{Q}{k_e} = \frac{1}{\alpha_e}\frac{\partial T}{\partial t}$$ at $L_s<x< L_i$ (1.7)

and the PVC container

$$\frac{\partial^2 T}{\partial^2 x} + \frac{\partial^2 T}{\partial^2 y} = \frac{1}{\alpha_c}\frac{\partial T}{\partial t}$$ at $L_i <x < L_o$ and $L_i <y< L_o$ (1.8)

Where

k : thermal conductivity of the sample,

k_c : thermal conductivity of the PVC container,

k_e : thermal conductivity of the electrode,

α_e : thermal diffusivity of the electrode,

α_c : thermal diffusivity of the container, and

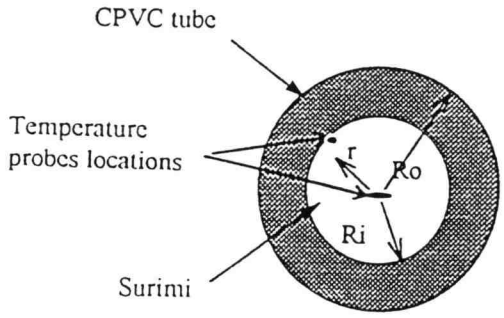
L_o, L_i, L_s : sample and PVC container dimensions.

To solve equations (1.4) and (1.6) we need to know the thermal and electrical properties of surimi as a function of temperature. The properties of CPVC, PVC and electrodes are assumed to be constant with temperature.

THERMAL CONDUCTIVITY (k)

Measuring Thermal Conductivity

Several techniques are commonly used to measure thermal conductivity. These can be grouped into steady state, transient or unsteady state, and quasi-steady state techniques. In the steady state technique, the sample material is placed between a heat source and a heat sink until it reaches a steady state condition. Thermal conductivity can be related to the rate of heat input and the temperature difference between the sample surfaces. This technique is not well suited for measuring thermal conductivity for food materials. Reaching a steady state condition in food materials with a low thermal conductivity and high moisture content, takes a long time resulting in moisture migration and property changes due to long exposure to high temperature (Murakami and Okos, 1989). The steady state technique is mostly suited for dry homogenous material having a high thermal conductivity. Transient and quasi-steady state techniques are more suitable for measuring thermal conductivity of food materials. In these techniques the running time is much shorter since reaching a steady state is not required.



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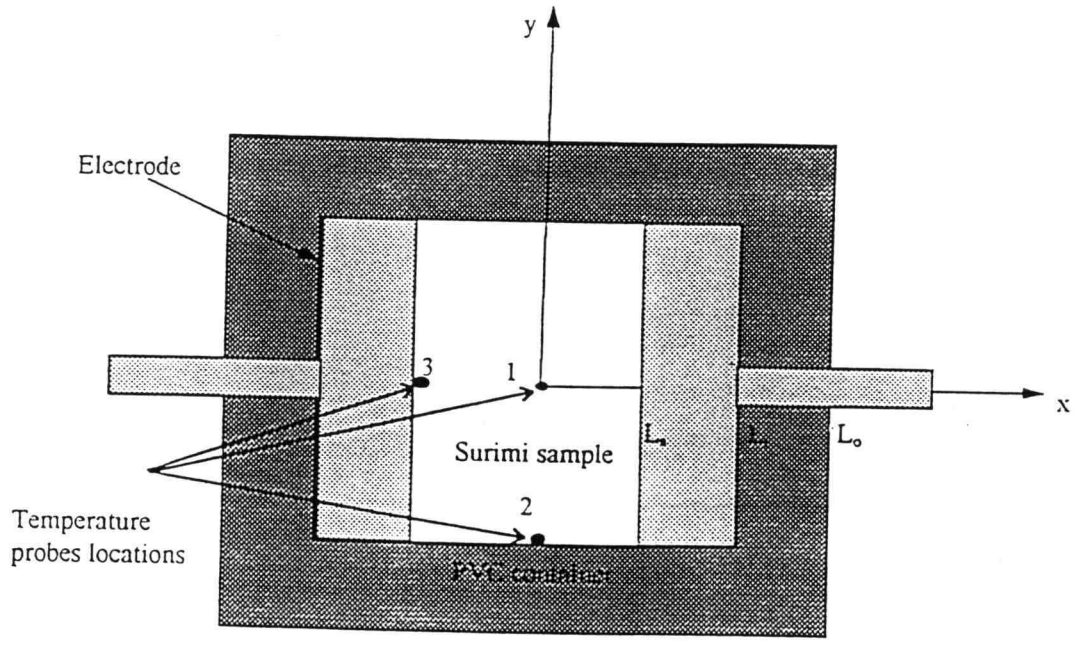

b

Figure 1.1 Cross sectional areas of a) cylindrical sample parallel to the electrodes
b) rectangular samples perpendicular to the electrodes.

The line heat source or probe method based on the transient technique has been widely used in measuring thermal conductivity of food materials due to its simplicity, speed and relatively small sample requirement. In this technique, a line heat source (heater) is introduced into a sample material resulting in a cylindrical temperature distribution. The rate in which the heat is conducted away from the source is related to the sample thermal conductivity. The probe is simply a heater wire and a thermocouple junction contained in a metal tube as shown in Figure 1.2. The theory behind the probe technique is based on the transient heat transfer equation

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T ; \qquad (1.9)$$

where α: thermal diffusivity defined by $k/\rho C_p$,

k: thermal conductivity,

C_p: Specific heat,

ρ: Density,

T: Temperature, and

t: time.

The initial and boundary conditions of the governing equation are as follow (Murakami et al. 1995):

$$T(r,t)=0 \qquad t \le 0 \qquad (1.10)$$

$$\lim_{r=0} \left(r \frac{\partial T}{\partial r}\right) = -\frac{Q}{2\pi k} \qquad t \ge 0 \qquad (1.11)$$

and

$$\lim_{r=\infty} \Delta T(r,t) = 0 \qquad t \geq 0 \qquad (1.12)$$

where ΔT is the change in temperature over a small change in the radial direction (Δr). The analysis assumes negligible thermal mass of the heater, constant power input (Q) and constant thermal properties of the sample at test temperature. This also assumes infinite length of the heat source (probe) to eliminate consideration of heat flow in the axial direction. The solution for Eq. (1.9) under these condition is therefore (Carslaw and Jaeger 1959)

$$T = \frac{Q}{4\pi k} \int_{\beta^2}^{\infty} \left[\frac{e^{-u} du}{u} \right] \qquad (1.13)$$

where $\beta = \dfrac{r}{2\sqrt{\alpha t}}$

Using series expansion, the first order exponential integral in Eq. (1.13) can be evaluated as follows: (Abramowitz and Stegun, 1964)

$$\int_{\beta^2}^{\infty} \left[\frac{e^{-u} du}{u} \right] = -C_e - \ln(\beta^2) - \sum_{n=1}^{\infty} \left[\frac{(-1)^n \beta^{2n}}{n n!} \right] \qquad (1.14)$$

where C_e is the Euler constant (0.5772).

The summation term in Eq. (1.14) can be neglected if β is kept small. β can be made small by either making the test duration as long as possible or by making the probe radius as small as possible. By satisfying the above condition, Eq. (1.14) can be rewritten as

$$\int_{\beta^2}^{\infty} \left[\frac{e^{-u} du}{u} \right] = -C_e - 2\ln\beta - \xi(\beta^2) \qquad (1.15)$$

where $\xi(\beta^2)$is the truncation error term. By neglecting the error term, Eq (1.13) reduce to

$$T = \frac{Q}{2\pi k}\left[\frac{-C_e}{2} - \ln(\beta)\right] \tag{1.16}$$

Still we cannot calculate the thermal conductivity from Eq. (1.16) because it is dependent on thermal diffusivity which is, in most cases, unknown for the test material. The thermal diffusivity term can be eliminated by evaluating Eq. (1.16) at an initial time (t_o)

$$T_o = \frac{Q}{2\pi k}\left[\frac{-C_e}{2} - \ln(\beta_o)\right] \tag{1.17}$$

then subtracting Eq. (1.17) from Eq. (1.16) to give

$$T - T_o = \frac{Q}{4\pi k}\left[\ln(\frac{t}{t_o})\right] \tag{1.18}$$

Rearranging Eq. (1.18) will give

$$k = \frac{Q}{4\pi S} \tag{1.19}$$

where S is the slope of the log-time temperature plot, $\frac{(T - T_o)}{Ln\left(\frac{t}{t_o}\right)}$.

When designing the linear heat source probe, the assumptions and simplifications made when deriving its working equation should be considered carefully. The

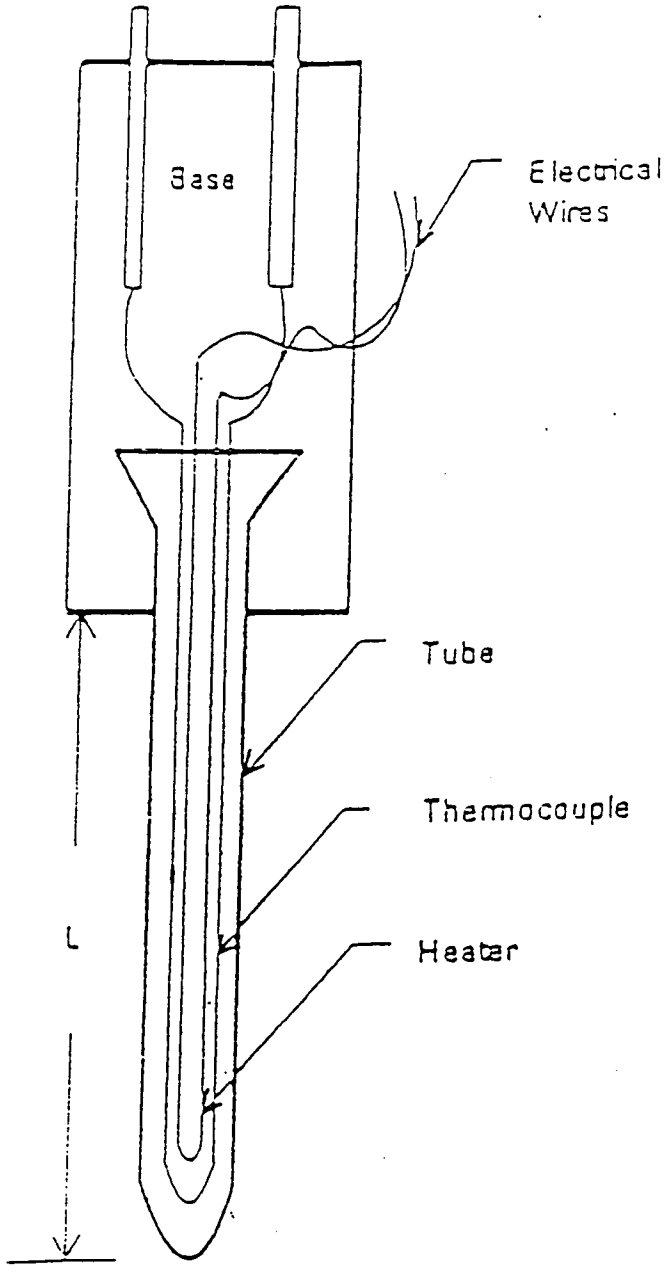

Figure 1.2 Thermal conductivity probe (Murakami and Okos, 1989)

truncation error term in Eq. (1.15) could be minimized by reducing the radius (R) of the probe to as small as possible. Voss (1955) suggested an r value less than $\frac{2}{5}\sqrt{\frac{\alpha t}{2}}$ to give a truncation error of less than 0.59%. The line heat source theory assumes no thermal mass for the heat source (probe). But in reality the probe has a finite thermal mass which absorbs some of the power output of the heater, causing a delay in heat penetration into the sample. Using an appropriate t_o corrects for this delay. Murakami et al. (1995) recommended setting t_o equal to the time when the time-temperature plot in a semi-log axis starts to become linear, as shown in Figure 1.3.

An infinite length of the heat source was assumed when deriving Eq (1.19) to eliminate the axial heat flow. But due to the finite length of the probe, heat flow in the axial direction is expected. Blackwell (1956) developed a relationship giving the axial flow error (ΔR) as a function of the probe length-to-diameter ratio ($\frac{L}{D}$) and the ratios of the thermal properties of the probe material and the sample:

$$|\Delta R|_{max} = 100\left[\frac{5.64 + 6.8x10^{-3}\delta\lambda(\varepsilon - \eta)}{\lambda \exp(0.01\lambda^2)}\right] \qquad (1.20)$$

where $\eta = \frac{k_p \alpha_s}{k_s \alpha_p}$,

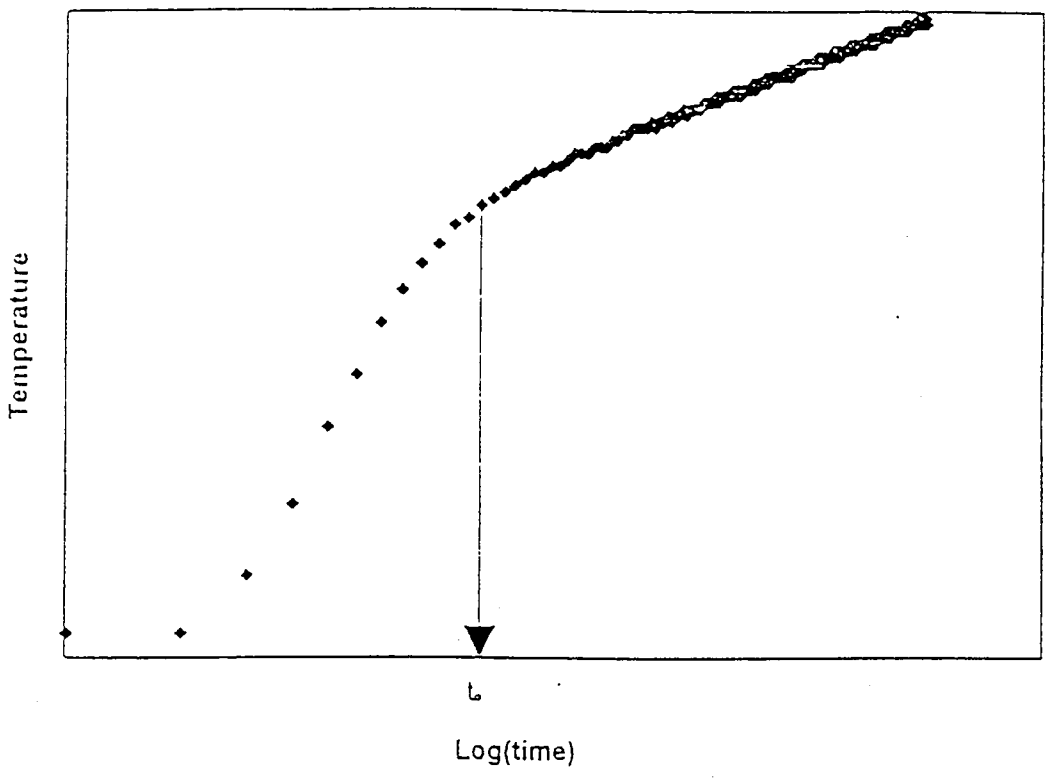

Figure 1.3 Thermal conductivity probe Log(time)-temperature plot

$$\lambda = \frac{L_P}{D_p},$$

$$\varepsilon = \frac{k_p}{k_s}, \text{ and}$$

$$\delta = \frac{2a}{r};$$

and ΔR: the error in thermal conductivity measurement.

k_p: the thermal conductivity of the probe tube,

α_p: the thermal diffusivity of the probe, and

a: the probe wall thickness.

r: distance of temperature sensor from heater.

Using this relation, Murakami et al. (1995) reported an axial flow error of less than 0.7% for a stainless steel probe with an $(\frac{L}{D})$ ratio of 30.

The probes used in this study, designed and constructed from stainless steel by V.E. Sweat (Texas A&M), had a diameter (D) of 0.6 mm and length (L) of 35mm, dimensions which satisfy the constraints discussed above. The thermal conductivity measurement apparatus used in this study is shown in Figure 1.4. Measurement procedures and experimental results for various moisture contents of surimi in the cooking temperature range are presented in Chapter 2.

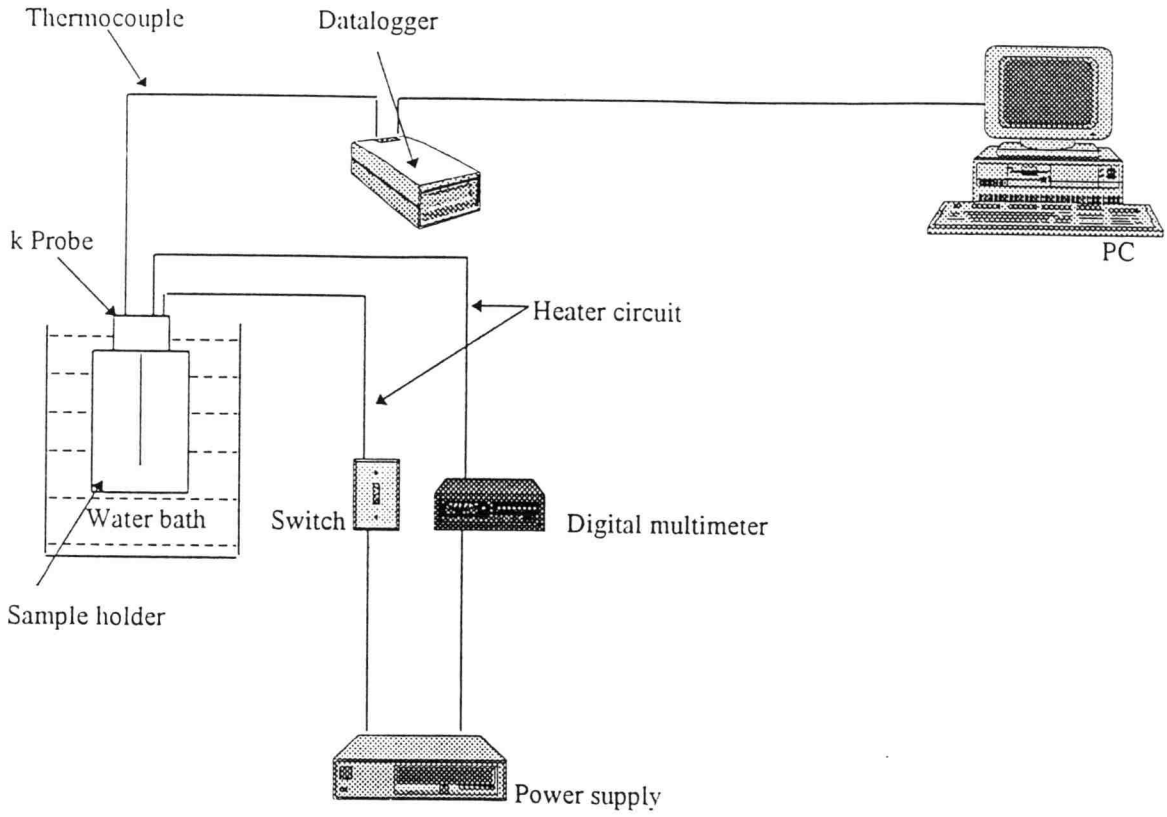

Figure 1.4 Thermal conductivity measurement apparatus.

Modeling Thermal Conductivity for Surimi

It is useful to represent the discrete experimental data points describing thermal conductivity into a continuous model over the cooking temperature range. This model then can be used in the heat transfer simulation. Several models have been proposed to predict thermal conductivity of food materials (Sweat, 1989). Some of those models were developed to predict thermal conductivity of specific food groups under specific conditions, and some were developed for general usage. Most are empirical models based on statistical curve fitting. For high moisture food materials, a linear model of the form $k=C_1+C_2M$ is commonly used (C_1 and C_2 are constants and M is the percentage of moisture content in the food material). To account for the variation of thermal conductivity with temperature a first order (or higher) temperature term is added to the above model.

Modeling thermal conductivity of food material as a function of thermal conductivities of its pure components has been investigated by several researchers. Choi and Okos (1986) expressed a relationship between thermal conductivity and the basic food components -- fat, protein, moisture, carbohydrate, fiber, and ash-- as follows

$$k = \sum_i k_i X_i^v \qquad (1.21)$$

where k_i and X_i^v are the ith component thermal conductivity and volumetric fraction respectively. The thermal conductivity of each component (k_i) is expressed

as a function of temperature. The accuracy in this model depends on the accuracy of describing thermal conductivity of each component. This assumption could limit the use of this kind of model to predict thermal conductivity for a wide range of food materials. Thermal conductivity of the components varies from one food material to another and depends on their chemical and physical forms (Sweat 1989).

A newly developed model (by S. K. Sastry) for predicting thermal conductivity of food material was also investigated in this study. The model is based on Kopelman's model (1966) by predicting thermal conductivity of food materials as the combination of continuous and discontinuous phases. The model works by breaking the food material into its basic components (water, carbohydrate, fat,...etc.). Starting with water as continuous phase and carbohydrate as discontinuous phase; then water and carbohydrate as continuous and fat as discontinuous, and continuing through all phases. Knowing thermal conductivity and volumetric percentage of each component, thermal conductivity of the food material can be calculated according to an iterative algorithm. Application of this model in predicting thermal conductivity of surimi is discussed in Appendix C.

Thermal conductivity of surimi is expected to vary with temperature, particularly in the presence of gelation (Nicklason and Pigott, 1989). Using one of the above models to predict thermal conductivity of surimi probably would not give an

accurate result since these models are built to describe thermal conductivity of homogenous food material without looking into structural changes, as we will see in Chapter 2. Predicting thermal conductivity of surimi accurately in this study is important because it affects the accuracy of the heat transfer simulation in surimi during ohmic and conventional heating. A more accurate way would be to fit an empirical model to experimental thermal conductivity data of surimi in the cooking temperature range.

Modeling thermal conductivity for surimi is discussed thoroughly in chapter 2. The accuracy of both an empirical and a composition model in predicting thermal conductivity of surimi are also presented.

APPARENT SPECIFIC HEAT (C_p)

Specific heat indicates how much heat is required to change the temperature of a material by one degree. Apparent specific heat on the other hand, includes in addition to the heat required to change the temperature, the heat required for structural or phase changes in the heated or cooled material. The specific heat has units of (J/kg-C) and is denoted by C_p.

Measuring Apparent Specific Heat

Specific heat of food material is commonly measured by one of the following methods: 1- Mixtures methods, 2- Modified mixture method, and 3- Differential

scanning calorimeter. In the mixture technique, hot water (heat exchange medium) is added to the sample material whose specific heat is to be determined. The change in the mixture temperature is then related to the sample specific heat. Since this method allows a direct contact between the sample material and the heat exchange medium, it is impossible to accurately determine the specific heat if the food material solublizes in the heat exchange medium.

The modified mixture method was developed based on the mixture method but avoiding direct contact between the sample and the heat exchange medium. One scheme is the vacuum bottle calorimeter. Based on the modified mixture method, it uses a modified household vacuum jar (thermos) in which the heat exchange medium is placed in the void between the vacuum bottle and a plastic cup holding the sample material (Wang and Hayakawa, 1979). Although the heat balance is straight-forward in this method, the heat lost or gained by the part of the vacuum bottle in contact with the sample is difficult to quantify because the entire vacuum bottle does not equilibrate to the same final temperature of the sample (Sweat, 1989).

The differential scanning calorimeter (DSC) is recommended for measuring specific heat for homogenous food materials. The DSC is well suited to determined the effect of temperature on the specific heat because it is very easy to scan over a wide range of temperature (Wang and Kolbe 1991). In the DSC, the

sample is subjected to a linear temperature increase, and the heat flow rate into the sample (relative to that into a similarly-scanned reference mass) is continuously measured; this heat flow rate is proportional to the instantaneous specific heat of the sample (O'Neill 1966). One type of "power -compensated" DSC uses two platinum alloy "cups" as the sample and reference holders . The cups are mounted in a solid aluminum block which contains a heater and a temperature sensor. A secondary temperature control system measures the temperature difference between the two sample and reference holders and adjusts this difference to zero by controlling a differential heating power. This differential power is measured and recorded. The procedure of measuring specific heat with DSC is as follows (McNaughton and Mortimer, 1975). The sample and reference mass holders with empty aluminum containers are subjected to a linear increase in temperature over a given range, and the heat flow rate with time is recorded. From the heat flow rate scan, a baseline is established as shown in Figure 1.5. The base line indicates the differential heat losses due to differences in thermal mass of the sample and reference holders. A weighed amount of sample material is then placed in one of the containers in the sample holder and then both sample and empty container are again scanned over the same temperature range. The measured heat flow rate into the sample (dH/dt) can be expressed as follows:

$$\frac{dH}{dt} = mC_p \frac{dT}{dt} \tag{1.22}$$

where dT/dt : the linear temperature increase rate, and

m : the sample mass.

The specific heat of the sample material could be evaluated using Eq. (1.22), but any systematic error in reading dH/dt or dT/dt would reduce the accuracy. To minimize such errors, the ratio method is used. In this method a reference material (sapphire is commonly used) having an accurately known specific heat, is scanned over the same temperature range. The ratio of the specific heat of the sample to that of the sapphire reference material is proportional to the ratio of the heat flows into the sample and reference as follows:

$$\frac{C_p}{C_{p_r}} = \frac{\frac{dH}{dt}}{\frac{dH_r}{dt}} \frac{m_r}{m} = \frac{y}{y_r} \frac{m_r}{m} \tag{1.23}$$

where y and y_r are the heights of the heat flow rate curve of the sample and the reference material (respectively) at a given time, as shown in Figure 1.5.

Modeling Specific Heat for Surimi

Similar to those describing thermal conductivity, models for predicting specific heat of food materials are commonly of the form C_p=C1+C2M, where the constants C1 and C2 depend on the food material being modeled. Temperature has less effect on specific heat than on thermal conductivity for moist food, because specific heat of water has less dependency on temperature. A first order temperature term added to the previous model would be sufficient (if needed).

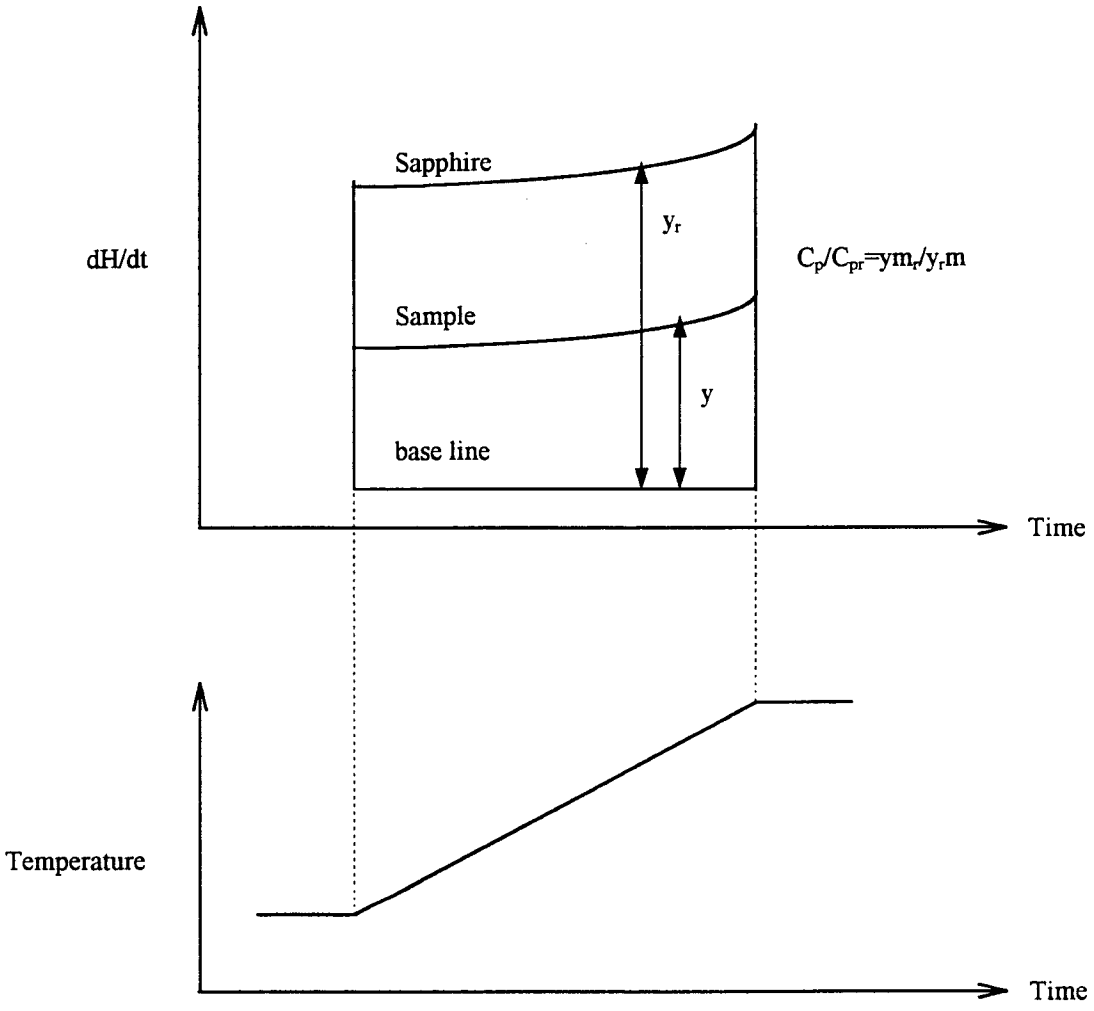

Figure 1.5 Specific heat determination by ratio method
(McNaughton and Mortimer, 1975)

Models based on food composition have also been presented. Leninger and Beverloo (1975) expressed specific heat as a function of water, fat and solid content of the food material. Choi and Okos (1986) developed a model similar to that describing thermal conductivity, except they used weight fraction instead of the volumetric fraction as follows:

$$C_p = \sum C_{p_i} X_i^w \tag{1.24}$$

Although this model would give a good estimate of specific heat for a known material composition, one cannot rely on it for accurate results. This is because the model assumes the same specific heat for the components when they are in different food materials, and this is not always true.

Apparent specific heat of surimi is expected to vary strongly with temperature due to structural changes represented by protein denaturation and gelation (Park and Lanier, 1989). Due to this structural change in surimi, modeling apparent specific heat based on its composition would not give accurate results. Structural changes in surimi and its effect on apparent specific heat are investigated in Chapter 2 of this study.

ELECTRICAL CONDUCTIVITY

Measuring Electrical Conductivity

Electrical conductivity of food materials can be found by simply applying a known voltage across the sample and measuring the current through it. The electrical resistance of the sample can then be found according to Ohms law

$$R = \frac{E}{I} \tag{1.25}$$

where R: resistance (Ω),

E: voltage across the sample (v), and

I: current through the sample (Am).

The electrical conductivity is calculated as follows (Palaniappan and Sastry 1991):

$$\sigma = \frac{1}{R}\frac{L}{A} \tag{1.26}$$

where σ: electrical conductivity (S/m),

L : sample length (m), and

A : sample cross sectional area (m^2).

Different instrument have been developed for measuring the electrical conductivity of food materials (Mitchell and de Alwis, 1989; Palaniappan and Sastry, 1991; and Yongsawatdigul et al., 1995b). The apparatus described by Yongsawatdigul et al (1995a) and shown in Figure 1.6, was used in this study. It is constructed of two

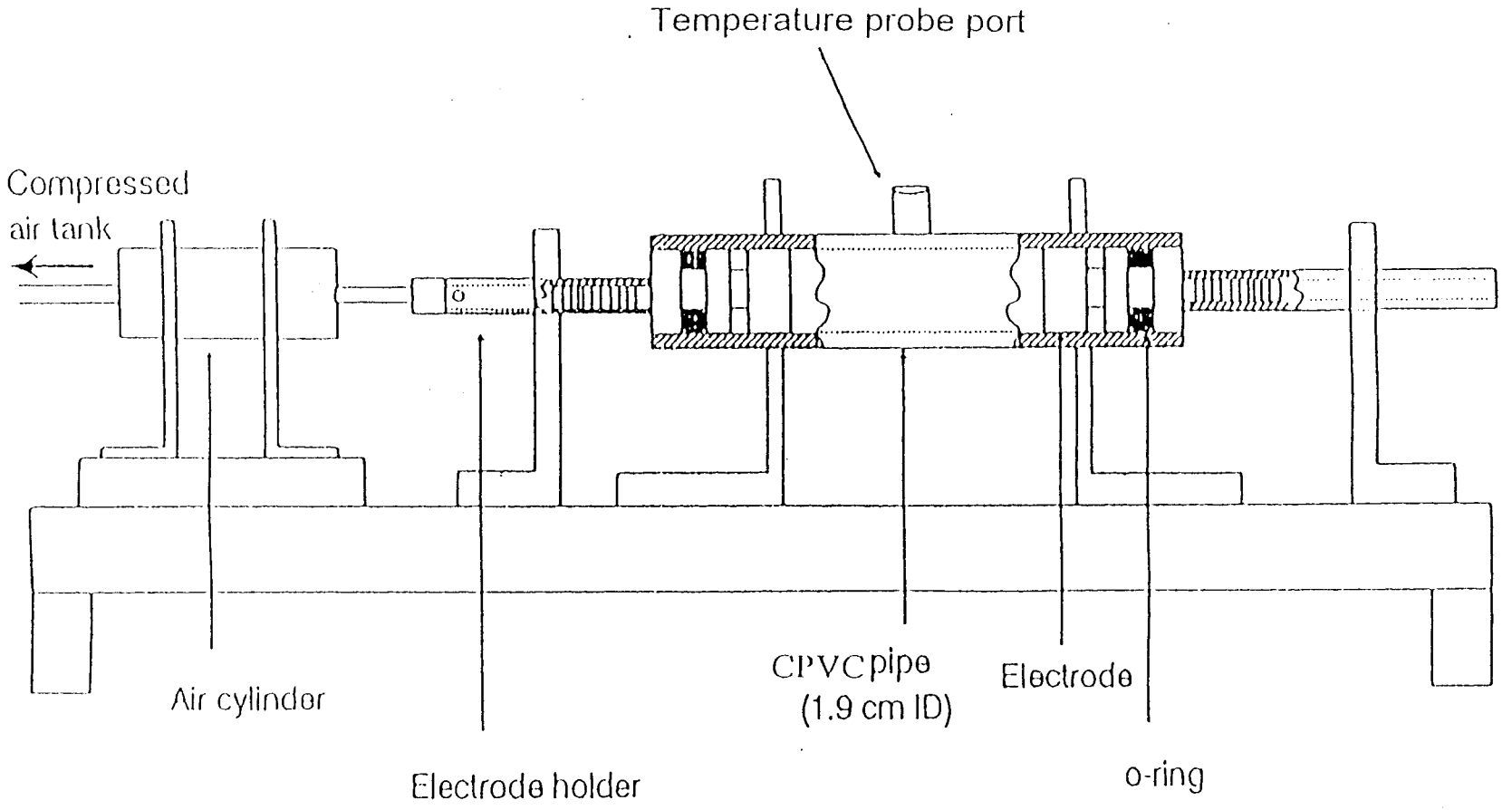

Figure 1.6 Ohmic heater apparatus

stainless steel electrodes connected to an alternating current source and pressed against sample material contained in an electrically insulating container . Voltage across, current through and temperature of the sample were measured continuously to obtain the electrical conductivity of the sample as a function of temperature. The temperature probe used to measure the temperature of the sample was sealed in a Teflon tube to eliminate electrical interference. The electrodes were electro-plated with Rhodium to minimize reaction with the food material. An air cylinder was used to apply pressure to the electrodes to ensure good contact. Construction and operation of the ohmic heater is described in detail in chapter 3 and Appendices A and B. Measured values of electrical conductivity of surimi with several moisture content in the cooking temperature range are also presented in Appendix A.

Modeling Electrical Conductivity for Surimi

Accurate prediction of electrical conductivity of surimi is important for accurate simulation of the ohmic heating process. Electrical conductivity influences the rate of heat generation as described by Palaniappan and Sastry (1991). Yongsawatdigul et al (1995b) investigated the effect of temperature and moisture and salt content in surimi. Increasing salt content increases the number of ions available for conducting electrical current, causing an increase in electrical conductivity. Ionic mobility increases with higher temperature and moisture content in surimi leading to higher electrical conductivity. The model used in this

study to predict internal heat generation in surimi during ohmic heating is presented in Appendix A of this study.

FINITE ELEMENT MODELING

The finite element method is a numerical technique for solving problems involving differential equations. For problems involving partial differential equation and complicated material properties and/or geometry it would not be possible to obtain analytical solutions (Logan 1992). In the finite element technique the body is divided into small elements and instead of solving the problem for the whole body, equations for each element within the body are formulated and combined to obtain the solution for the whole body. The elements into which the body is divided could be lines for a one-dimension (1-D) problem, areas of different shapes for a two-dimension (2-D) problem and volumes for a three-dimension (3-D) problem. This study used the PDEase package, a finite element analysis for partial differential equations (Macsyma Inc. Arlington, MA). For our 2-D problem, the cross sectional area of the sample is divided into triangular areas. The governing equation to be solved for each element will appear as

$$\frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right)+\frac{\partial}{\partial y}\left(k\frac{\partial T}{\partial x}\right)+Q=\rho C_p\frac{\partial T}{\partial t} \tag{1.27}$$

Temperature within each element is defined as follows

$$T=[N]\{t\} \tag{1.28}$$

where N is the shape function matrix and {t} is the nodal temperature vector. For a triangular element shown in Figure 1.7 (Logan 1992),

$$[N] = [N_1 \quad N_2 \quad N_3] \qquad \text{and} \qquad \{t\} = \begin{Bmatrix} t_1 \\ t_2 \\ t_3 \end{Bmatrix} \tag{1.29}$$

where $N_1 = \frac{1}{2A}(\alpha_1 + \beta_1 x + \gamma_1 y)$ (1.30)

$$N2 = \frac{1}{2A}(\alpha_1 + \beta_2 x + \gamma_2 y) \tag{1.31}$$

$$N_3 = \frac{1}{2A}(\alpha_3 + \beta_3 x + \gamma_3 y) \tag{1.32}$$

and

$$\alpha_1 = x_2 y_3 - y_2 x_3, \qquad \alpha_2 = x_1 y_3 - y_2 x_1, \qquad \alpha_3 = x_1 y_2 - y_1 x_1,$$

$$\beta_1 = y_2 - y_3, \qquad \beta_2 = y_3 - y_1, \qquad \beta_3 = y_1 - y_2,$$

$$\gamma_1 = x_3 - x_2, \qquad \gamma_1 = x_1 - x_3, \qquad \text{and } \gamma_1 = x_2 - x_1. \tag{1.33}$$

PDEase used the Galerkin method to solve the governing equation of our problem. Using the nodal function as the weighted residual function (Stasa 1985), we get

$$\int_{A^e} [N]^T \left[\frac{\partial}{\partial x}\left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y}\left(\frac{\partial T}{\partial y} \right) + Q - \rho C_p \frac{\partial T}{\partial t} \right] dxdy = 0. \tag{1.34}$$

By integration over an element area (A^e), and using the Green-Gauss theorem we get

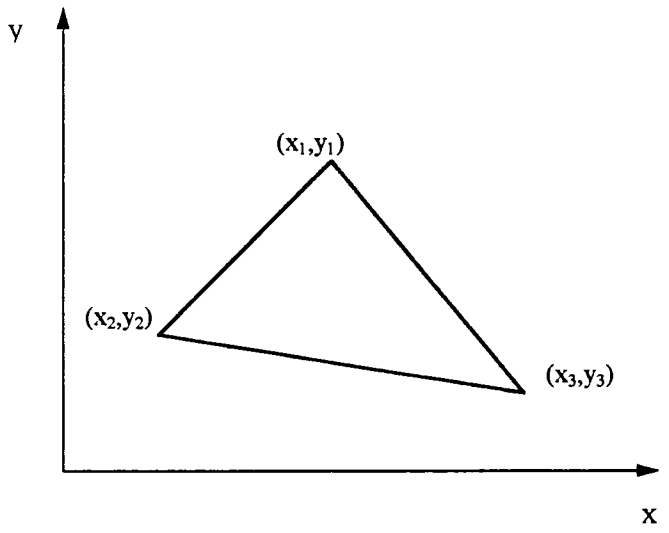

Figure 1.7 Basic triangular element

$$\int_{C^e}[N]^T k\frac{\partial T}{\partial x}dC - \int_{A^e}\frac{\partial[N]^T}{\partial x}k\frac{\partial T}{\partial x}dxdy + \int_{C^e}[N]^T k\frac{\partial T}{\partial y}dC - \int_{A^e}\frac{\partial[N]^T}{\partial y}k\frac{\partial T}{\partial y}dxdy + \int_{A^e}[N]^T Q dxdy - \int_{A^e}[N]^T \rho C_p \dot{T} dxdy = 0 \quad (1.35)$$

where C is the element boundary.

From the definition of the outward heat flux (q_n)

$$q_n = -k\frac{\partial T}{\partial x} - k\frac{\partial T}{\partial y} \quad (1.36)$$

the two integrals around the element boundary in Eq.(1.35) can be written as

$$\int_{C^e}[N]^T\left(k\frac{\partial T}{\partial x} + k\frac{\partial T}{\partial y}\right)dC = \int_{C^e}[N]^T(-q_n)dC. \quad (1.37)$$

Describing a convection boundary condition, and performing energy balance on the global boundary follows as

$$q_n = h(T - T_\infty). \quad (1.38)$$

Substituting Eq. (1.38) in Eq. (1.37), we get

$$\int_{C^e}[N]^T(-q)dC = -\int_{C^e}[N]^T hT dC + \int_{C^e}[N]^T hT_\infty dC \quad (1.39)$$

Substitute Eqs. (1.38) and (1.39) in Eq. (1.35) and rearrange,

$$\left[\int_{A^e}\left(\frac{\partial[N]^T}{\partial x}k\frac{\partial[N]}{\partial x} + \frac{\partial[N]^T}{\partial y}k\frac{\partial[N]}{\partial y}\right)dxdy + \int_{C^e}[N]^T h[N]dC\right]\{t\} + \left[\int_{A^e}[N]^T\rho C_p[N]dxdy\right]\left\{\dot{t}\right\} = \int_{A^e}[N]^T Q dxdy + \int_{C^e}[N]^T hT_\infty dC \quad (1.40)$$

Now define an element conduction [k] and lumped mass [m] matrices and an element nodal force vector {f} as follows:

$$[k]=\left[\int_A \left(\frac{\partial[N]^T}{\partial x} k \frac{\partial[N]}{\partial x}+\frac{\partial[N]^T}{\partial y} k \frac{\partial[N]}{\partial y}\right) dxdy+\int_C [N]^T h[N] dC\right] \tag{1.41}$$

$$[m]=\left[\int_A [N]^T \rho C_p [N] dxdy\right] \tag{1.42}$$

$$\{f\}=\int_A [N]^T Q dxdy+\int_C [N]^T h T_\infty dC \tag{1.43}$$

Rewriting Eq. (40) in terms of Eqs. (1.41), (1.42) and (1.43) we get

$$\{f\}=[k]\{t\}+[m]\left\{\dot{t}\right\} \tag{1.44}$$

Similarly for cylindrical coordinates the conduction and the lumped mass matrices and the nodal force vector will be

$$[k]=2\pi\left[\int_A \left(\frac{\partial[N]^T}{\partial r} k \frac{\partial[N]}{\partial r}+\frac{\partial[N]^T}{\partial z} k \frac{\partial[N]}{\partial z}\right) drdz+\int_C [N]^T h[N] dC\right] \tag{1.45}$$

$$[m]=2\pi\left[\int_A [N]^T \rho C_p [N] drdz\right] \tag{1.46}$$

$$\{f\}=2\pi\left[\int_A [N]^T Q drdz+\int_C [N]^T h T_\infty dC\right] \tag{1.47}$$

For an (n) element body we define the global conduction and lumped mass matrices as follows:

$$[K]=\sum_{e=1}^{n}[k] \tag{1.48}$$

and

$$[M]=\sum_{e=1}^{n}[m] \tag{1.49}$$

The global force matrix{F}can be written as follows

$$\{F\} = [K]\{T\} + [M]\left\{\dot{T}\right\} \tag{1.50}$$

Now we need to numerically integrate Eq.(1.50) with respect to time. Assuming temperature T_i and T_{i+1} at time t_i and t_{i+1} respectively, using the Galerkin method for numerical time integration we get

$$T_{i+1} = T_i + \left[\frac{1}{3}\dot{T}_i + \frac{2}{3}\dot{T}_{i+1}\right]\Delta t \tag{1.51}$$

Now we rewrite Eq. (1.50) for time t_i and time t_{i+1}, then multiplying the first of these equations by 1/3 and the second by 2/3, we get

$$\frac{1}{3}F_i = \frac{1}{3}\left(K_i T_i + M_i \dot{T}_i\right), \text{ and} \tag{1.52}$$

$$\frac{2}{3}F_{i+1} = \frac{2}{3}\left(K_{i+1} T_{i+1} + M_{i+1} \dot{T}_{i+1}\right) \tag{1.53}$$

Adding Eqs. (1.52) and (1.53) and using Eq. (1.51) to eliminate the time derivative term, we get

$$\frac{M_{i+1}T_{i+1} - M_i T_i}{\Delta t} + \frac{1}{3}K_i T_i + \frac{2}{3}K_{i+1}T_{i+1} = \frac{1}{3}F_i + \frac{2}{3}F_{i+1} \tag{1.54}$$

Rewriting Eq. (1.54) to give

$$\left(\frac{1}{\Delta t}M_{i+1} + \frac{2}{3}K_{i+1}\right)T_{i+1} = \left[\frac{1}{\Delta t}M_i - \frac{1}{3}K_i\right]T_i + \frac{1}{3}F_i + \frac{2}{3}F_{i+1} \tag{1.55}$$

Given a known initial temperature T_o at t=0 and a time step Δt, Eq. (1.55) can be solved for T_1 at time $t=\Delta t$. Using T_1, T_2 can be found at time $t=2(\Delta t)$ and so on.

The matrix Eq.(1.50) is solved at each time step using the Gauss elimination method.

THESIS OUTLINE

Besides the introduction, this Thesis includes two chapters and three appendices. In Chapter 2, thermal and physical properties (thermal conductivity, specific heat and density) of surimi are measured and models as a function of temperature. An additional modeling technique for thermal conductivity of surimi is presented in Appendix C. In Appendix A, a model for electrical conductivity of surimi is developed. Appendix B is a coauthered and published paper that discusses the effect of heating rate on gelation in surimi. Using the thermal, physical, and electrical property models for surimi described in Chapter 2 and Appendix A., a heat transfer simulation for surimi heated using ohmic and water bath heating is developed in Chapter 3.

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Chapter 2

Thermophysical Properties of Surimi Paste at Cooking Temperature *

by

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ABSTRACT

Thermal conductivity, specific heat and density of Pacific whiting surimi paste with 74, 78, 80 and 84% moisture content were measured and modeled over the cooking temperature range. Thermal conductivity and specific heat were measured using a linear heat source probe and differential scanning calorimitry (DSC) respectively. Both thermal conductivity and specific heat were found to increase with increasing moisture content and temperature. Surimi density was found to decrease with increasing moisture content and temperature. Empirical models for each property, as a function of temperature and moisture content, were fitted based on the experimental data.

INTRODUCTION

Surimi is an intermediate raw material used to make seafood analogs. It is made from minced and washed fish meat with up to 8% added sugar and sorbitol as cryoprotectant. When ground with salt, the myofibrillar protein in surimi becomes solubleized. The resulting paste is valued for its ability to form an elastic gel during cooking. Surimi made from Pacific whiting (*Merluccius productus*) has a protease enzyme throughout its tissue, and this tends to destroy the gel network during heat setting of surimi-based product, such as crabsticks and imitation shrimp (Lee et al., 1990). Enzyme inhibitors, such as beef plasma protein, whey protein concentrate and potato extract, are used to control the softening effect of the enzyme (Morrissey et al., 1993). These enzyme inhibitors may have some limitation due to cost, labeling restrictions or sensory effects. A rapid and controlled rate of heating through the enzyme-active temperature range has been shown to be an alternative, since rapid heating inactivates the enzyme before it can affect the gel network(Yongsawatdigul et al., 1995).

One method of effecting a rapid and controlled rate of heating is with the used of ohmic "resistance" heating, in which an alternating current passes through the food medium between electrodes (Shiba 1992). Utilizing ohmic heating in the industry will require a full understanding and control of the process. Simulating the ohmic heating process can result from a numerical solution for the partial differential

equations. However, for accurate results we need an accurate prediction of temperature-dependent thermal properties (thermal conductivity "k", specific heat "C_p" and density "ρ") for surimi paste in the cooking temperature range.

Models to predict thermal properties for each of a large variety of food materials cannot be found in the literature. Thus general models have been developed to predict thermal properties of food materials based on their composition (fat, protein, water, etc.). Using these models, thermal properties for any food material with known composition can be predicted. Choi and Okos (1986) expressed relationships between thermal conductivity and specific heat as a function of the basic food components (fat, protein, moisture, carbohydrate, fiber and ash) as follows:

$$k = \Sigma\, k_i X_i^{v} \qquad (2.1)$$

$$C_p = \Sigma\, C_{pi} X_i^{w} \qquad (2.2)$$

where k_i and C_{pi} are the thermal conductivity and specific heat values of each component as a function of temperature. X_i^{v} and X_i^{w} are the volumetric and weight fraction of the ith component respectively. In the above models, it is assumed that each component has the same thermal properties in different food materials, but this is not always true. For example, thermal conductivity of beef protein is different than that of milk protein (Sweat 1986).

Empirical models of thermal conductivity developed for each specific food material would give more accurate prediction. The utility of both general and empirical thermal property models for surimi paste are investigated in this study.

We found no published reports concerning the measurement and modeling of thermal properties of surimi paste at cooking temperatures. Wang and Kolbe (1990, 1991) measured thermal conductivity and specific heat for frozen surimi. Nicklason and Pigott (1989) predicted thermal conductivity and specific heat for surimi paste using the equations of Riedel and Dickerson (respectively) as reported by Charm (1978). They used those predicted values to calculate the heating rate in surimi paste during conventional cooking. Their calculated rate was within 20% of the experimental values. The researchers concluded that the change in thermal properties of surimi paste with temperature was responsible for this error.

Several methods are available to measure thermal conductivity, and these fall into general categories of steady state and transient techniques (Murakami and Okos 1989). The steady state technique works well for non-biological materials but is not well suited for food materials because of long temperature equilibration time required, moisture migration in the sample, and large sample size required (Sweat 1986). This method is thus most suitable for dry homogenous materials having a moisture content no more that 10% (Mohsenin 1980). One commonly used transient technique --the linear heat-source probe-- has been frequently used for

thermal conductivity measurements in solids, plastics and other materials (Sweat et al., 1973). In this technique, a line heat source (heater) is introduced into a sample material resulting in a cylindrical temperature distribution (Murakami and Okos 1989). The rate at which the heater temperature rises is related to the sample thermal conductivity. The linear source probe has gained popularity in measuring thermal conductivity for food materials because of its simplicity, speed and relatively small sample requirement. Some such as probe and sample sizes and test duration have been recently addressed by Murakami et al. (1994). Sweat et al. (1973, 1974) used this technique to measure thermal conductivities of fruit, vegetables and chicken meat in the non-frozen range.

For specific heat measurement, differential scanning calorimetry (DSC) as described by McNaughton and Mortimer (1975) has been commonly used. The DSC method works by comparing the heat flow rate into a sample material to that of a standard material when both are subjected to the same linear rate of temperature increase. The specific heat for the sample material can then be obtained as a function of temperature. DSC is well suited for determining the effect of temperature on specific heat of food samples. It works rapidly and simply and a very small sample can give accurate results. Total enthalpy change will also result from DSC as shown by Iso et al. (1991) who measured these data for fish and chicken paste. This then enables calculation of an "apparent specific heat" which includes both a temperature change and a thermal transition. Wang and

Kolbe (1991) used DSC in partially frozen surimi to find an apparent specific heat that included latent heat of fusion for the water fraction.

The objective of this study is to measure thermal conductivity, specific heat and density at cooking temperature for surimi having a range of moisture contents. paste under cooking temperatures. From the measured data a suitable model for each property is investigated.

MATERIALS AND METHODS

Materials

Pacific whiting was supplied by local fishermen to a plant in Waranton, OR within 12 hours of catch. Minced and washed product in their surimi line was then packed in ice and delivered to OSU Seafood Lab (Astoria, OR) within 30 minutes of processing. Surimi was then prepared by mixing the washed mince with 4% sucrose, 4% sorbitol (ICI Specialties, New Castle, DE) and 0.3% sodium tripolyphosphate (B.K. Ladenburg Corp. Cresskill, NJ). Surimi samples were vacuum packed in 500g trays , frozen and stored in a -30°C freezer.

Sample Preparation

Frozen surimi samples were thawed at ambient temperature (22°C) for 2 hours. A weighed amount of salt (NaCl) and beef plasma protein (BPP) were mixed with

each surimi sample for three minutes in a Stephan chopper (model UM 5 universal, Stephan Machinery Co. Columbus, OH). Ice was added to the sample to adjust the final moisture content, and then mixed for three minutes under vacuum (addition of ice ensured that the mixture remains at temperature below 10°C). Four different surimi paste samples were prepared with 2% salt, 1% BPP, and moisture contents of 74, 78, 80 and 84% , wet weight basis. BPP was added to inhibit the softening enzyme in surimi (Morressey et al., 1993). Having a proper gel network is important in our study to find the effect of gelation on thermal properties.

Thermal Conductivity

Apparatus: The linear heat source probe technique was used to measure thermal conductivity for surimi paste. The equipment used in this study appears in Figure 2.1. The thermal conductivity probes were purchased from V.E. Sweat (Texas A&M University). The probe encloses a heater wire and thermocouple junction contained in a hypodermic needle (D= 0.6 mm, L= 35.5 mm). Construction of the line heat-source probe is described by Sweat (1989).

The sample holder was a film capsule (5 cm x 3 cm diameter) insulated at both ends. The sample temperature was controlled by a VWR Scientific 1120 water bath (VWR Scientific Inc., Niles, Il) to within ± 1°C. For current source and measurement in the heater circuit we used a Micronta power supply with 0 -1.4 Amps range and Micronta digital multimeter (DMM) respectively. An external

switch was used to minimize any time delay in the circuit. Time-temperature data were recorded using a Campbell 21X datalogger (Campbell Scientific, Inc., Logan, UT) with a maximum scanning rate of 25 reading per second. The datalogger was interfaced with a PC and the data analyzed using Quattro Pro spread sheet. The apparatus was calibrated against a 0.4% agar gel sample.

Method: Thermal conductivity values for Pacific whiting surimi paste with four different moisture contents (74,78,80 and 84%) were measured over the temperature range of 30 to 80°C. Surimi paste samples were packed in sample holders (film capsules) within minutes of mixing, then a thermal conductivity probe was inserted into each sample through a hole in the film capsule lid. Four samples for each moisture content surimi were then placed in thin latex bags, immersed in the controlled temperature water bath and allowed to equilibrate to the 30C bath temperature over a period of 45-60 min. The power for the heater wire in the k probe was turned on, and time-temperature data for the four samples were recorded by datalogger at a rate of 20 reading per second. After bath temperature adjustment and equilibration (another 45-60 min.), reading were next taken at temperatures of 40, 50, 60, 70 and 80°C. Because preliminary experiments indicated no difference in k values when using a new sample vs. the same sample at each temperature, the same sample for each moisture content was used for k measurement at all temperatures Thermal conductivity (k) was then calculated from,

$$k = \frac{q^{\backprime}}{2\pi} \frac{\ln(t_e / t_o)}{(T_e - T_o)}$$ (Sweat 1986). (2.3)

Where

$\ln(t_e/t_o)/(T_e-T_o)$ is the slope of the t-T Plot.

Power level ($q^{\backprime}$) in the heater circuit was 7.2 W/m. A short experiment time was chosen to avoid edge effect, caused by heat transfer at the outer sample surface (Murakami et al., 1995). To linearize the t-T plot, the initial time (t_o) in the above equation was set to equal the time when the nonlinear portion of t-T plot ends (Murakami et al, 1995). For each t-T plot, the slope was found using simple linear regression.

Specific Heat

Specific heat for surimi paste was measured using a DuPont 910 differential scanning calorimeter (DSC) (DuPont Company, Wilmington, DE). Three surimi paste samples (8-10 mg) for each moisture content value were sealed in aluminum pans and weighed on a Mettler microbalance (model AE 240, Mettler-Toledo Inc., Highstown, NJ). Five scans were run for each moisture content value: a baseline (empty aluminum pan), standard material (Sapphire), and three surimi paste sample replicates. Each sample was scanned from 10 to 90°C at a heating rate of 10°C/min. Prepared samples were kept packed in ice throughout the experiment to prevent pre-setting (low temperature gelling). Specific heat (C_p) was calculated using the ratio method,

$$C_p = \frac{E\,q}{H\,m} \qquad \text{(McNaughton and Mortimer 1975)} \qquad (2.4)$$

DSC heat capacity software (TA Instruments Inc., New Castle, DE) was used for these calculation of specific heat.

Density

Density of surimi paste was measured at three different temperatures (25, 60 and 90°C) for each moisture content value. Surimi paste was extruded into a known weight stainless steel cylinder (D=19 and L=178 mm) using a sausage stuffer with horn diameter of 12.4 mm. Although vacuum packing of the samples would give a higher density and perhaps better quality gel (Babbitt and Reppond 1988), it was not used in this study to insure similarity with procedure used in the seafood analog industry. The samples were then placed in a controlled water bath and allowed to expand freely as it gelled. At each test temperature the excess surimi was termed and the sample weighed using Mettler balance (model PM 2000, Mettler-Toledo Inc., Highstown, NJ). Four replicates were used for each moisture content level.

RESULTS AND DISCUSSION

Thermal Conductivity

Thermal conductivity values for Pacific whiting surimi paste at several moisture contents and temperatures appear in Table 1. Standard deviations ranged between

0.1 to 5% with higher deviations found at the higher temperatures. Thermal conductivity of surimi paste increased with increasing temperature and moisture content, a behavior seen in other high moisture content foods. The increase in thermal conductivity with increasing moisture content is due to the higher thermal conductivity of water compared to that of other surimi paste components.

Earlier experiments investigated the effect of gelation on thermal conductivity by recording more data points around the expected gelling temperature range (40 to 50°C). No sudden change in thermal conductivity was observed. This indicates a possible pre-setting in the samples, in which gelation starts at a low temperature, due to the slow heating rate. It is possible that there is little difference in thermal conductivity between paste and gel at given temperature.

Two different models conceded for prediction of thermal conductivity in surimi paste: the Choi and Okos (1986) model and an empirical model fitted to the experimental data. The Choi and Okos model, based on a multi-component system, describes the thermal conductivity of food material as a function of the thermal conductivity of each component and its volumetric fraction. The thermal conductivity of each component, in this model, is expressed as a function of temperature.

A second order multiple regression model for thermal conductivity as a function of moisture content and temperature was fitted as follows:

$$k=1.33- 4.82x10^{-3}T + 5x10^{-5}T^2 - 2.45x10^{-2}M + 1.7x10^{-4}M^2 + 2.4x10^{-5}MT \quad (2.5)$$

The second order terms of both temperature and moisture content were included for a better fit. A positive coefficient of MT indicates a higher increase in thermal conductivity of surimi paste with increasing temperature at higher moisture level. The regression has a coefficient of determination (r^2) of 0.93.

The predicted thermal conductivity values from the two models are plotted along with the experimental values($\pm$ standard deviation) for 74 and 84% moisture content surimi paste in Figures 2.2a-b. Since the regression model is based on the experimental data, it has better fit with an average error of 1.6%, while the Choi and Okos model has an average error of 4.3%. This deviation in the Choi and Okos model suggests that the structural change in surimi paste during cooking, such as gelation and protein denaturation, has an effect on the thermal conductivity. The Choi and Okos model was meant to describe change in thermal conductivity of homogenous material without consideration of structural change (Gratzek and Toledo 1993).

Apparent Specific Heat

Apparent specific heat recorded on the DSC will include both heat capacity and any endothermic gelation; these values for different moisture contents and

temperatures are listed in Table 2. Specific heat for surimi paste was found to increase with both moisture content and temperature, a behavior found with most moist foods (Sweat 1986). The temperature-specific heat graphs for 74 and 84% moisture content surimi paste, Figures 2.3a-b , show the effect of myosin and actin denaturation, endothermic reactions with characteristic maxima around 45 and 75°C respectively (Park and Lanier 1989). The endothermic peaks are higher at low moisture content due to higher protein concentration (Akahane et al., 1980).

A linear model for the specific heat of Pacific whiting surimi paste as a function of temperature and moisture content was fitted to the experimental specific heat data,

$$C_p = 2.33 + 0.006\ T + 0.0149\ M \qquad (2.6)$$

Although the linear regression did accommodate the denaturation peaks, it has a good overall fit with an average error of 0.75%, and an r^2 of 0.92, and considered a workable engineering model in most design circumstances. Johnsson and Skjoldebrand (1983) suggested a correlation between specific heat of any food material and the individual specific heat values of water and solids,

$$C_p = X_w C_{pw} + (1-X_w) C_{ps} \qquad (2.7)$$

C_p for water is almost constant (4.2 J/g-C) in the temperature range 30 to 80°C. C_p for the solid substance was assumed to have a linear relationship with temperature,

$$C_{ps} = aT + b \qquad (2.8)$$

Using our experimental data for specific heat, a and b were found to be 0.0295 and 0.8651 respectively with an average error of 0.92%. The Choi and Okos (1986) model for specific heat was also considered. A plot of the regression model, the Johnsson and Skjoldebrand (J&S), the Choi and Okos models and the experimental data (± standard deviation) for 74 and 84% moisture content surimi paste samples are shown in Figures 2.3a-b. The Choi and Okos model did not fit the experimental data well in the high temperature range, with a maximum deviation from the experimental data of 9% at 90°C. This support the assumption that the structural change in surimi paste during cooking affects its thermal properties. The regression model has slightly better fit than that of Johnsson and Skjoldebrand.

Density

Experimental data for Pacific whiting surimi paste density at various moisture contents and temperatures are listed in Table 3. A multiple linear regression model was fitted to the experimental data as follows:

$$\rho = 1511.2 - 1.16\,T - 5.4\,M \qquad (2.7)$$

Both the temperature and moisture content terms have a negative coefficient indicating a decrease in the density with increasing moisture content and temperature. Experimental density data (± standard deviation) and the regression model for 74 and 84% are appears in Figure 2.4. The regression has r^2 of 0.87.

The density of Pacific whiting surimi paste decreased with increasing moisture content due to lower density of water than the rest of the component except for fat. Protein denaturation, a process in which the spatial arrangement of the protein chains within the molecule is changed from that typical of the native protein to a more disordered arrangement (Ziegler and Acton 1984), was responsible for the decrease in density with increasing temperature.

In the absence of experimental thermal properties data for surimi paste made from other fish species, models developed in this study could give a good prediction of these properties. This is valid because of the similarity in the composition of different kinds of surimi paste.

ACKNOWLEDGMENT

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Moisture	74%		78%		80%		84%	
T (C)	k	%SD	k	%SD	k	%SD	k	%SD
30	0.524	1.9	0.534	0.2	0.536	1.0	0.567	1.0
40	0.525	2.4	0.539	2.0	0.570	2.0	0.577	0.5
50	0.550	1.5	0.570	2.4	0.571	0.9	0.577	0.5
60	0.601	1.3	0.565	6.4	0.587	1.3	0.613	3.1
70	0.600	1.8	0.610	0.9	0.610	1.2	0.632	2.7
80	0.630	2.0	0.680	3.5	0.683	0.7	0.708	4.8

Table 1. Thermal conductivity of Pacific whiting surimi (W/m-C)

Moisture	74%		78%		80%		84%	
T (C)	C_p	%SD	C_p	%SD	C_p	%SD	C_p	%SD
25	3.53	3.4	3.542	1.7	3.571	3.4	3.697	1.9
30	3.594	3.3	3.651	2.8	3.682	4.1	3.827	1.8
35	3.669	3.3	3.780	4.8	3.759	4.3	3.867	1.8
40	3.747	3.2	3.798	4.2	3.766	3.5	3.853	1.3
45	3.784	2.6	3.813	2.6	3.800	2.9	3.876	1.3
50	3.771	2.7	3.808	1.8	3.798	2.6	3.886	1.3
55	3.779	2.9	3.811	1.6	3.817	2.4	3.909	1.3
60	3.801	2.9	3.848	1.6	3.843	2.3	3.942	1.3
65	3.833	2.9	3.879	1.5	3.875	2.1	3.977	1.3
70	3.890	3.1	3.920	1.5	3.910	2.0	4.018	1.2
75	3.905	3.1	3.953	1.5	3.921	2.0	4.045	1.2
80	3.906	3.3	3.959	1.5	3.965	2.0	4.096	1.5
85	3.939	3.6	3.985	1.5	3.993	1.8	4.132	1.5
90	3.980	3.5	4.033	2.0	4.040	1.7	4.182	1.4

Table 2. Apparent specific heat of Pacific whiting surimi (J/g-C)

Moisture	74%		78%		80%		84%	
T (C)	ρ	%SD	ρ	%SD	ρ	%SD	ρ	%SD
30	1080	1.0	1067	1.1	1047	1.1	1043	1.2
60	1053	0.9	1036	1.0	1005	1.3	1002	1.3
90	1010	0.6	993	1.3	962	0.5	947	0.4

Table 3. Density of Pacific whiting surimi (kg/m^3)

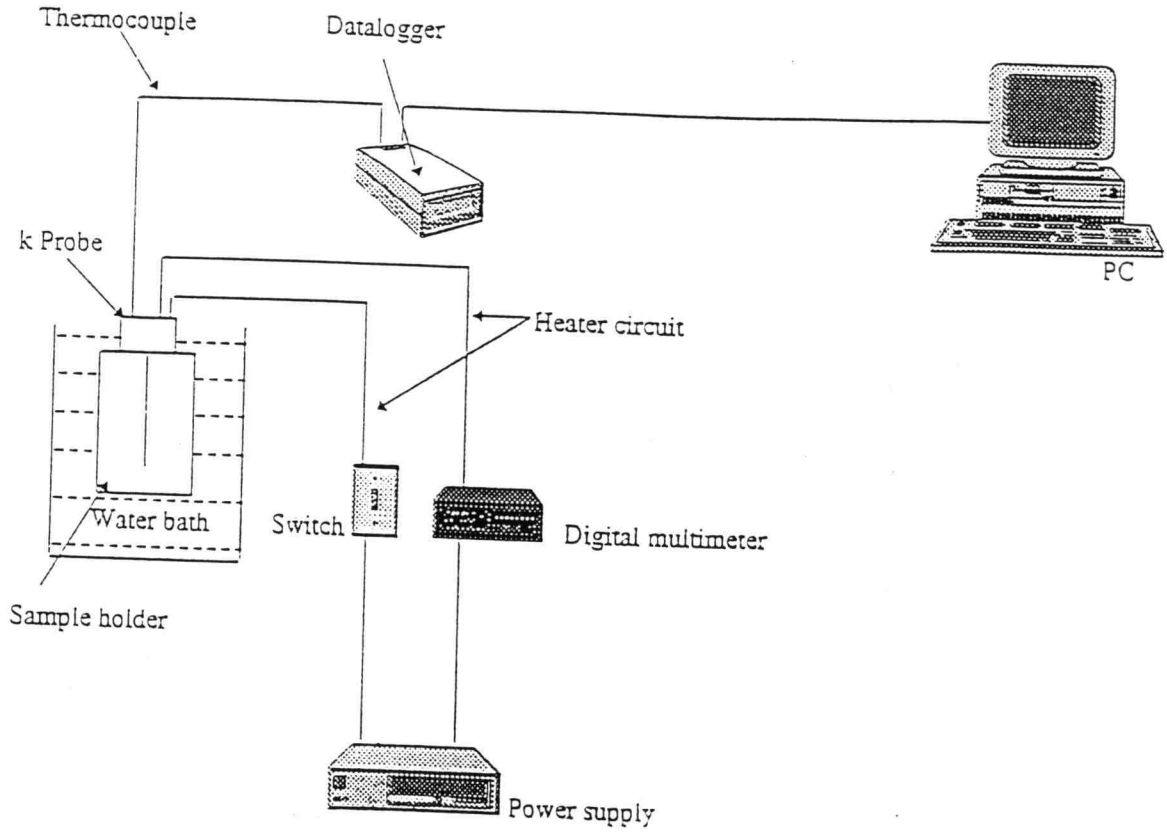
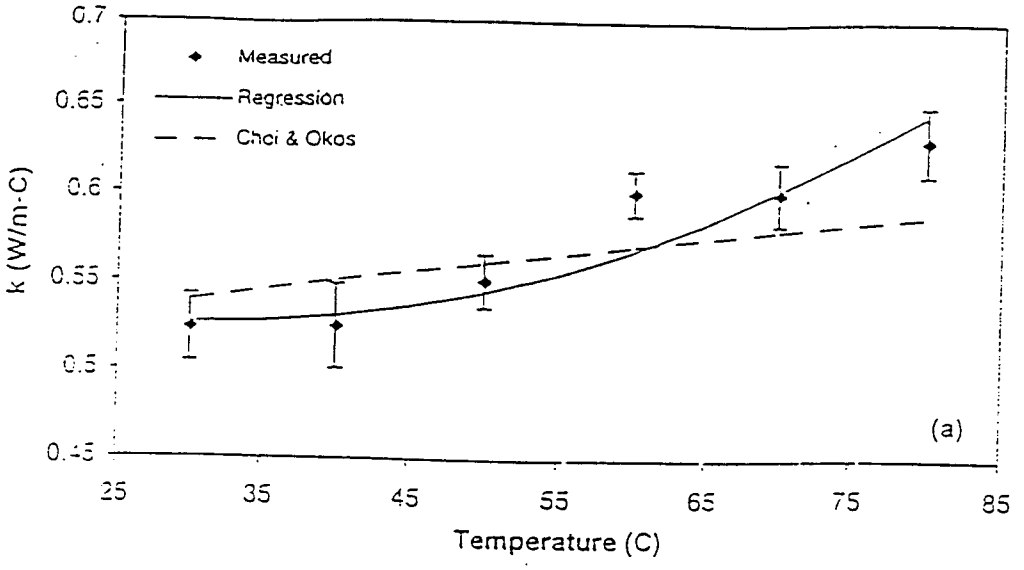
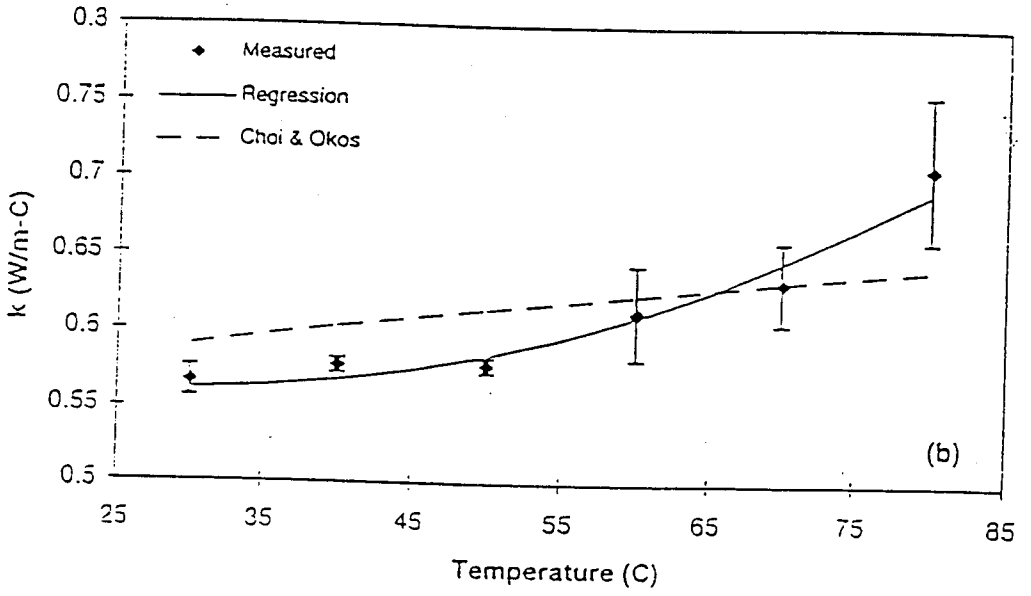
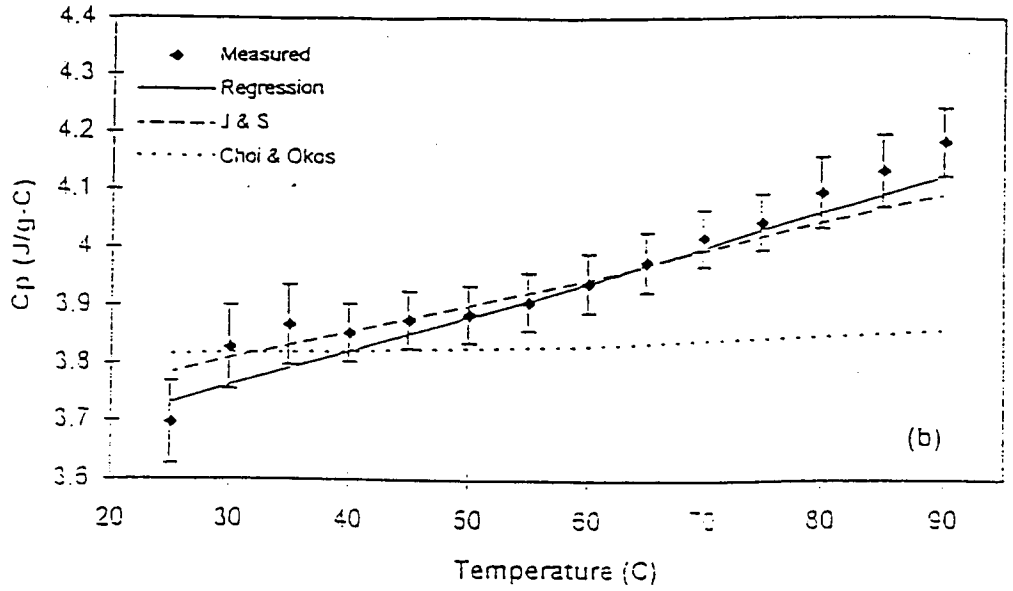


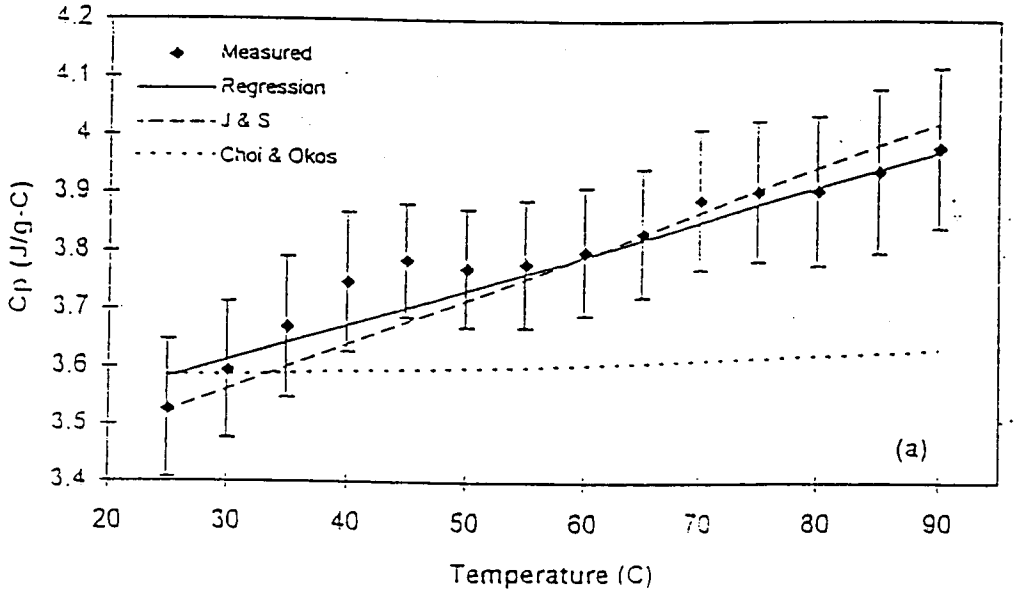
Fig. 2.1 Thermal conductivity measurement apparatus.



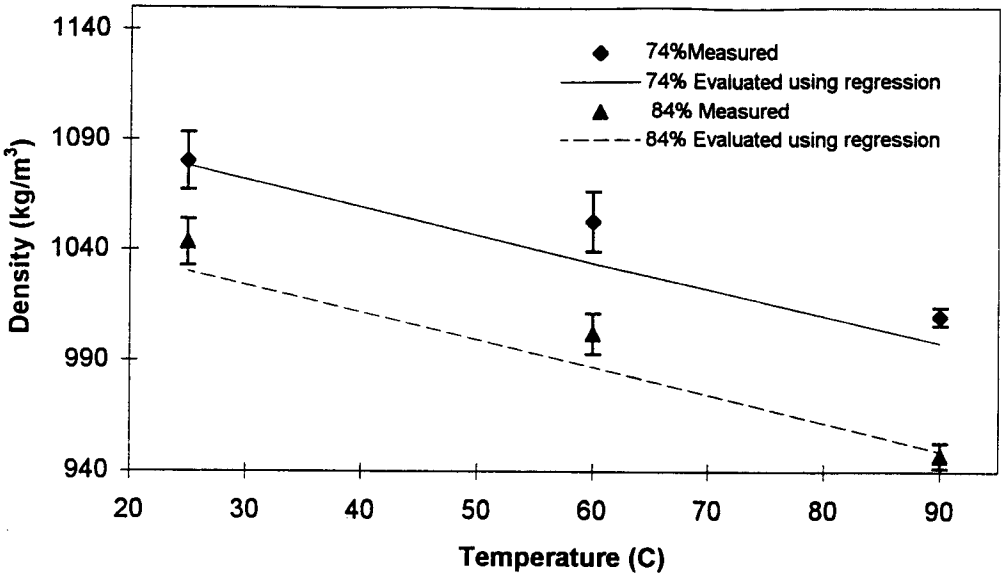


Figures 2.2a-b Thermal conductivity of pacific whiting surimi paste. (a) 74% moisture; (b) 84% moisture





Figures 2.3a-b Specific heat of pacific whiting surimi paste. (a) 74% moisture; (b) 84% moisture



Figures 2.4 Density of Pacific whiting surimi paste with 74% and 84% moisture content

NOTATION

C_p: Specific heat (J/g-°C)

C_{pi}: Specific heat of the ith component (J/g-°C)

C_{ps}: Specific heat of solid substance (J/g-°C)

C_{pw}: Specific heat of water (J/g-°C)

D: Diameter (m)

E: DSC constant

k: Thermal conductivity (W/m-°C)

k_i: Thermal conductivity of the ith component (W/m-°C)

H: Heating rate (°C/min.)

L: Length (m)

M: Moisture content (%)

m: Sample mass (kg)

q: Heat flow rate (W)

$q^{\backprime}$: Heat generation rate per unit length (W/m)

T, T_e, T_o :Temperature, final temperature, initial temperature(°C)

t, t_e, t_o: Time, final time, initial time(sec)

t-T plot: Time-temperature plot in a semi-log scale.

X_w: Water weight fraction

X_i^v: Volumetric fraction of the ith component.

X_i^w: Weight fraction of the ith component

ρ: Density (kg/m^2)

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Chapter 3

Analysis of Heat Transfer in Surimi Paste Heated by Conventional and Ohmic Means*

by

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ABSTRACT

Heating rates by conventional and ohmic means were measured and modeled over the cooking temperature range for Pacific whiting surimi paste having moisture contents of 74% and 80% and salt content of 2%. A good comparison with simulation results was found using a model derived from finite element analysis. An ohmic heating rate (under 1200V/m) was 11 times higher than that of conventional (90°C water bath) heating for cylindrical sample of 19mm diameter. The effects of voltage gradient across the sample, moisture content, heat leakage to the surrounding and electrode design were also investigated. Heat leakage to the sample holder and surroundings caused a significantly lower heating rate in the outer edges of the sample compared to the center. A good electrode design is essential to avoid heat loss to the electrodes.

INTRODUCTION

Pacific whiting represents the largest biomass of commercial stock on the west cost of the United States, but it has had limited usage, due to a protease-related tissue softening after harvest (Lee et al., 1989). The principal problem relates to protease enzymes that are present throughout the muscle tissue and which cause rapid softening upon heating. Pacific whiting is widely used for surimi, a commercially valuable washed minced product. When solublized with salt (the surimi "paste") and heated, it has the ability to form an elastic gel, used in the seafood analog industry to manufacture surimi-based products such as crabsticks and imitation shrimp. Typically, enzyme inhibitors are added to Pacific whiting surimi to inhibit the protease activity, preventing distruction of the gel network during heat setting. The protease enzyme has a maximum activity in the temperature range between 45-60° C (Wasson, 1992).

Several protease inhibitors have been tested and used in surimi; these include beef plasma protein (BPP), egg white, whey protein concentrate and potato starch (Morrissey et al 1993). The inhibitors generally control the softening effect of the enzyme, but there have been limitations in their use due to labeling concerns, expense, and high concentration required. Thus, a processing alternative is needed when the addition of inhibitors becomes undesirable. An alternative could be a rapid and controlled heating process which could inactivate the softening enzyme

before it affects the gel network. Ohmic heating, which passes an alternating current between electrodes through the food medium, is a potential method of rapid heating (de Alwis and Fryer 1990a, Parrot 1992, Sastry and Palaniappan 1992a). The electrical resistance of the medium causes " *resistance heating*" that increases its temperature more rapidly and more uniformly than is possible when heat is conducted from the outer boundaries.

Most of the recent applications of ohmic heating are in the sterilization of liquid-solid food mixtures. Use of conventional heating to sterilize food mixtures in steam jacketed tubing may result in food quality loss due to overcooking of the liquid phase and particle surfaces (Halden et al., 1990). In the ohmic heating process, the heat is internally generated, and the problem of conducting heat from outside boundaries is avoided. The rate of heat generated depends on the electrical conductivity of the food material.

Recently, Japanese investigators have used ohmic heating in cooking Pollock surimi paste. Shiba (1991) reported a very rapid heating rate using ohmic heating (47°C/min.) compared to conventional water-bath heating (0.9°C/min.). Yongsawatdigul et al. (1995a & b) also used ohmic heating to cook Pacific whiting surimi. Both studies reported higher gel quality in surimi cooked by ohmic heating.

To use ohmic heating in industry, a full understanding of the process is needed. Trying to experimentally determine the heating rate for industrial-scale equipment would be costly and time consuming. Developing a heat transfer model for the process will help reduce the experimental work. De Alwis and Fryer (1990b), Sastry and Palaniappan (1992b), Sastry (1992) and Fryer and Li (1993) modeled the heating process for ohmically-heated liquid-solid food mixtures.

To model the ohmic heating process, the transient heat transfer equation with an internal heat source must be solved. This in turn requires an accurate prediction of temperature-dependent thermal and electrical properties of the heated material.

The objective of this study was to support design of industrial-scale processes by simulating the heat transfer process in surimi paste during ohmic and conventional heating under different conditions. The parameters that most affect the heating rate are also investigated. The simulation was carried out numerically using finite element methods within a software package called PDEase (Macsyma Inc. Arlington, MA).

MATERIALS AND METHODS

Materials

Pacific whiting was supplied by local fishermen to a plant in Waranton, OR within 12 hours of catch. Minced and washed product in their surimi line was then packed in ice and delivered to OSU Seafood Lab (Astoria, OR) within 30 minutes of processing. Surimi was then prepared by mixing the washed mince with 4% sucrose, 4% sorbitol (ICI Specialties, New Castle, DE) and 0.3% sodium tripolyphosphate (B.K. Ladenburg Corp. Cresskill, NJ). Surimi samples were vacuum packed in 500g trays , frozen and stored in a -30°C freezer.

Sample Preparation

Frozen surimi samples were thawed at ambient temperature (22°C) for 2 hours. A weighed amount of salt (NaCl) was mixed with surimi for three minutes in a Stephan chopper (model MU 5 Universal, Stephan Machinery Co. Columbus, OH). When mixed with salt the myofibrillar protein in surimi solublized, forming a paste. Ice was added to the resulting paste, to adjust the final moisture content, then mixed for three minutes under vacuum. Two different surimi paste samples were prepared with 2% salt and moisture contents of 74 and 80% , wet weight basis.

Conventional Heating

Surimi paste was stuffed into a stainless steel tube (ID=19mm, L=178mm) using a sausage stuffer with horn diameter of 12.4mm. The sample was then sealed and heated in a 90°C water bath. The temperatures at the geometric center and at the outer edge of the sample were measured using 0.04 in. diameter T-type temperature probes (Omega Engineering Inc. Stanford, CT), recorded every 30 seconds in a Campbell 21X datalogger (Campbell Scientific Inc., Logan, UT). The samples were kept in the water bath until the temperature at the center reached 90°C. Two replicates were used for 74 and 84% moisture content.

Ohmic Heater Apparatus

The Ohmic heater apparatus was developed by the authors at Oregon State University. A schematic diagram of the ohmic heating apparatus for the cylindrical sample is shown in Figure 3.1. The electrodes were made from type 316 stainless steel. Two different geometric sample holders were used; one, a 3/4-inch CPVC tube (ID=19mm, L=205mm); the second, a PVC cubic container (L=51mm). A cross sectional view of each appears in Figure 3.2a-b. Temperatures at several locations in the samples were measured by T-type temperature probes and recorded in a Campbell 21X datalogger. Each temperature probe was sealed in a 0.05 in. inner diameter Teflon tube to eliminate any electrical interference. The voltage across the sample was controlled by a 0-300 V transformer. Voltage

across and current through the sample were measured by transducers and recorded by the datalogger. An air cylinder (Bimba Mfg. Co., Monee, IL) connected to a compressed air tank was used to press electrodes against the sample to insure good contact. The ohmic heater apparatus for the cylindrical sample is described in detail by Yongsawatdigul et al (1995a). The same apparatus was modified for the cubic sample by replacing the circular cross sectional electrodes with square ones.

Ohmic Heating Procedure

Two different sample holders were used; a CPVC cylindrical tube and a PVC cubic container. Surimi paste was stuffed into the cylindrical sample holder using a sausage stuffer. Two temperature probes were inserted into the sample through holes in the sample tube walls. One of the probes was placed at the geometric center and the other at the outer edge of the sample, Figure 3.2a. For the cubic sample holder, surimi paste were packed by hand. Three temperature probes were inserted into the sample, one at the geometric center, the second at the electrode face at its center and the third at the inner surface of the PVC container, as shown in Figure 3.2b. The electrodes were then inserted into each end of the sample holders, pressurized using the air cylinder, then heated to 90°C using alternating current of 60 Hz. Heating rates for surimi paste with moisture contents of 74% and 80% (two replicates of each) were studied under two voltage levels. Time-temperature data were recorded every second using the datalogger.

MATHEMATICAL MODELING

Simulating the heating rate in ohmically heated surimi calls for solving the general transient heat transfer equation with an internal heat generation source. The transient heat transfer equation, is a second-order partial differential equation defined as follows:

$$\nabla(k\nabla T) + Q = \rho C_p \frac{\partial T}{\partial t} \tag{3.1}$$

Thermal conductivity (k), specific heat (C_p) and density (ρ) of surimi paste in the cooking temperature range are described as a function of temperature and moisture content by AbuDagga and Kolbe (1995) as follows:

$$k = 1.33 - 4.82 \times 10^{-3} T + 5 \times 10^{-5} T^2 - 2.45 \times 10^{-2} M + 1.7 \times 10^{-4} M^2 + 2.4 \times 10^{-5} MT \tag{3.2}$$

$$C_p = 2.33 + 0.006 T + 0.0149 M \tag{3.3}$$

$$\rho = 1511.2 - 1.16 T - 5.4 M \tag{3.4}$$

The internal heat generation per unit volume (Q) can be found according to the following relation:

$$Q = \sigma V^2 \tag{3.5}$$

where V is the voltage gradient across the sample and σ is the electrical conductivity per unit length. For Pacific whiting surimi paste, this has been determined as a function of temperature, moisture content and salt content by Yongsawatdigul et al (1995a) as follows

$$\sigma = 0.1168 + 0.0083\ T - 2.511\ N + 0.0385\ MN +$$
$$0.02229\ TN + 0.0282\ N^2 \qquad (3.6)$$

A constant voltage gradient across the sample was assumed.

Sample Geometry

Cylindrical Sample: In this case we need to solve Eq (3.1) in the cylindrical coordinate, assuming infinite cylinder (no heat loss to the electrodes). Eq (3.1), in the surimi region (as shown in Figure 3.2a), can be written in cylindrical coordinates as:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(k\frac{r\partial T}{\partial r}\right) + Q = \rho C_p \frac{\partial T}{\partial t} \qquad (3.7)$$

For the outer CPVC tube region, there is no heat generation and assuming constant properties; Eq (3.1) then can be written as:

$$\left(\frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2}\right) = \frac{1}{\alpha}\frac{\partial T}{\partial t} \qquad (3.8)$$

Although surimi is a homogenous material, temperature, and thus temperature-dependent thermal properties are expected to vary in the radial direction.

Since the temperature solutions in each region (surimi and CPVC) are coupled, solutions to Eqs (3.7) and (3.8) need to be equal at the boundary. The boundary conditions for these equation are: a symmetric boundary at the center (r=0), an equal heat flux an temperature value at the contact between the two regions ($r=R_i$)

assuming perfect contact (Ozisik 1992), and convection heat transfer at the outer surface of the CPVC tube ($r=R_o$) as shown in Figure 3.2a.

Rectangular cross section sample: A cross sectional drawing of the sample container and the electrodes is shown in Figure 3.2b. A two dimensional model was built for this case. Although a three dimensional model would be more accurate, the heat loss in the Z direction is about 0.2 % of the internally generated heat in worst case. In two dimensional Cartesian coordinates Eq. (3.1) for the surimi region is written as follow:

$$\frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right)+\frac{\partial}{\partial y}\left(k\frac{\partial T}{\partial y}\right)+Q=\rho C_p\frac{\partial T}{\partial t} \tag{3.9}$$

For the electrodes

$$\frac{\partial^2 T}{\partial x^2}+\frac{Q}{k_e}=\frac{1}{\alpha_e}\frac{\partial T}{\partial t} \tag{3.10}$$

and for the PVC container

$$\left(\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}\right)=\frac{1}{\alpha_c}\frac{\partial T}{\partial t} \tag{3.11}$$

A perfect contact between the sample, electrodes and the container walls was assumed in simulating this case. Constant thermal properties of CPVC and PVC were assumed. For CPVC: ρ=1400 kg/m^3, k= 0.13 W/m-C and C_p = 1340 J/kg-C; for PVC: ρ=1540 kg/m^3, k= 0.14 W/m-C and C_p = 1340 J/kg-C (Modern Plastic Encyclopedia, McGraw Hill, Highstone, NJ).

RESULTS AND DISCUSSION

Conventional Heating

Two different moisture content surimi cylindrical samples were heated in the 90°C water bath in a horizontal position. The free convection heat transfer coefficient (h in W/m^2-C) between the cylinder and the hot water was measured as a function of surface temperature using the lumped mass method and found to be as follows

$$h = (1.94 \times 10^{10})/ T^5 \quad (W/m^2\text{-}C) \qquad (3.12)$$

where T is the stainless steel tube surface temperature (°C).

The average heating rate was 6.25 and 4°C/min. for the 80% and 74% moisture content samples respectively. The sample with higher moisture content had higher heating rate because it has higher thermal conductivity (AbuDagga and Kolbe, 1995). Under the free convection boundary condition and assuming perfect contact between the surimi sample and the stainless steel tube, Eq (3.7) was solved without the internal heat generation term (Q). Results appear in Figure 3.3a-b. The simulation agrees with the experimental temperature within 5%.

The center of the sample was in the protease enzyme active temperature range (45-60°C) for an average of 85 sec. This time was found to be enough for the softening enzyme to affect the gel network in surimi resulting in a low gel strength as reported by Yongsawadigul (1995b). A simulation of heat transfer in Conventionally-cooked surimi packed in 30mm and 48 mm diameter casing shows

even slower heating rates and longer times in the enzyme active temperature range (210 and 390 seconds, respectively), as shown in Figure 3.3c. These casing sizes are actually more-frequently used in the surimi industry to test gel strength than the smaller stainless steel tubes.

Ohmic Heating

Cylindrical sample: Samples of 74 and 80% moisture content were heated using the ohmic heater under two different voltage levels. Because of the Teflon shielding on the temperature probes, there was a time constant of about 4 sec and this was used to adjust for the time delay in temperature readings. The average heating rates of the 74% moisture content surimi under 1200 and 680 V/m were 55 and 16°C/minute respectively, while the average heating rates for the 80% moisture content surimi under the 1200 and 630 V/m were 58 and 12 °C/sec. With the assist of the commercial partial differential equation package (PDEase) the calculated heating rate along with the experimental data are plotted in Figure 3.4 for the 74% moisture sample and in Figure 3.5 for the 80% moisture content sample. The calculated heating rate for the center of the sample had lower deviation from the experimental data with an average error of 3.5% (in the temperature range between 20 to 90), while that of the edge has a higher error (6.5%). Error in predicting thermal and electrical properties of surimi paste is probably partially responsible for this error. Slow response in temperature probes and uncertainty in their location may also account for part of this error. Using

constant thermal, physical and electrical properties for surimi at 50°C (an average error of about 4.25% in thermal diffusivity "$k/\rho C_p$" and 20% in electrical conductivity) in simulating the heat transfer results in a large error (more than 25%) compared to the experimental data as shown in Figure 3.4

The electrically-heated samples were kept in the enzyme-active temperature range (45-60°C) for an average of 24 sec which is much less than that of the conventional heating. The temperature difference between the center and the edge of the sample is due to the heat loss to the CPVC tube and convection to the surroundings (a constant free convection heat transfer coefficient of 5 W/m^2-°C was used in this model according to Osizik 1993). Figure 3.6 shows the temperature distribution in a cross sectional area of ohmically heated cylindrical sample predicted by the heat transfer model for 80% moisture surimi after 80 sec.

Cubic Sample: The sample thickness in the cubic configuration was 25mm; voltage was adjusted to give a gradient of 1200 V/m. The heating rate was measured in three locations in the surimi region. The measured heating rate of surimi in contact with the electrode is close to that of the center as can be seen in Figure 3.7. For ideal conditions (perfect contact and no resistance between the electrodes and surimi) the heating rate of surimi in contact with the electrode should be lower than that at the center due to the heat loss to the electrodes, as shown by calculation in Figure 3.7. A possible explanation of the lower heating

rate could be due to a build up of gases resulting from electrolytic activity between electrodes and sample. Those gases reacted with the electrode surfaces, causing a corrosion. Consequently a high voltage drop is expected at the electrodes surfaces due to the heigh electrical resistance. This voltage drop would lead to a lower heat generation in the sample itself. The decrease in voltage drop across the sample sample with time shown in Figure 3.8, suggests that the built up gas layer and corrosion problem gets worse with time, creating an unstable system. This might suggest that any gases in the cylindrical case would have been immediately pushed out into edge and annulus in the electrodes. The design of the electrodes(flat in the rectangular sample, convex in the cylinder) and the higher pressure (250 kPa maximum pressure in the rectangular sample compared to 450 kPa for the cylindrical one) helps to push the gases out in the cylindrical case.

Parameters affecting heating rate

Heat leakage to the surroundings: Heat leakage through the sample holder walls to the surroundings affects the heating rate of the sample, especially at the edges. This heat leakage could be greatly diminished by using a sample holder made of high heat insulation material. A simulation of ohmic heating for the cylindrical sample and assuming perfect insulation, shows an increase in heating rate of approximately 25%. Externally heating the sample holder walls during ohmic heating would also eliminate heat leakage to the surroundings. Using a 90°C water

jacket as an added heat source around the sample during ohmic heating would result in a predicted 40 % increase in the heating rate of the sample.

Voltage Gradient: Increasing the voltage (or voltage gradient) across the sample results in a higher heating rate. Increasing the voltage by an average of 1% resulted in 3.7% increase in the heating rate. This large increase in the heating rate with voltage results from the quadratic dependency of the internal heat generation on the voltage as shown in Eq (3.5).

Moisture Content: Although electrical conductivity and consequently the internal heat generation increase with moisture content, moisture content did not have a big effect on the heating rate (a 1% increase in moisture content results in 0.6% increase in heating rate). This is because the specific heat also increases with moisture content. Higher specific heat means higher energy is needed to increase the temperature of surimi. Moisture content level in surimi is constrained by the product and typically ranges from 74 % to 84%.

Electrodes: Any practices which improve the assumed "perfect" contact between electrodes and sample is highly recommended to prevent resistance heating of the interface. A near-perfect electrode contact can be achieved by designing the electrodes in a way that allows an escape for trapped gases. A high pressure on the electrode surface will also help force a good contact. Electrodes are typically

considered a heat sink due to their high diffusivity, so decreasing the electrode mass would lower the heat loss to it.

CONCLUSION

Application of ohmic heating was found to provide a higher rate of heating than that of conventional heating in a 90°C water bath. Surimi heated conventionally is thus expected to have a lower gel quality because it is kept in the softening enzyme active temperature region for longer time, as summarized in Table 1. Voltage gradient across the sample, moisture content, heat leakage to the surrounding, and electrode design were all shown to affect the heating rate. The heating rate increased with voltage gradient, moisture content, a reduced leakage to the sample holder and the surrounding. A poor contact between sample and electrodes also causes heat generation at the electrode surface and resulted in a lower heating rate in surimi.

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Heating Method	*ID (mm)*	*Moisture (%)*	*Time in enzyme active range (exp.) in sec.*	*Time in enzyme active range (model) in sec.*
Ohmic heating (1200v/m)	19	80	11	10
Ohmic heating (1200v/m)	19	74	13	12
Conventional	19	80	80	72
Conventional	19	74	90	83
Conventional	30	80	-	210
Conventional	48	80	-	390

Table 3.1 Time the center of cylindrical sample kept in the softening enzyme-active temperature range (45-60°C) using different heating methods and sample sizes.

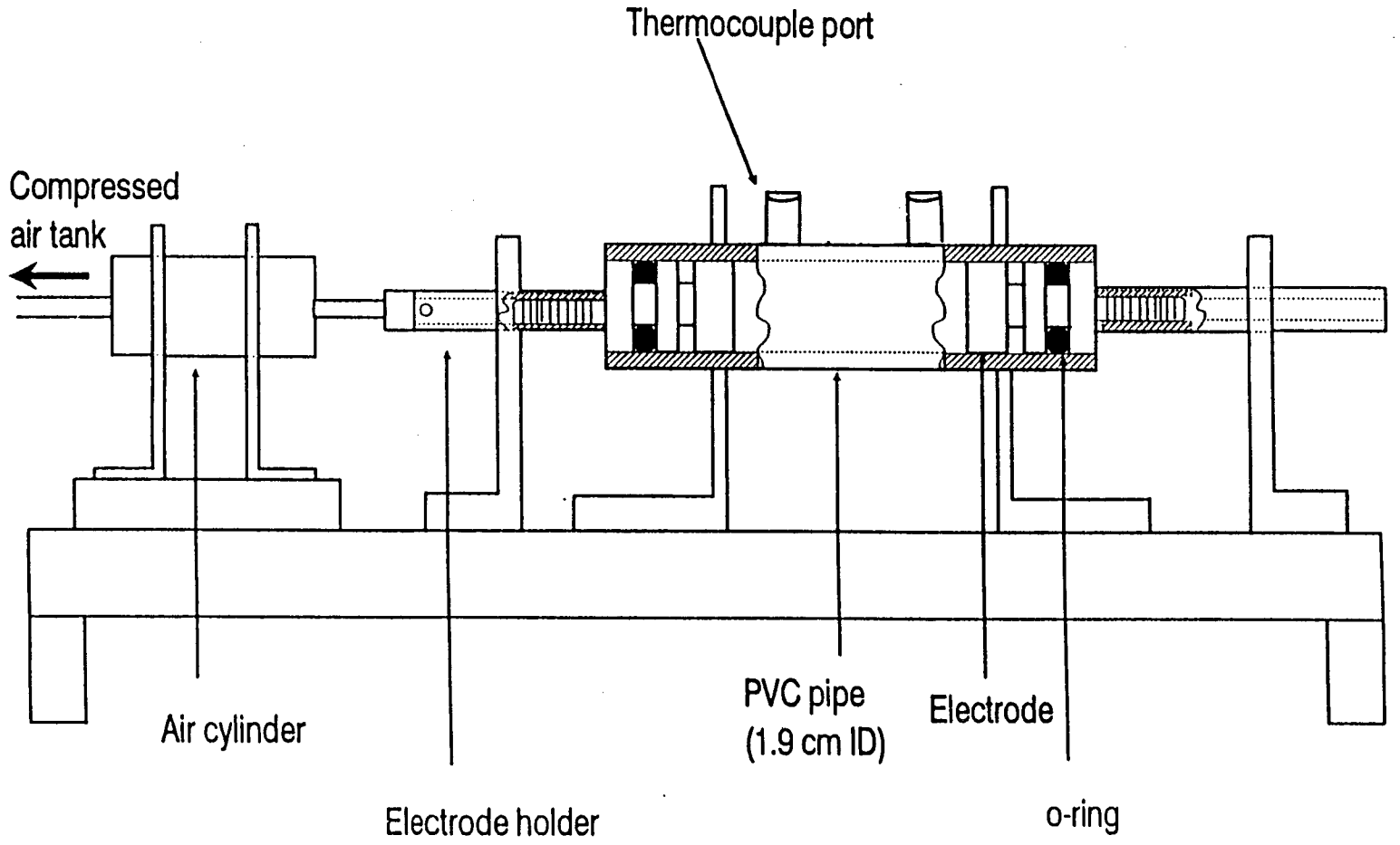
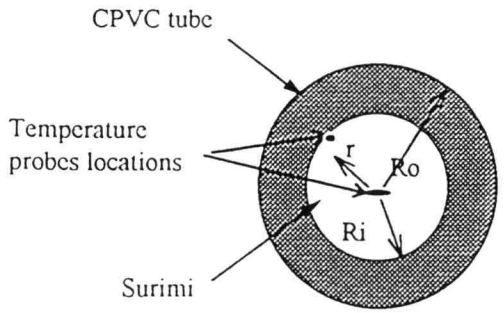
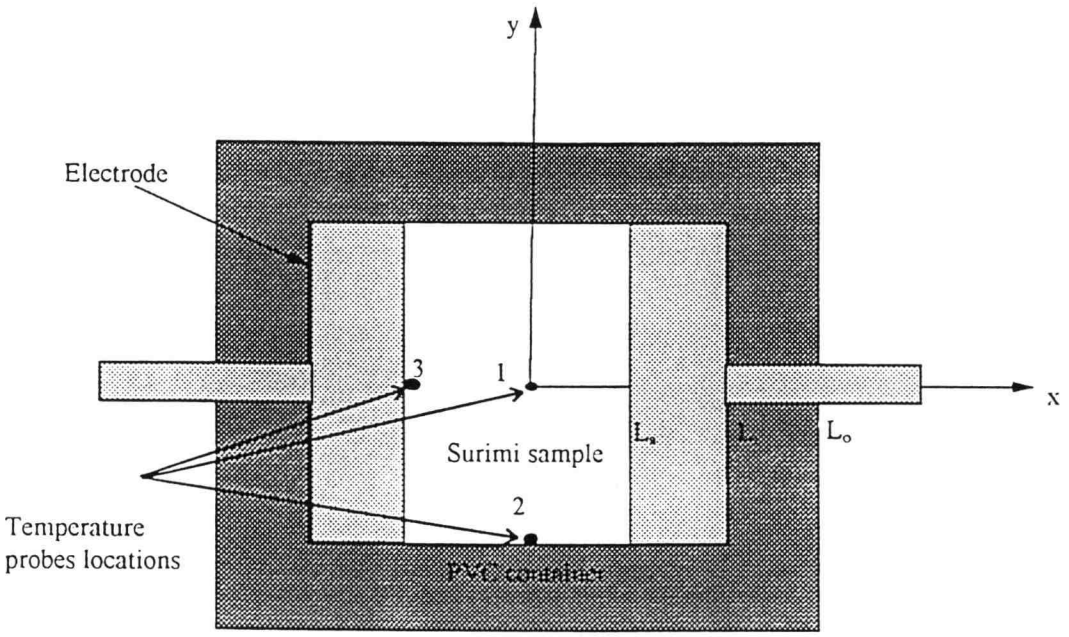


Figure. 3.1 Schematic drawing of ohmic heater apparatus.

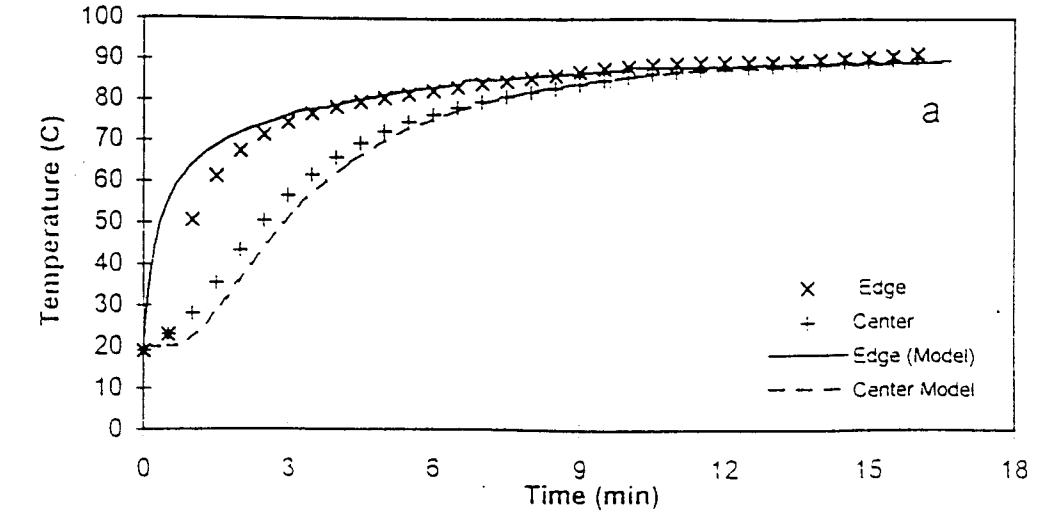


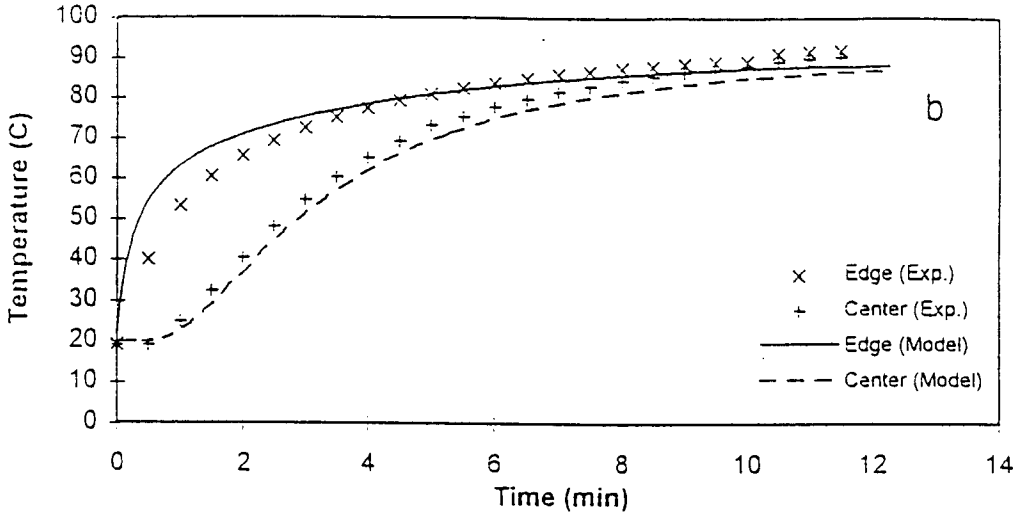
a

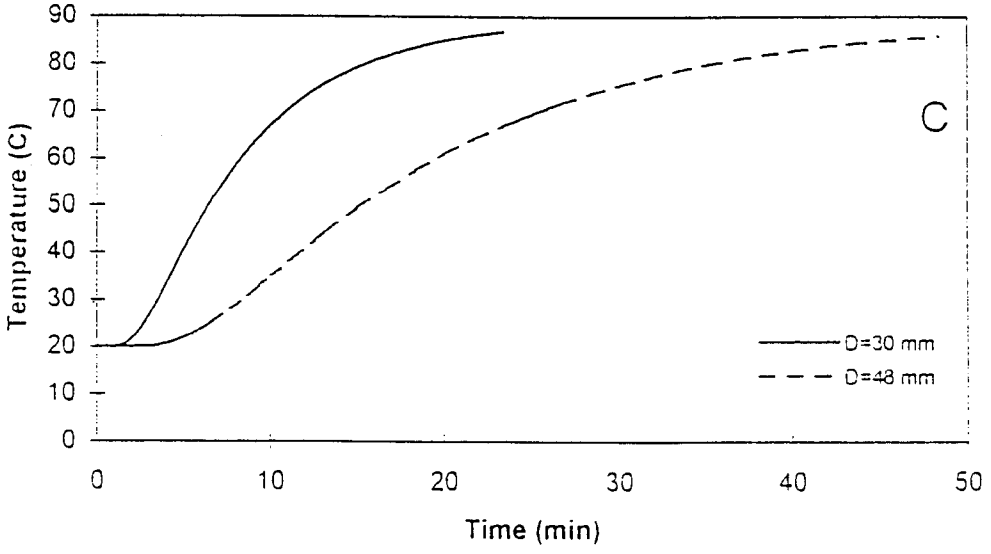


b

Figures 3.2a-b Cross sectional view of (a) cylindrical sample (b) cubical sample with temperature probes locations.







Figures 3.3a-c Conventional heating using 90°C water bath. (a) 74% moisture surimi in 19 mm ID tube; (b) 80% moisture surimi in 19mm ID tube; (c) 80% moisture surimi in 30mm and 48mm ID tube.

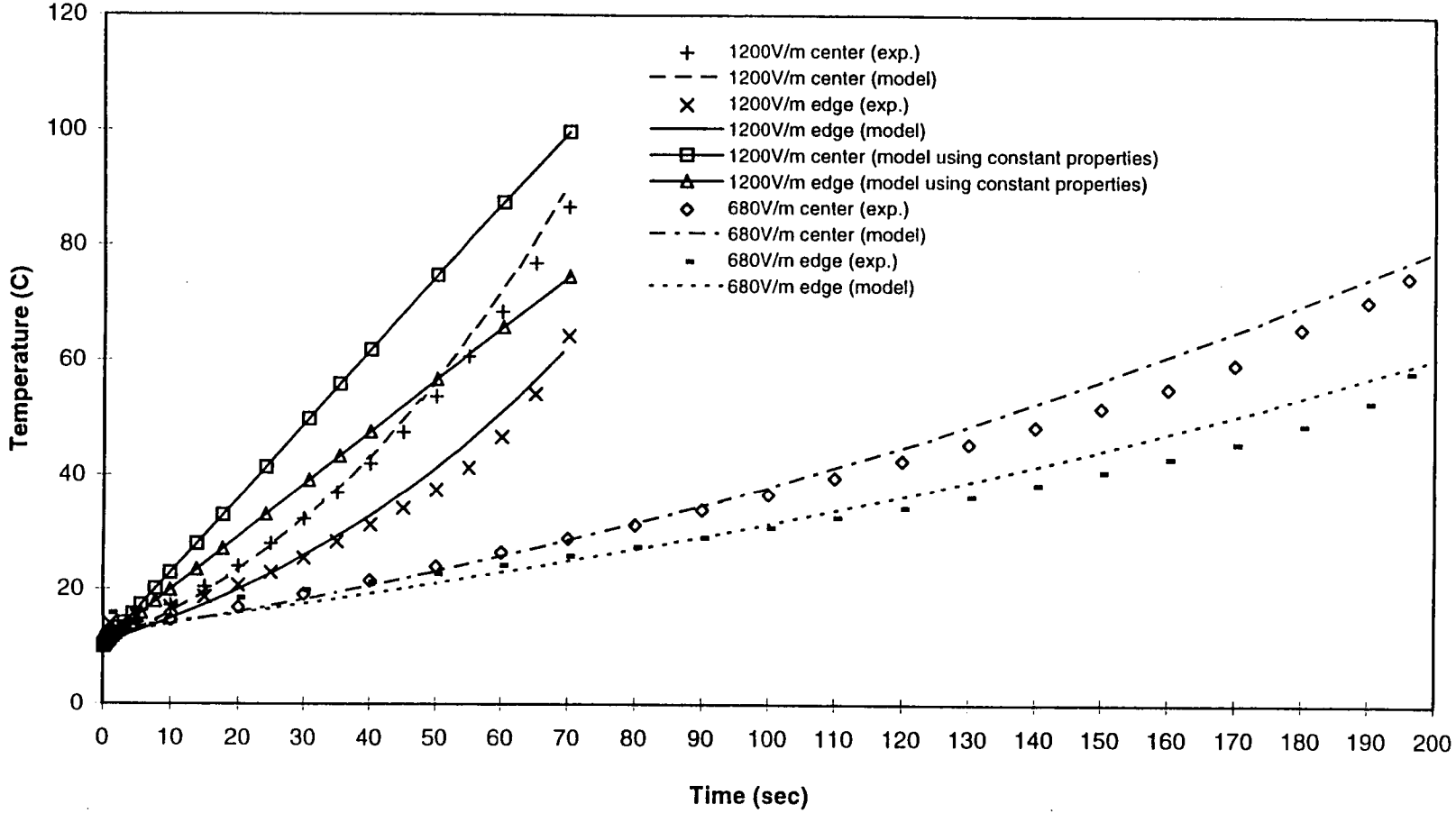


Figure. 3.4 Effect of voltage gradient on heating rate of 74% moisture content surimi.

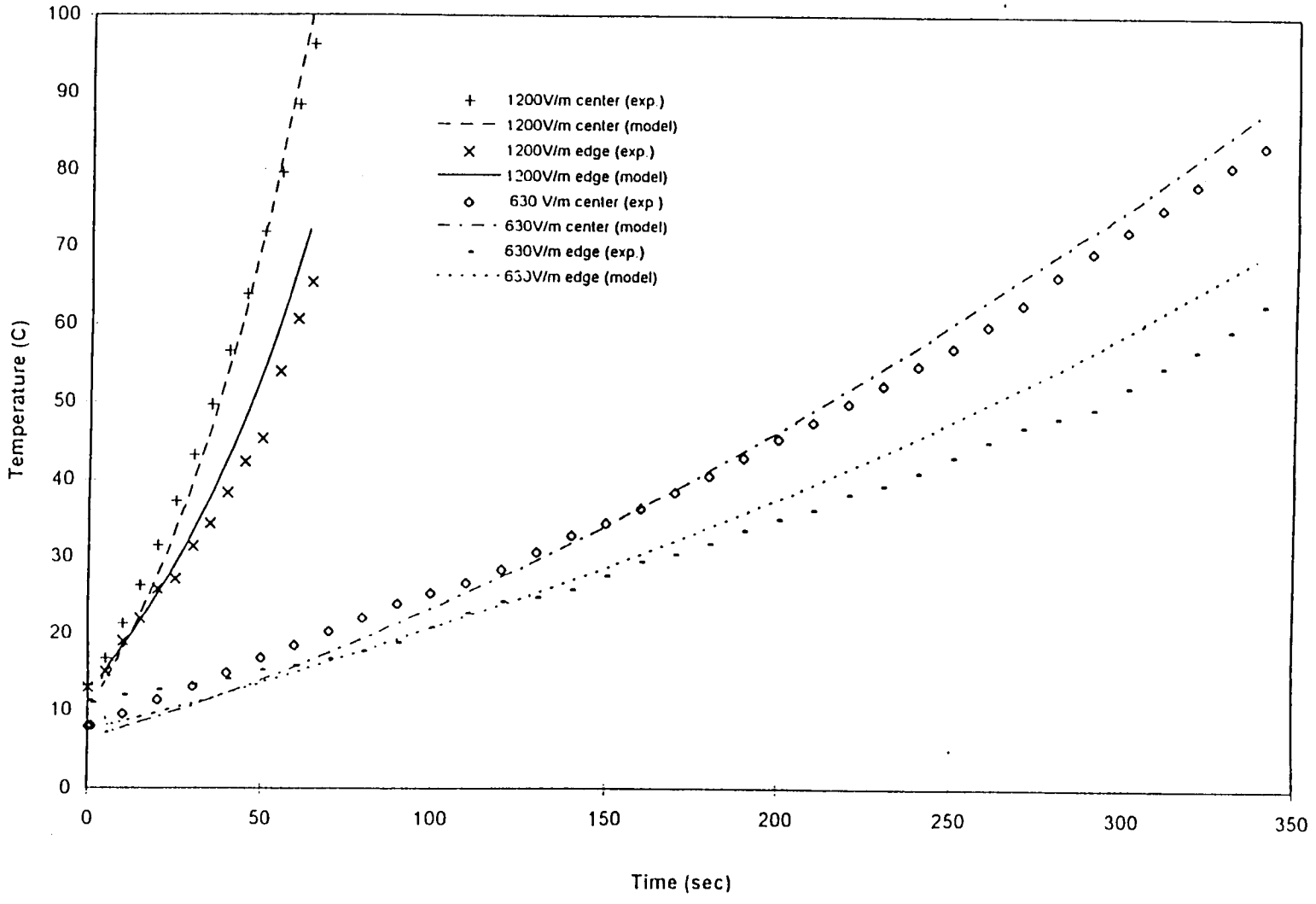


Figure 3.5 Effect of voltage gradient on heating rate of 80% moisture content surimi.

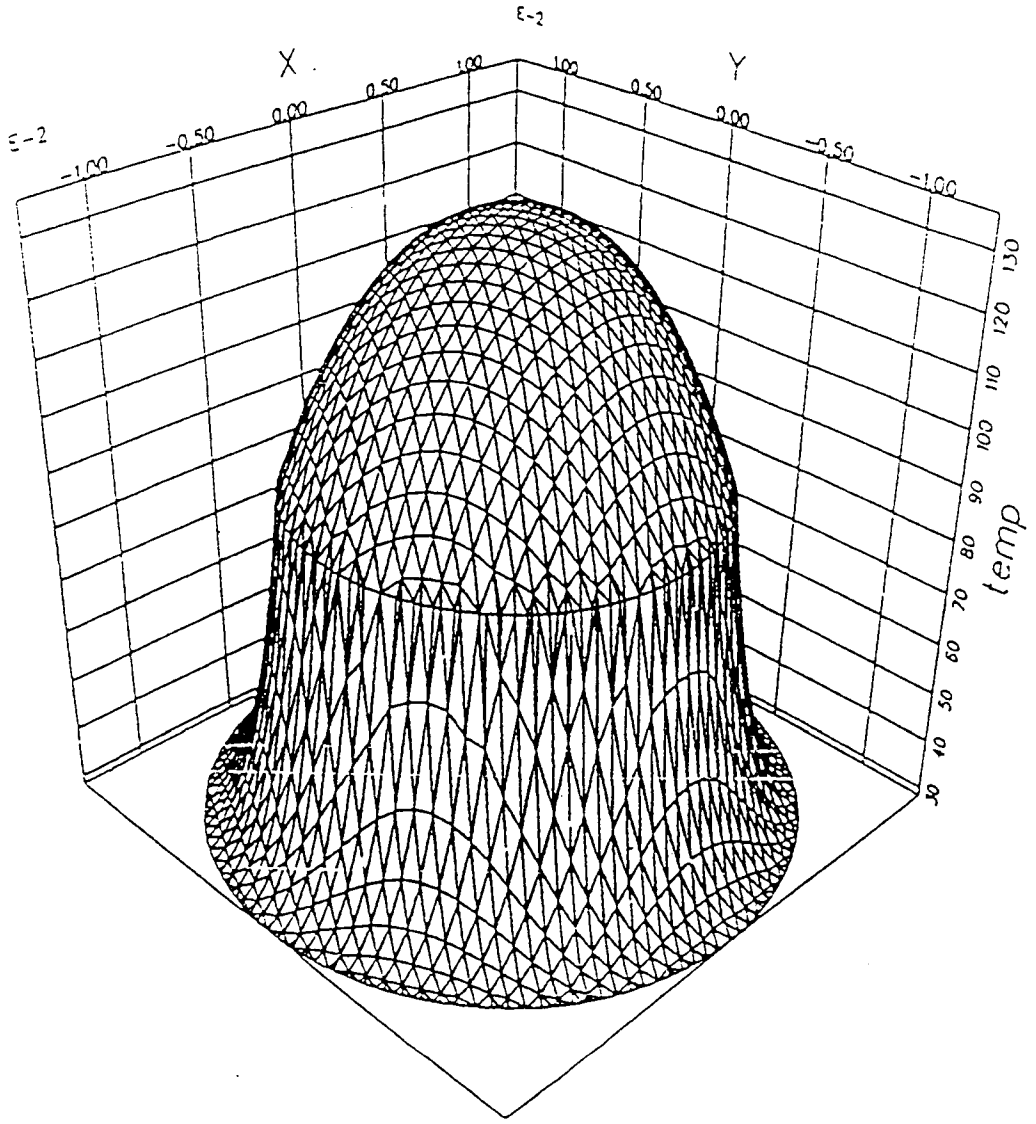


Figure 3.6 Temperature distribution in 80% moisture content surimi in CPVC cylindrical tube ohmically heated under 1200V/m after 80 sec.

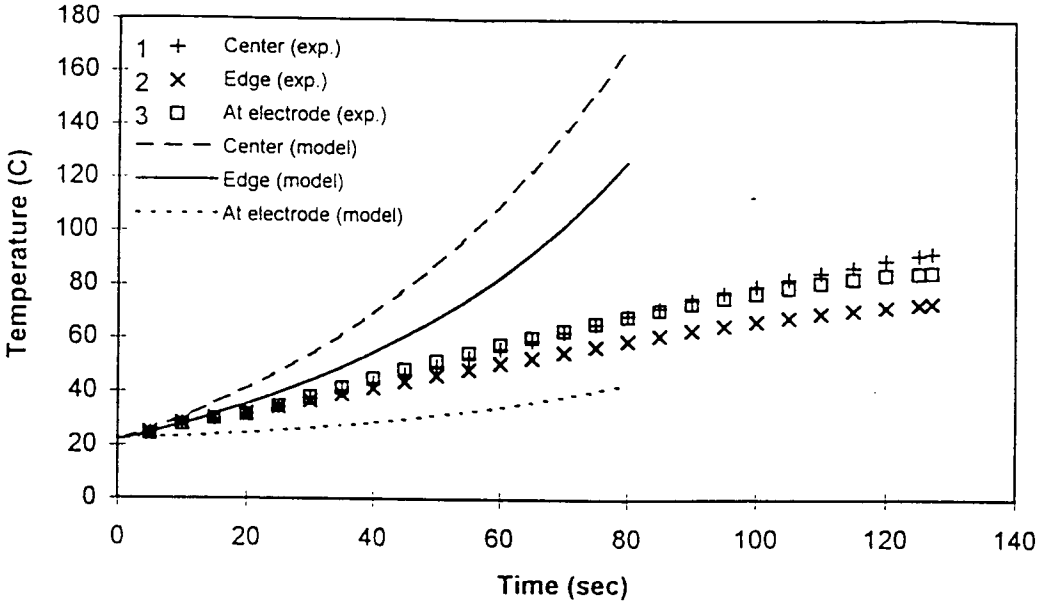


Figure 3.7 Heating rate of 74% moisture content surimi in a cubic container in locations marked in Figure 2b.

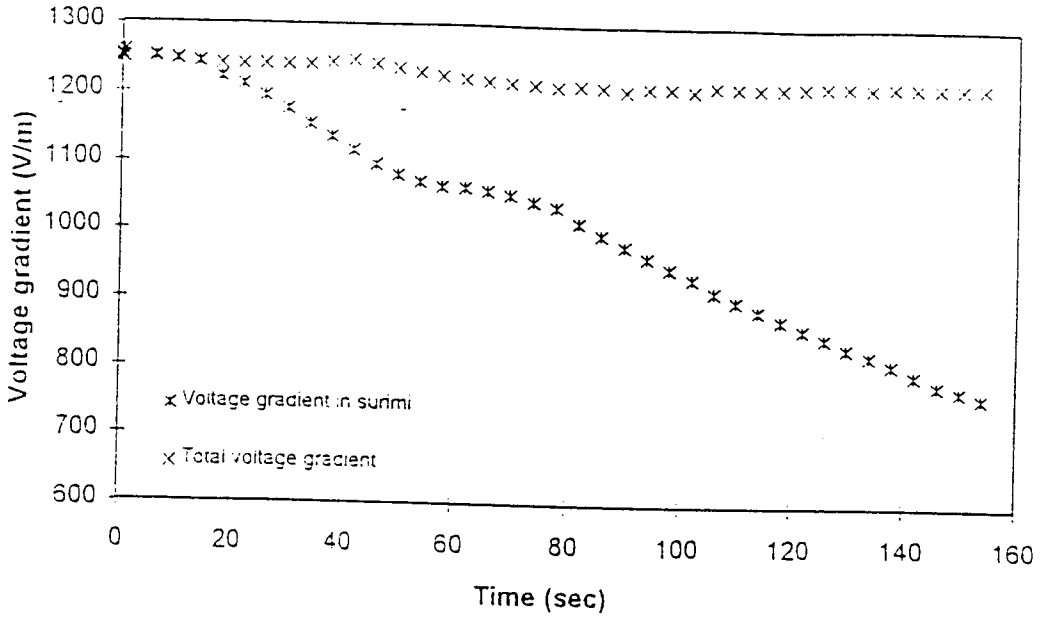


Figure 3.8 Voltage gradient across electrodes and sample and sample only in the cubic container.

NOTATION

C_p : Specific heat of surimi paste (J/kg-°C)

L_i, L_o, L_s : The cubic container dimensions (m) as shown in Figure 3.2b.

Q : Internal heat generation per unit volume (W/m^3)

h : convection heat transfer coefficient (W/m^2- °C)

k : Thermal conductivity of surimi (W/m-°C)

k_e : Thermal conductivity of electrode (W/m-°C)

k_c : Thermal conductivity of PVC (W/m-°C)

k_t : Thermal conductivity of CPVC (W/m-°C)

M : Moisture content (%)

N : NaCl content (%)

R_i, R_o : The cylindrical sample tube dimensions (m) as shown in Figure 3.2a.

T : Temperature (°C)

T_∞ : Room temperature (~22°C)

t : Time (sec)

V :Voltage gradient (v/m)

α :Thermal diffusivity of surimi (m^2/sec)

α_c :Thermal diffusivity of PVC (m^2/sec)

α_e :Thermal diffusivity of electrode (m^2/sec)

α_t :Thermal diffusivity of CPVC (m^2/sec)

ρ : density of surimi (kg/m^3)

σ : Electrical Conductivity of Surimi (S/m)

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Chapter 4

Conclusion and Recommendations

Thermal and Electrical properties of surimi was found to be affected strongly by temperature and moisture contents. Restructuring of surimi (gelation and protein denaturation also affected these properties. Application of ohmic heating on surimi paste was found to provide a higher rate of heating than that of conventional heating in a 90°C water bath. Surimi heated conventionally is thus expected to have a lower gel quality because it is kept in the softening enzyme active temperature region for longer time, as summarized in Table 1. Voltage gradient across the sample, moisture content, heat leakage to the surrounding, and electrode design were all shown to affect the heating rate. The heating rate increased with voltage gradient, moisture content, a reduced leakage to the sample holder and the surrounding. A poor contact between sample and electrodes also causes heat generation at the electrode surface and resulted in a lower heating rate in surimi.

A good electrode design with a small thermal mass would help reduce heat lose to the electrode and interface region. Introducing a heat source to the outer boundaries of the sample would help eliminate the heat loss to the sample case and the surrounding

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APPENDICES

APPENDIX A

Electrical Conductivity of Pacific Whiting Surimi Paste during Ohmic Heating

J. YONGSAWATDIGUL, J.W. PARK, and E. KOLBE

ABSTRACT

Electrical conductivities of Pacific whiting surimi paste with various moisture contents (75, 78, 81, and 84%) and added salt (1, 2, 3, and 4%) were measured using ohmic heating at alternating current of 3.3, 6.7, and 13.3 V/cm. Electrical conductivity of surimi increased with temperature and salt content and slightly increased with moisture content. Electrical conductivity correlated linearly with temperature ($r^2 \geq 0.99$). Generally, voltage gradient did not affect conductivity. However, variations of conductivity with voltage gradient observed in surimi containing 3–4% salt, were probably caused by electrochemical reactions at electrode surfaces. The empirical model of electrical conductivity predicted values ±16% of independent experimental results.

Key Words: ohmic heating, electrical conductivity, surimi, whiting

INTRODUCTION

SURIMI made from Pacific whiting (*Merluccius productus*) normally undergoes textural degradation due to the presence of a heat-stable endogenous protease in the flesh (Chang-Lee et al., 1989; Patashnik et al., 1982). The protease has been identified as cathepsin L with an optimum temperature at 55°C (Seymour et al., 1994). A breakdown of myofibrillar proteins, caused by proteolysis, inhibits proper development of a three-dimensional gel structure (Niwa, 1992). As a result, the gel forming ability of Pacific whiting surimi is low unless food grade enzyme inhibitors, such as beef plasma proteins, egg white, and potato extract are added (Chang-Lee et al., 1989; Morrissey et al., 1993; Porter, 1992).

In conventional heating methods, heat is transferred from the heating medium to the product interior by means of both convection and conduction. Yongsawatdigul et al. (1995) illustrated that temperature at the center of a cylindrical sample (I.D. = 1.9 cm, length = 17.9 cm) of whiting surimi paste heated in a 90°C water bath took ≈10 min to reach 70°C. The protease is completely inactivated at that temperature (Seymour et al., 1994). For two min of this process, surimi was exposed to a temperature range in which the protease is most active: 40–60°C. Thus, a typical slow heating rate activates the protease to degrade myofibrillar proteins before the protease can be thermally inactivated. To minimize proteolytic activity without use of enzyme inhibitors, the protease would need to be thermally inactivated quickly. This could be achieved through rapid heating methods as reported by Greene and Babbitt (1990) and Yongsawatdigul et al. (1995).

Ohmic heating is a method in which an alternating electrical current is passed through an electrically conducting product (de Alwis and Fryer, 1992). Heat is internally generated due to electrical resistance of the sample, supporting a rapid heating rate. Moreover, ohmic heating can provide uniform temperature distribution because both liquid and solid phases are heated simultaneously (Parrott, 1992). Such characteristics have led to development of commercial ohmic sterilization for particulate foods (Biss et al., 1989; de Alwis and Fryer, 1990). Application of ohmic heating in seafoods has also been investigated. Gel strength of surimi made from walleye pollock, white croaker, threadfin bream, and sardine was improved when samples were ohmically heated, as compared with samples heated in a 90°C water bath (Shiba, 1992; Shiba and Numakura, 1992). Pacific whiting surimi heated ohmically with an applied voltage gradient of 13.3 V/cm had good gel quality (shear stress of 30.5 kPa; shear strain of 2.8). Those gels heated conventionally had shown shear stress and strain values of 13.9 kPa and 1.3, respectively (Yongsawatdigul et al., 1995). Improved gel functionality was accompanied by retention of myosin heavy chain, indicating that the endogenous protease was quickly inactivated by rapid heating associated with ohmic heating.

To design the ohmic process optimally, electrical conductivity of food materials during ohmic heating must be elucidated. Conductivity is a critical parameter influencing the rate of heat generation (Palaniappan and Sastry, 1991a and de Alwis and Fryer, 1992). Electrical conductivities measured using alternating current (50 or 60 Hz) have been studied on various food products (Halden et al., 1990; Palaniappan and Sastry, 1991a, b; Schreier et al., 1993). However information about electrical conductivity of seafoods, particularly surimi paste, is lacking. Therefore, our objectives were: (1) to investigate effects of temperature, voltage gradient, moisture, and added salt content on electrical conductivity of Pacific whiting surimi paste and (2) to establish an empirical model of electrical conductivity as a function of composition.

MATERIALS & METHODS

Surimi paste preparation

Pacific whiting (*Merluccius productus*) surimi was taken from a process line of a local manufacturer and mixed with 4% sucrose, 4% sorbitol (ICI Specialties, New Castle, DE), and 0.3% sodium tripolyphosphate (B.K. Ladenburg Corp., Cresskill, NJ) at the OSU Seafood Laboratory. No food grade enzyme inhibitors were added. Samples were frozen and kept in a −30°C room throughout the experiment. Frozen surimi samples were thawed at room temperature (~23°C) for 2 hr and cut into small pieces (about 3 cm cubes). Sixteen batches of surimi paste representing four different moisture contents (75, 78, 81, and 84% wet basis) and added NaCl (Mallinckrodt Inc., Paris, KY) (1, 2, 3, and 4% w/w) were randomly prepared. One kg of partially thawed surimi was chopped for 1.5 min in a Stephan vertical vacuum cutter (model UM 5 universal, Stephan Machinery Co., Columbus, OH). Salt was added and mixed with surimi for another 1.5 min. Then ice was added to adjust final moisture content to the desired level and the sample was further chopped at high speed under vacuum of 600 mmHg for 3 min. Final moisture content of each batch was determined using the standard oven method (AOAC, 1984). The paste was stuffed into PVC tubes (1.9 cm i.d. × 20.5 cm long) and heated using an ohmic heating apparatus.

Electrical conductivity measurement

A sample tube containing surimi paste was placed on the sample holders (Fig. 1). An electrode was inserted into each end of the tube to provide a sample length of 15 cm. The minimum pressure that would maintain an air-free contact between the rhodium-coated stainless steel electrodes and the paste, 448 kPa, was applied to the sample. The sample was heated to 90°C using alternating current of 60 Hz at applied voltages of 50, 100, and 200 V, corresponding to voltage gradients of 3.3, 6.7,

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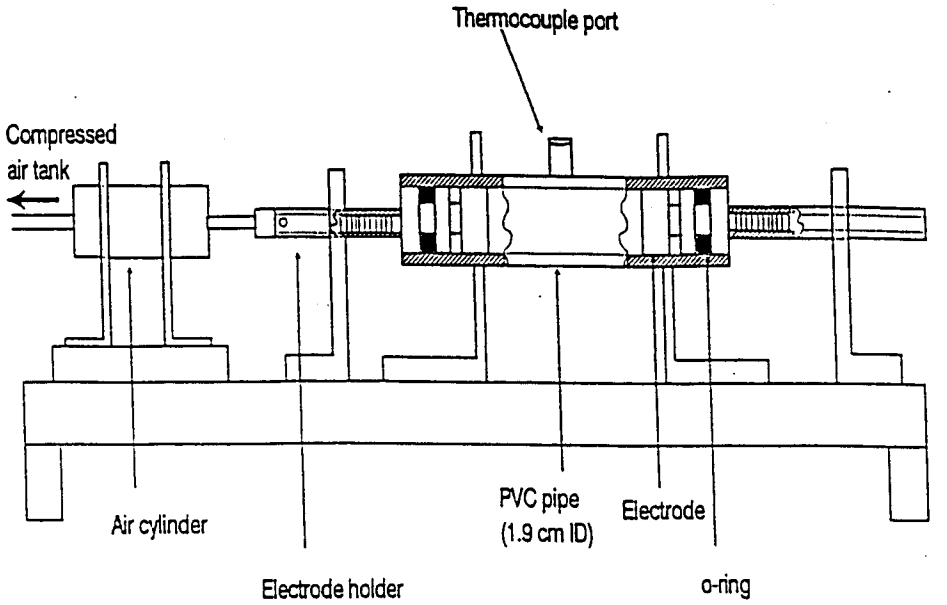


Fig. 1—Diagram of ohmic heating apparatus.

and 13.3 V/cm, respectively. Temperature at the geometric center of the samples was continuously measured with a T-type thermocouple covered with teflon to prevent interference from the electrical field. Voltage and current were measured using voltage and current transducers, respectively. Temperature, voltage and current data were recorded on a datalogger (model 21X, Campbell Scientific, Inc., Logan, UT) at 10, 2, and 1 sec intervals, according to the applied voltage gradient of 3.3, 6.7, and 13.3 V/cm, respectively. Electrical conductivity of surimi paste during ohmic heating was measured twice at each voltage gradient.

The accuracy of the voltage and current transducers was tested against a portable multimeter (John Fluke Manufacturing, Everett, WA). The voltage was applied to the circuit connected with a known 500 Ω resistor. Voltage and current transducers were calibrated to provide the same readings as those from the multimeter. Surimi paste is a homogenous material and electric field was assumed to be uniform along the sample tube, thus temperature variation within the sample tube was neglected.

Data analysis

Electrical conductivities of the samples were calculated from voltage and current data using the equation described by Palaniappan and Sastry (1991a):

$$\sigma = (1/R)(L/A)$$

where, σ = electrical conductivity (S/m); L = sample length (m); A = cross-sectional area of the sample (m^2); R = resistance of the sample (ohm).

A large number of the data points (6,073) were obtained from 96 measurements and thus the data splitting technique (Bowerman and O'Connell, 1990) was used to develop and validate the empirical model. One-third of the experimental runs (32 runs, 1,849 data points) were randomly separated and used to validate the model, which was developed from the rest of the data using a Statistical Analysis System computer program (SAS Institute, Inc., 1990). Nine variables including three main effects temperature (T), moisture content (M), and added NaCl content (N), three interactive effects (TM, TN, MN), and second order polynomial terms (T^2, M^2, N^2), were initially analyzed for statistical significance using stepwise and backward regression. Residual plot of the model was evaluated to assure that the assumption of constant variance and normality were satisfied.

RESULTS & DISCUSSION

SURIMI is washed and dewatered minced flesh consisting primarily of myofibrillar proteins. Due to three cycles of washing and dewatering, ionic constituents originally present in the fish are removed with wash water, resulting in a low ion content of surimi (Lin, 1992). The sodium content of Pacific whiting surimi without enzyme inhibitors was 0.002% (Chung et al., 1993); this is relatively low considering the amount of NaCl used (1–4%). For this reason, the effect of added NaCl content was studied instead of total ion content.

Linear relationships between temperature and electrical conductivity were evident (r^2 0.987 to 0.999, Table 1). Electrical conductivity of Pacific whiting surimi paste changed with respect to temperature at various added NaCl (Fig. 2) and moisture contents (Fig. 3). Since variation between two replicates (Table 1) was low, the raw data from only one were presented. Electrical conductivity increased as temperature and added salt content increased, and slightly increased as moisture content increased.

As salt content increased, the ions (Na^+ and Cl^-) for conducting electrical current increased, which increased conductivity. Increased conductivity at high temperature was due to ionic mobility (Palaniappan and Sastry, 1991a). This linearly increasing trend agreed with results of Fryer et al. (1993) and Palaniappan and Sastry (1991a, b).

However, electrical conductivity of purified proteins, such as wool, collagen, and elastin varied with temperature according to an Arrhenius-type equation (Pethig, 1979). Differences in the trend could be due to differences in electrical conducting mode of the materials. Ionic constituents were important in conducting electrical currents through the surimi paste and other food materials during ohmic heating. On the other hand, electrical conductivity in the purified proteins (Pethig, 1979) was mainly attributed to negative and positive charges associated with the protein molecules. According to Shiba (1992), impedance of surimi paste linearly decreased as it was heated ohmically from 5°C to 50°C, indicating an increase of electrical conductivity with increased temperatures. However, electrical conductivity of surimi above 50°C is not directly comparable with our results because electrical current in Shiba's (1992) study was controlled below 3 A to achieve a desired heating rate.

Electrical conductivity tended to increase with moisture content (Fig. 3). Ion solvation could increase when more water molecules are available, resulting in increased ionic mobility. An

Table 1—Means of estimated parameters of electrical conductivity modeled as a function of temperature

Moisture (%)	Salt (%)	Coeff. (°C)$^{-1}$ Voltage gradient (V/cm) 3.3	6.7	13.3	Intercept (S/m) Voltage gradient (V/cm) 3.3	6.7	13.3
75	1	0.030±0*	0.030±0	0.028±0	0.540±0.003	0.606±0.039	0.649±0.062
	2	0.052±0.002	0.049±0	0.050±0.001	1.099±0.041	1.204±0.007	1.267±0.033
	3	0.074±0.001	0.067±0.004	0.069±0.002	1.704±0.018	1.904±0.020	1.921±0.037
	4	0.092±0	0.090±0	0.104±0.003	2.264±0.028	2.533±0.009	2.160±0.071
78	1	0.033±0.001	0.031±0	0.029±0.001	0.613±0.007	0.645±0.025	0.696±0.024
	2	0.053±0.001	0.051±0.001	0.051±0.004	1.257±0.014	1.326±0.026	1.449±0.042
	3	0.080±0	0.072±0.002	0.087±0.003	1.653±0.059	1.869±0.032	1.894±0.042
	4	0.099±0.003	0.096±0.001	0.100±0	2.285±0.176	2.651±0.069	2.709±0.065
81	1	0.032±0.001	0.031±0	0.029±0.001	0.629±0.009	0.682±0.034	0.767±0.010
	2	0.058±0	0.054±0	0.057±0.002	1.327±0.016	1.381±0.038	1.499±0.028
	3	0.083±0.003	0.076±0.003	0.082±0.003	1.933±0.023	2.239±0.256	1.984±0.079
	4	0.112±0.005	0.110±0.003	0.131±0.001	2.540±0.046	2.556±0.046	2.404±0.125
84	1	0.036±0.001	0.034±0.001	0.032±0	0.678±0.034	0.758±0.038	0.832±0.024
	2	0.060±0.001	0.057±0	0.056±0	1.433±0.028	1.623±0.004	1.708±0.008
	3	0.074±0.001	0.081±0.001	0.088±0.002	2.006±0.056	2.433±0.062	2.418±0.301
	4	0.092±0.002	0.107±0.001	0.106±0.008	3.343±0.107	3.495±0.112	3.051±0.268

* 0 indicates values less than 0.001.

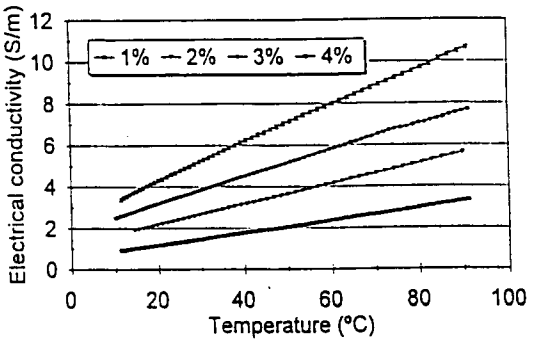


Fig. 2—Effect of salt content on electrical conductivity of surimi paste containing 75% moisture content, measured at 6.7 V/cm.

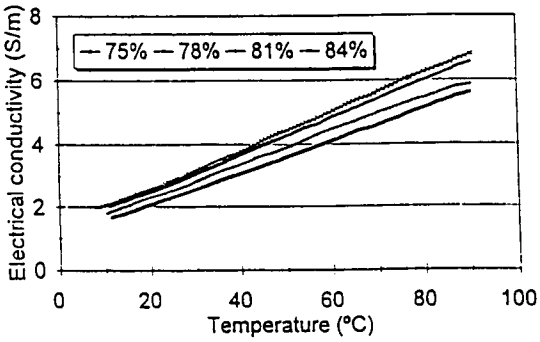
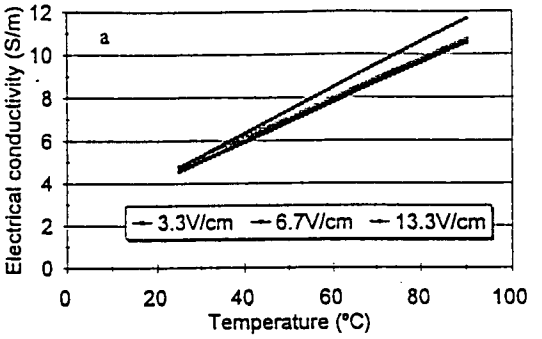


Fig. 3—Effect of moisture content on electrical conductivity of surimi containing 2% salt at voltage gradient of 3.3 V/cm.



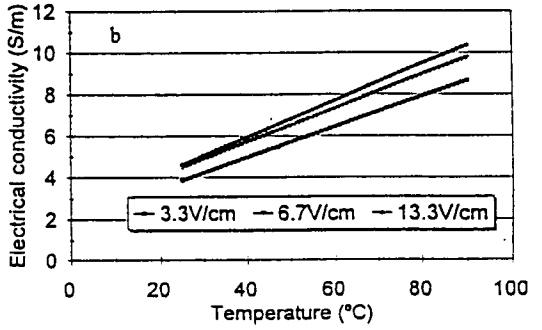


Fig. 4—Effect of voltage gradient on electrical conductivity. (a) 75% moisture and 4% salt; (b) 84% moisture and 3% salt.

increase in electrical conductivity with increased moisture was also reported in various proteins, such as hemoglobin, keratin, and bovine plasma albumin (Pethig, 1979). This was due to ionic conduction effects associated with salts in hydrated proteins. Such hydration allowed protons and other ionic species to migrate around the surface of the proteins (Pethig, 1979). Our study demonstrated that changes in electrical conductivity were greater with respect to salt content than moisture content in the studied ranges.

Temperature coefficients at various voltage gradients of each moisture-salt combination were very similar (Table 1), indicating that the voltage gradients had no effect on electrical conductivity. However, the effect of voltage gradient was notable in samples containing 3–4% NaCl (Figs. 4a-b). The effect of voltage gradient on electrical conductivity of fruit and vegetable products was reported by Palaniappan and Sastry (1991b) and Halden et al. (1990). High applied electric field enhanced cell fluids motion within plant cells and ruptured cell membranes, resulting in release of cell fluids (Halden et al., 1990). Electrical conductivity of fruits and vegetables increased with increasing voltage gradient. Differences in electrical conductivity at varied voltage gradients we observed were unlikely to have arisen from the enhanced motion of the cell fluids. Surimi paste was finely comminuted and was a homogeneous material which was quite different from vegetables or fruits that retained the integrity of

plant cells during ohmic heating. Dependence of electrical conductivity on voltage gradient could have been caused by corrosion of the electrodes which often occurred in samples containing 3 and 4% NaCl (Figs. 4a-b). Faradaic current generated by electrolytic reactions was observed when current density >8,000 A/m² passed in a platinized-titanium electrode immersed in saturated sodium chloride solution (Stirling, 1987). Thus, an electrical current measured under corroded conditions included both applied alternating current and Faradaic current (Oldham and Myland, 1994). To minimize corrosion of the electrode, the maximum current density was recommended at 4,000 A/m² (de Alwis and Fryer, 1992).

Relationships between applied voltage and electrical current of surimi pastes at 25°C were studied (Fig. 5). For the sample containing 4% NaCl and 84% moisture, electrode corrosion and deviation from Ohm's law were observed when electrical current exceeded 1 A, corresponding to a current density of about 3,500 A/m². However, Ohm's law was followed for the sample containing 1% NaCl and 75% moisture, when the total current was <1 A and electrode corrosion was not noticed. To obtain accurate electrical conductivity values, it is critical to measure conductivity such way that electrochemical reactions at the electrodes and any other polarization phenomena do not occur.

A model was developed for electrical conductivity of Pacific whiting surimi as a function of temperature (T), added NaCl content (N) and moisture content (M). Voltage gradient was not included because it did not appear to affect electrical conductivity. The empirical model can be written as:

$$\sigma = 0.1168 + 0.0083T - 2.5115N + 0.0385MN + 0.0229TN + 0.0282N^2$$

where σ = Electrical conductivity (S/m); N = Salt content (% w/w); M = Moisture content (% wet basis); T = Temperature (°C).

All variables were significant ($P < 0.001$). Positive coefficient of TN indicated that an increase in electrical conductivity with temperature was greater at higher salt content. Although the effect of moisture content was not significant, a positive coefficient of MN suggested that an increase in electrical conductivity with salt content was greater in samples with higher moisture content. Furthermore, electrical conductivity increased quadratically with salt content. Statistical insignificance of T^2 confirmed that electrical conductivity of whiting surimi pastes, with compositional characteristics in these ranges, linearly increases with temperature. Predictability of the model was illustrated (Fig. 6a-b). The model satisfactorily predicted electrical conductivity of Pacific whiting with an error ranging from 0–16%. Error of prediction was relatively large in the sample containing 3–4% NaCl and 84% moisture (Fig. 6b). This was probably due to the electrode corrosion problem. Although the model was primarily developed for Pacific whiting surimi paste, it could be used to estimate electrical conductivity of surimi from other species. This inference was based on the fact that ionic content of surimi from various fish could be similar due to washing and dewatering. Furthermore, electrical conductivity of surimi-based seafoods, such as, imitation crabmeat, could be predicted from the model because the main factors affecting electrical conductivity of such products are only salt and moisture content.

CONCLUSION

ELECTRICAL CONDUCTIVITY was highly dependent on temperature and added salt content and slightly dependent on moisture content. The effect of applied voltage was insignificant. Changes of electrical conductivity affected by heating and compositional characteristics indicated the importance of such factors in design and operation of ohmic heaters for surimi-based seafood products. The empirical model adequately predicted the electrical conductivity of whiting surimi based on temperature, salt and moisture.

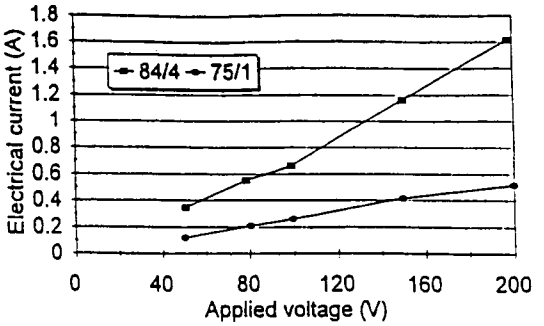


Fig. 5—Polarization of electrodes: 84/4: surimi paste containing 84% moisture and 4% salt at 25°C; 75/1: surimi paste containing 75% moisture and 1% salt at 25°C.

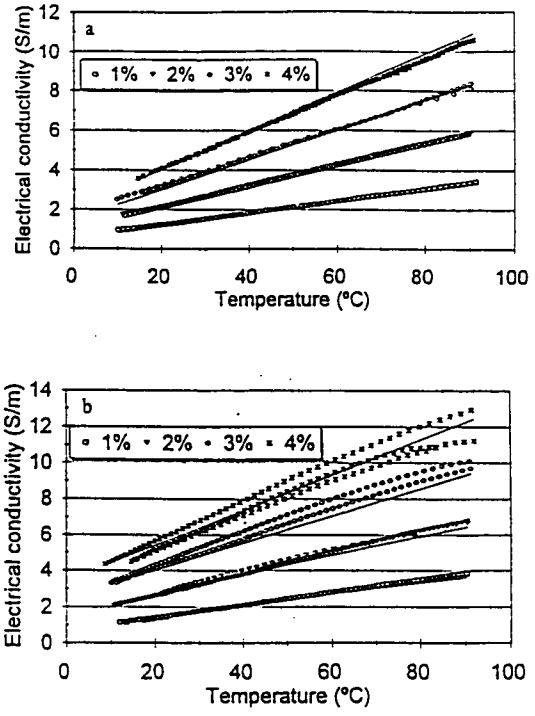


Fig. 6—Predictability of the electrical conductivity model as compared with experimental values. (a) 75% moisture; (b) 84% moisture; line: predicted values; symbol: experimental values.

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APPENDIX B

Ohmic Heating Maximizes Gel Functionality of Pacific Whiting Surimi

J. YONGSAWATDIGUL, J. W. PARK, E. KOLBE, Y. ABU DAGGA, and M. T. MORRISSEY

ABSTRACT

Surimi without enzyme inhibitors containing 78% moisture and 2% NaCl was heated conventionally and ohmically to 90°C after holding at 55°C for 0, 1, 3 and 5 min. Gels heated slowly in a water bath exhibited poor gel quality, while the ohmically heated gels without holding at 55°C showed more than a twofold increase in shear stress and shear strain over conventionally heated gels. Degradation of myosin and actin was minimized by ohmic heating, resulting in a continuous network structure. Ohmic heating with a rapid heating rate was an effective method for maximizing gel functionality of Pacific whiting surimi without enzyme inhibitors.

Key Words: ohmic heating, surimi, proteolysis, whiting

INTRODUCTION

PACIFIC WHITING (*Merluccius productus*) is the most abundant fishery resource off the West Coast of the U.S. with an allowable biological catch of 140,000 to 250,000 metric tons for the last three years (NMFS, 1993). The major portion of the harvested fish is used to produce surimi, a washed and dewatered fish mince, which is further utilized as a raw ingredient for surimi seafood products (Pacheco-Aguilar et al., 1989). Due to the presence of heat-stable endogenous protease in the flesh (Nagahisa et al., 1981; Patashnik et al., 1982; Erickson et al., 1983), Pacific whiting surimi normally exhibits undesirable textural properties unless food grade enzyme inhibitors are added (Chang-Lee et al., 1989; Morrissey et al., 1993). The protease responsible for textural degradation was purified and characterized as cathepsin L with an optimum temperature at 55°C (Seymour et al., 1994). A gel weakening at around 55–60°C has also been reported in threadfin bream (*Nemipterus bathybius*) (Toyohara and Shimizu, 1988), Atlantic menhaden (*Brevoorti tyrannus*) (Boye and Lanier, 1988), arrowtooth flounder (*Atheresthes stomias*) (Greene and Babbitt, 1990), white croaker (*Micropogon opercularis*) and oval filefish (*Navodon modestus*) (Toyohara et al., 1990).

Beef plasma proteins, egg white, and other food grade enzyme inhibitors have been used to inhibit proteolytic activity (Nagahisa et al., 1981; Chang-Lee et al., 1989; Hamann et al., 1990; Porter, 1992; Morrissey et al., 1993). However, these enzyme inhibitors used commercially have some negative effects such as high cost, off-odor, off-color and labeling concerns. Consequently, processing alternatives to overcome the textural deterioration of Pacific whiting surimi are needed.

Ohmic heating is a method in which alternating electrical current is passed through an electrically conducting food product (Biss et al., 1989). Heat is internally generated, resulting in a rapid heating rate. Because heat is simultaneously generated in liquid and solid phases, the temperature increase in the product is uniform, compared with the conventional process in which heat is applied at the external boundary (de Alwis and Fryer, 1990; Parrot, 1992).

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To minimize proteolysis, thermal inactivation of the enzyme should be quickly achieved (Patashnik et al., 1982). Greene and Babbitt (1990) demonstrated that textural degradation caused by proteolysis in arrowtooth flounder was notably reduced when cooked by microwaves. However, microwave processes can create non-uniform heating patterns because of differences in dielectric properties of the sample and nonuniform microwave field distribution (Decareau, 1985). In addition, microwave heating rates are so rapid that conductive heat transfer cannot uniformly take place (Datta and Hu, 1992). Since ohmic heating provides a rapid heating rate with more uniform temperature distribution than microwave heating, it could be an alternative to overcome the protease problem. Our objective was to investigate the feasibility of ohmic heating to maximize gel functionality of whiting surimi without enzyme inhibitors.

MATERIALS & METHODS

UNFROZEN PACIFIC WHITING (*Merluccius productus*) surimi (100 kg) without food grade enzyme inhibitors and cryoprotectants was obtained from Point Adams Packing Co. (Hammond, OR). Surimi was packed in polystyrene foam containers with ice and delivered to the OSU Seafood Laboratory (Astoria, OR) within 30 min. Each 17 kg of surimi was mixed with cryoprotectants, 4% sucrose, 4% sorbitol (ICI Specialties, New Castle, DE), and 0.3% sodium tripolyphosphate (B.K. Ladenburg Corp., Cresskill, NJ) using a Hobart vertical mixer (Hobart Manufacturing Co., Troy, OH) for 2 min. Mixing was carried out in a cold room (3°C). Mixed surimi was then divided into ~ 500-g portions and vacuum-packed in plastic trays. Samples were frozen and stored in a −30°C room.

Surimi gel preparation

Frozen surimi samples were thawed at room temperature (~23°C) for 2 hr and cut into small pieces. Moisture content of surimi was determined using the microwave procedure described by Morrissey et al. (1993). One kg of surimi was chopped for 1.5 min in a Stephan vertical vacuum cutter (model UM 5 universal, Stephan Machinery Co., Columbus, OH) at low speed. Salt was added and mixed with surimi another 1.5 min. Then, ice was added to adjust final moisture to 78%, and the sample was further chopped at high speed under vacuum of 600 mm Hg for 3 min. The paste was maintained below 8°C during chopping. An aliquot of the paste (~300g) was stuffed into stainless steel cooking tubes (1.9 cm i.d. × 17.5 cm long) and heated in a 90°C water bath for 15 min. Change in temperature at the geometric center of the tube sample

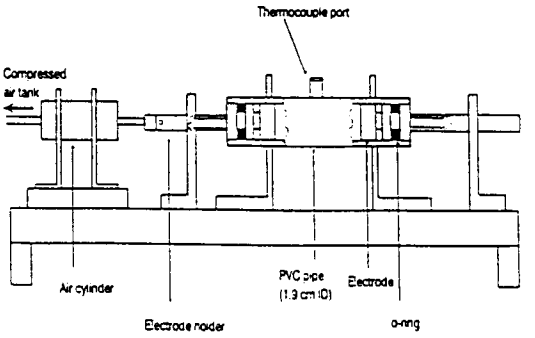

Fig. 1—Sample tube and electrodes.

was measured using a T-type thermocouple, and recorded every 30 sec in a datalogger (model 21x, Campbell Scientific Inc., Logan, UT). The remainder was stuffed into PVC tubes (1.9 cm i.d. × 20.5 cm long) and heated using an ohmic heating apparatus. Surimi gels heated by both heating methods were kept at 4°C for torsion tests, scanning electron microscopy, and gel electrophoresis within 24 hr. Gel preparation was replicated twice.

Ohmic heating apparatus

An ohmic heating apparatus was developed from two rhodium-coated stainless steel electrodes at each end of a PVC tube (1.9 cm i.d. × 20.5 cm long), a variable transformer (Powerstat F246, Newark Electronics, Eugene, OR), a current transducer (CT5-010A, Syntex Co., Wilsonville, OR), and a voltage transducer (VT-240A, Syntex Co., Wilsonville, OR). To minimize electrical hazards, the sample tube and electrodes were housed inside a plexiglass enclosure equipped with an open-snap action switch, which was activated when the plexiglass box was closed.

A 1.6-mm-diameter hole was drilled at the center of the PVC tube, and a saddle (diameter = 1.9 cm) was glued in that position to make a thermocouple port. To measure temperature at the geometric center of the sample, a 30-gauge Teflon-sealed type-T thermocouple (OMEGA Engineering Inc., Stamford, CT) with a compression fitting (OMEGA Engineering Inc., Stamford, CT) was used. Sixty-Hz alternating current at 240 V was supplied to a variable transformer. Voltage output ranged from 0 to 280 V. Voltage and current transducers were used to measure voltage across and current through the sample, respectively.

Ohmic heating procedure

A sample tube containing surimi paste was placed on the sample holders (Fig. 1). An electrode was inserted into each end of the tube to obtain a sample length of ≈15 cm. One of the electrode support rods was connected to an air cylinder. Pressure of 448 kPa was applied to the sample to maintain an air-free contact between the electrodes and the paste. Based on preliminary studies, gel strength of surimi and corrosion of the electrodes increased with applied voltage gradient. However, at voltage gradient >13.3 V/cm, corrosion was so severe that it interrupted electrical circuits. Therefore, the apparatus was operated at the voltage gradient of 13.3 V/cm (applied voltage of 200 V). The pastes were heated to 55°C, and were held at 55°C for 0, 1, 3, and 5 min. Temperature was controlled by manually adjusting the variable transformer. After each holding time was achieved, the sample was heated to 90°C by re-applying 200 V. Each heating treatment was replicated 3 times. Temperature, voltage, and current changes during heating were recorded at 1 sec intervals on a datalogger (model 21X, Campbell Scientific, Inc., Logan, UT).

Torsion test

Torsion failure tests were performed as described by NFI (1991). Gels were equilibrated to and tested at room temperature. Ten hourglass samples were used for each treatment. Shear stress and shear strain at failure were calculated from equations described by Hamann (1983).

Sodium dodecyl sulfate-gel electrophoresis (SDS-PAGE)

Unheated surimi paste and heated samples were analyzed by SDS-PAGE. Twenty seven mL of heated (95°C) 5% sodium dodecyl sulfate solution was added to 3g sample. The mixtures were homogenized for 1 min at a speed setting of 3–4 by a Polytron (Brinkmann Instruments, Westbury, NY). The homogenates were incubated in an 80°C water bath for 1 hr, and were centrifuged at 7,000 × *g* (Sorvall, DuPont Co., Newton, CT) for 10 min at room temperature. The protein concentration of supernatants was measured by the Lowry method (Lowry et al., 1951), using bovine serum albumin (Sigma Chemical Co., St. Louis, MO) as a standard.

Electrophoresis was carried out according to the procedure of Laemmli (1970). Stacking gels and separating gels were 4% (w/v) and 10% (w/v) polyacrylamide, respectively. The amount of protein loaded on the polyacrylamide gel was 60 µg. The separated proteins were stained with 0.125% Coomassie brilliant blue R-250 (Bio-Rad, Richmond, CA), and destained in a solution containing 25% ethanol and 10% acetic acid.

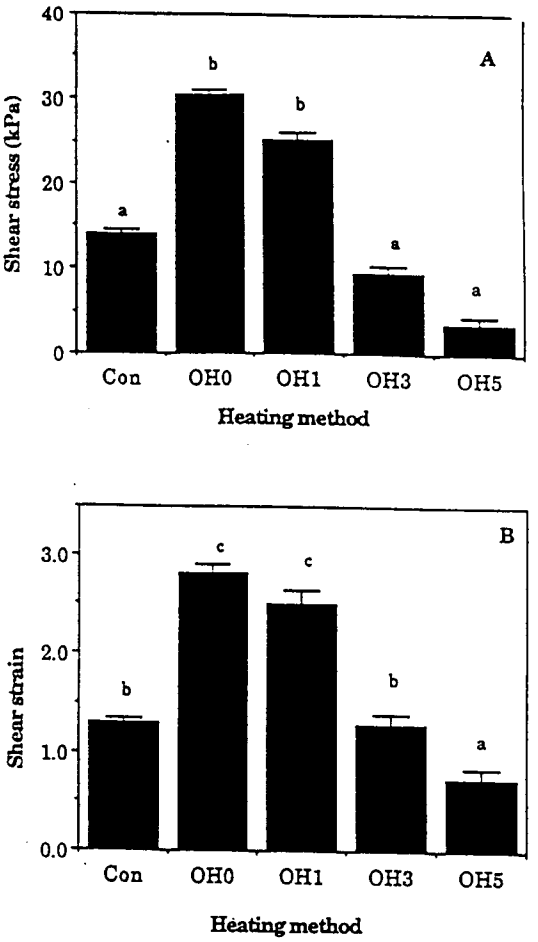

Fig. 2—Shear stress (A) and strain (B) of surimi gels heated by various heating methods. Means with the same letter (a,b,c) are not significantly different (P>0.05). CON = conventional heating (heated in a 90°C water bath for 15 min). OH0 = heated ohmically with voltage gradient of 13.3 V/cm (applied voltage = 200V) to reach 90°C. OH1 = heated ohmically with voltage gradient of 13.3 V/cm and held for 1 min at 55°C before heating to 90°C. OH3 = heated ohmically with voltage gradient of 13.3 V/cm and held for 3 min at 55°C before heating to 90°C. OH5 = heated ohmically with voltage gradient of 13.3 V/cm and held for 5 min at 55°C before heating to 90°C

Scanning electron microscopy

Small samples of heated gels were cut with a razor blade and fixed for 2 hr in 1% osmium tetroxide solution buffered with 0.125 cacodylate buffer pH 7.2. Samples were immersed for 20 min in 1,1-dimethoxypropane to remove unreacted osmium tetroxide and water. They were then soaked in absolute acetone twice, (10 min each). The samples were freeze-dried (model 500, Refrigeration for Science Inc., Island Park, NY) at a vacuum of 750 mm Hg and −73°C for 6 hr. Dried samples were mounted on aluminum specimen stubs (Ted Pella Inc., Redding, CA) using DUCO cement (Devcon Corp., Wood Dale, IL), and coated with gold in a sputter (model S150B, Edwards High Vacuum, West Sussex, England) for 45 sec at 10 kV and 40 mA. The samples were examined at 7,500× using a scanning electron microscope (Amray 1000A, Bedford, MA) at an accelerating voltage of 10 kV.

Statistical analysis

Since there were no significant differences ($P > 0.05$) between two replications, data were evaluated by one-way analysis of variance using

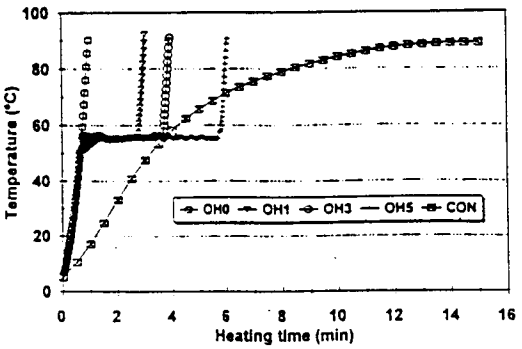

Fig. 3—Temperature profiles of surimi gels heated by various heating methods (abbreviations indicated in Fig. 2).

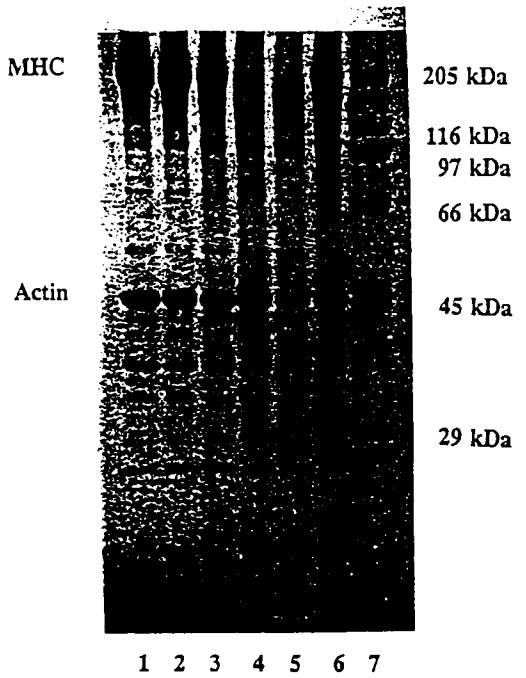

Fig. 4—SDS-PAGE separation pattern of surimi gels heated by various heating methods: (1) unheated surimi paste; (2) surimi heated ohmically with 13.3 V/cm to 90°C; (3) surimi heated ohmically with 13.3 V/cm and held at 55°C for 1 min before heating to 90°C; (4) surimi heated ohmically with 13.3 V/cm and held at 55°C for 3 min before heating to 90°C; (5) surimi heated ohmically with 13.3 V/cm and held at 55°C for 5 min before heating to 90°C; (6) surimi heated conventionally; (7) High molecular weight standard; MHC: Myosin heavy chain.

STATGRAPHIC Version 6.0 (Manugistics Inc., Rockville, MD). Differences within heating methods were determined using the least significant difference (LSD) multiple range test (Box et al., 1978).

RESULTS & DISCUSSION

Effects of heating methods on gel strength and myosin heavy chain

Shear stress and shear strain values of surimi gels heated conventionally (CON) were compared with those heated ohmically (Fig. 2A and 2B). Shear stress and shear strain are correlated with surimi gel hardness and cohesiveness, respectively (Hamann and MacDonald, 1992). Hardness of OH0 and OH1 gels was significantly higher than that of CON, OH3, and OH5 gels ($P<0.05$). No significant differences occurred in cohesiveness between CON and OH3 gels ($P>0.05$). However, cohesiveness of these two gels was significantly lower than that of OH0 and OH1, and higher than that of OH5 gels ($P<0.05$). Since an acceptable surimi gel should have a strain value of at least 2.0 (Hamann et al., 1990), textural properties of surimi gels heated in a 90°C water bath and those held ohmically at 55°C for 3 and 5 min were very poor. Low shear stress and shear strain in OH3 and OH5 illustrated the effect of protease activity at 55°C on textural characteristics of Pacific whiting surimi gel. Those gels heated ohmically to 90°C with a voltage gradient of 13.3 V/cm (200 V) and those held in ohmic heating at 55°C for 1 min showed good textural properties with strain values of 2.81 and 2.50, respectively. These were more than twice the value of conventionally heated surimi gels. Based on torsion test results, Pacific whiting gels without enzyme inhibitors heated ohmically without holding at 55°C were slightly better than those heated conventionally with incorporation of enzyme inhibitors such as beef plasma proteins, egg white, and potato extract. These had a maximum strain value around 2.5 (Morrissey et al., 1993).

Seymour et al. (1994) illustrated that activity of the protease purified from Pacific whiting gradually increased as temperature increased until peaking at 55°C. It then started decreasing and reached a minimum at 70°C. The myosin and actin have been reported as a substrate of endogenous protease found in threadfin-bream surimi (Toyohara and Shimizu, 1988; Toyohara et al., 1990), and of cathepsin L purified from rabbit skeletal muscle (Okitani et al., 1980) and Pacific whiting (An et al., 1994). Temperature profiles of conventional heating (Fig. 3), indicate that surimi was slowly heated in a 90°C water bath and was exposed to a temperature range of 40–60°C for ~2 min. Moreover, it took about 6 min to reach 70°C at which the protease could be inactivated. Due to the slow heating rate, the enzyme was activated and started degrading the myosin before thermal inactivation occurred. Since the myosin plays an important role in gel network formation (Niwa, 1992), severe degradation of the myosin heavy chain (Fig. 4) resulted in low gel strength (Fig. 2A and 2B). When holding time at 55°C in ohmic heating was prolonged, integrity of the myosin heavy chain and actin were diminished (Fig. 4). The OH0 and OH1 samples exhibited higher intensity of myosin and actin than the CON sample, while less intensity was observed in the OH3 and OH5. As surimi was subjected to optimum temperature of the enzyme for a longer period of time, more degradation of myosin and actin occurred. For the sample held at 55°C for 5 min, the myosin heavy chain and actin almost disappeared. These results suggest that gel-weakening associated with breakdown of the myosin heavy chain and actin in Pacific whiting surimi was due to proteolytic activity. The highest gel strength and the most intense myosin heavy chain and actin bands were observed in OH0 gels that were heated to 90°C within 1 min. The myosin and actin bands of the OH0 were comparable to those of unheated surimi paste (Fig. 4). Probably rapid thermal inactivation minimized degradation of the myosin and actin.

The effect of ohmic heating on surimi gel quality was also reported by Shiba (1992). Gel strength of surimi made from walleye pollock, white croaker, and sardine was increased when ohmically heated at a heating rate of 47°C/min was applied. Shiba and Numakura (1992) illustrated that walleye pollock surimi (diameter = 3 cm, length = 18 cm) heated by ohmic heating within 1 min exhibited a 33.1% increase in gel strength and a 38.1% increase in myosin heavy chain content in comparison with that heated conventionally 50 min. Gel strength and the myosin heavy chain content were decreased when the samples were heated ohmically with a slow heating rate. Since there is no substantial evidence of the presence of endogenous prote-

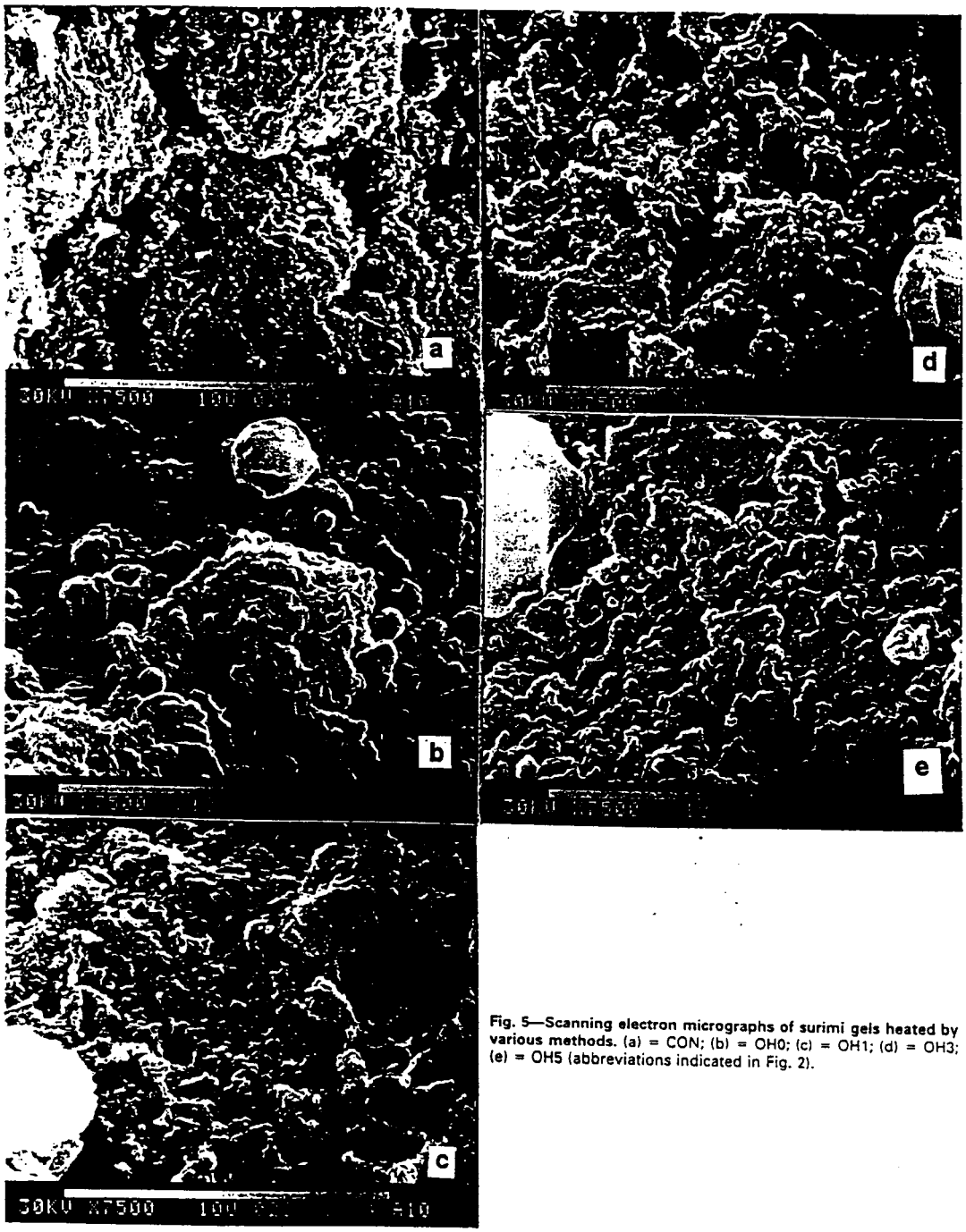

Fig. 5—Scanning electron micrographs of surimi gels heated by various methods. (a) = CON; (b) = OH0; (c) = OH1; (d) = OH3; (e) = OH5 (abbreviations indicated in Fig. 2).

ase(s) in walleye pollock, an increased gel quality may not be solely affected by rapid inactivation of the protease(s). However, ohmic heating with a rapid heating rate can evidently improve surimi gel quality.

Although the intensity of the myosin heavy chain band of CON gels was visually greater than that of OH3 gels, no differences ($P > 0.05$) occurred in shear strain and shear stress between those two gels. Toyohara and Shimizu (1988) also found a similar discrepancy. They indicated that the intensity of myosin did not accordingly correlate with gel strength. We could hypothesize that, once the myosin was degraded by the enzyme to a specific level, the gel network could not be properly

formed regardless of degree of degradation. This would agree with the fact that intact myosin is required for gel formation (Ziegler and Acton, 1984). When the myosin is severely hydrolyzed to smaller protein fragments (OH3 and OH5 in Fig. 4), a gel network was hardly developed, resulting in extremely low gel strength and very mushy texture.

Effects of heating methods on gel microstructure

Scanning electron micrographs of surimi gels heated by various heating methods were compared (Fig. 5). Microstructure of CON gels showed a sponge-like structure with several voids (Fig. 5a). The protein particles appeared to be randomly aggregated, without ordered network formation. This corresponded to a poor gel strength observed in the conventionally heated samples. On the other hand, OH0 gels involved formation of a continuous network exhibiting some definite degree of order (Fig. 5b). Microstructures of ohmically heated gels showed more openings and discontinuity as holding time at 55°C increased (Fig. 5c, 5d, 5e), particularly the samples held at 55°C for 5 min. These micrographs suggested that poor gel network formation resulted from degradation of myofibrillar proteins caused by proteolysis.

CONCLUSIONS

PACIFIC WHITING GELS rapidly heated to 90°C by ohmic heating with a voltage gradient of 13.3 V/cm demonstrated superior shear stress and shear strain. Degradation of the myosin heavy chain and actin was significantly minimized. Scanning electron micrographs showed a continuous gel structure corresponding to its gel strength. A decreased gel strength associated with poor gel network and degradation of the myosin heavy chain and actin was noticed as holding time at optimum temperature of the protease, 55°C, was prolonged. Surimi gels were susceptible to proteolysis under conventional heating since a slow heating rate allowed the enzyme to degrade more myosin heavy chain and actin.

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APPENDIX C

THERMAL CONDUCTIVITY MODELING USING SASTRY'S MODEL

Sastry's Model was used to predict thermal conductivity for different moisture content surimi paste samples. The model predicts thermal conductivity of food materials based on their composition. It is assumed that all food material can be broken down to its basic components, which are Water, Carbohydrate, Protein, Fat, Ice (For frozen foods), Ash, and Air. The model describe the thermal conductivity of a composite as the combination of continues and discontinuous phases. Starting with water as continuous, carbohydrate discontinuous; then water and carbohydrate continuous, protein discontinuous, and continuing through all phases. Knowing thermal conductivity and the volumetric percentage of each component in the food material, thermal conductivity for this material (a system of i+1 component) can be calculated according to the following iterative algorithm:

$$k_{i+1} = \frac{k_i[1 - Q_{i+1}]}{1 - Q_{i+1}[1 - (X_{i+1})^{1/3}]}$$

Where

$$Q_{i+1} = (X_{i+1})^{2/3}\left[1 - \frac{k_{i+1}}{k_i}\right]$$

$$X_{i+1} = \frac{V_{i+1}}{\Sigma V_i}$$

and V_i is component volume

Thus for an N-component material, thermal conductivity for this material is given by:

$$k_N = \frac{k_{N,1}[1-Q_N]}{1-Q_N[1-(X_N)^{1/3}]}$$

Thermal conductivities for four different moisture content surimi paste samples were calculated using this method and compared to values obtained experimentally using linear heat source prob.

Sample Analyses:

Four samples were prepared from Pacific whiting surimi with 2% NaCl, 1% Beef Plasma Protein (BPP) and 74, 78, 80 and 84% moisture. The ingredients of the samples are listed in Table (1). Compositions of both surimi and BPP are listed in Table (2). Composition of BPP was provided by American Meat Processing company (AMPC) and composition analysis for surimi were done in the OSU Seafood lab in Astoria according to AOAC standard method. Based on surimi and BPP composition, the compositions of the four samples were calculated and listed in Table (3). Samples densities are listed in Table (4) (See Appendix for density measurement procedure).

%Moisture	BPP	Surimi	Water	NaCl	Total
74	5.6	515.6	28	11.2	560.4
78	8.5	621.8	203.6	17	850.8
80	9.7	656.4	286.5	19.3	965.3
84	9.65	501.3	435.2	19.3	965.5

Table C.1 Ingredients of different moisture contents surimi paste samples (in grams)

	Surimi	BPP
% moisture	75.15	7.69
% Fat	1.04	2.5
% Ash	0.55	12
%Carbohydrate	7.52	9
% Protein	15.74	68.8

Table C.2 Proximate composition for surimi and BPP

% Moisture	% Protein	% Ash	% Carbohydrate	% Fat
74	15.2	2.12	7.13	1.0
78	12.2	2.0	6.4	0.7
80	11.4	1.9	6.0	0.7
84	8.8	1.9	4.1	0.5

Table C.3 Composition of different moisture content surimi paste sample.

% Moisture	Density (g/cc)
74	1.066±0.017
78	1.058±0.021
80	1.037±0.005
84	1.033±0.01

Table C.4 Densities for Different moisture content surimi paste samples.

Results:

Experimental and predicted thermal conductivities for four different moisture content surimi paste samples were compared and the results are listed in Table (5). The error in the predicted values ranges between 0 and 10%. The model mostly over-predicted thermal conductivity. Comparing the results obtained by Sastry for cake and ice cream, the errors in predicting thermal conductivity for surimi paste is much lower. This model works fairly good in predicting thermal conductivity for surimi paste based on its composition, and it can be used for our heat transfer model.

Sample moisture content	Temp (C)	Thermal conductivity k (exp.) (W/m-K)	Thermal conductivity k (model) (W/m-K)	% Error
74	30	0.524±0.019	0.540	3.0
	40	0.525±0.024	0.560	6.7
	50	0.550±0.015	0.579	5.3
	60	0.601±0.013	0.600	-0.16
	70	0.600±0.018	0.622	3.7
	80	0.630±0.020	0.645	2.5

(a)

Sample moisture content	Temp(C)	Thermal conductivity k (exp.) (W/m-K)	Thermal conductivity k (model) (W/m-K)	% Error
78	30	0.534±0.002	0.555	3.9
	40	0.539±0.020	0.575	6.6
	50	0.570±0.024	0.595	4.3
	60	0.565±0.064	0.617	9.2
	70	0.610±0.009	0.640	4.9
	80	0.680±0.035	0.660	-2.9

(b)

80	30	0.536±0.010	0.557	3.9
	40	0.570±0.020	0.577	1.2
	50	0.571±0.009	0.598	4.7
	60	0.587±0.013	0.620	5.6
	70	0.610±0.012	0.643	5.4
	80	0.683±0.007	0.667	-2.3

(c)

84	30	0.567±0.010	0.567	0
	40	0.577±0.005	0.586	1.6
	50	0.577±0.005	0.608	5.4
	60	0.613±0.031	0.630	2.8
	70	0.632±0.027	0.653	3.3
	80	0.708±0.048	0.678	-4.2

(d)

Table C.5 Comparison between experimental and predicted thermal conductivity for (a) 74, (b) 78, (c) 80 and (d) 84% Moisture content surimi paste samples.