LWT - Food Science and Technology 75 (2017) 417–424

Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

Development of model food systems for thermal pasteurization applications based on Maillard reaction products

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ARTICLE INFO

Article history:
Received 1 July 2016
Received in revised form
12 September 2016
Accepted 13 September 2016
Available online 14 September 2016

Keywords:
Mashed potato
Egg white
Gellan
Chemical marker
Microwave-assisted pasteurization

ABSTRACT

Model food systems with Maillard reaction products have been an effective tool to assess process lethality for microwave-assisted thermal sterilization. However, model food systems used for sterilization temperatures (110–130 °C) are not optimal for pasteurization temperatures (70–100 °C). The purpose of this research was to develop and assess model food systems to quantify process lethality and food quality for pasteurization applications, such as microwave-assisted pasteurization. Chemical marker M-2 (4-hydroxy-5-methyl-3(2H)-furanone) and color reaction kinetics were determined for egg white, mashed potato, and gellan model foods. M-2, L*, and a* value changes followed first order reaction kinetics and were significantly correlated to thermal lethality and cook value. Mashed potato was the optimal model food, in part because it had the greatest range of L* and a* reaction rates at 90 °C. Mashed potato model foods developed in this study could be used in the future to describe safety and quality reactions during pasteurization process evaluation.

1. Introduction

Products of the Maillard reaction have been used as indicators of heat treatment for process lethality evaluation for about 25 years (Kim & Taub, 1993; Kim, Taub, Choi, & Prakash, 1996). Newer thermal processing technologies, such as aseptic with particulates, ohmic heating, and microwave heating, have generated significant interest in the food industry, but it is challenging to use traditional direct temperature measurement methods in developing thermal processes (Kim et al., 1996). Time-temperature integrators (e.g. Maillard reaction products) are an effective alternative developed to quantify the change in a safety or quality attribute due to a variable time-temperature history (Van Loey, Hendrickx, De Cordt, Haentjens, & Tobback, 1996).

Researchers at the United States Army Natick Research Center found three Maillard reaction products that could be used to evaluate process lethality for sterilization of low-acid foods using continuous thermal processing: M-1 (2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one), M-2 (4-hydroxy-5-methyl-3(2H)-furanone), and M-3 (5-hydroxymethylfurfural) (Kim & Taub, 1993; Kim et al., 1996). These chemical markers have been evaluated for prediction of process lethality at sterilization temperatures for thermal pulses (Ross, 1993), canned food with particulates (Wnorowski & Yaylayan, 2002), aseptic processing of particulate foods (Kim & Taub, 1993; Ramaswamy, Awuah, Kim, & Choi, 1996), high pressure assisted thermal processing (Gupta, Mikhaylenko, Balasubramaniam, & Tang, 2011), microwave-assisted sterilization (Pandit, Tang, Mikhaylenko, & Liu, 2006; Prakash, Kim, & Taub, 1997; Wang, Lau, Tang, & Mao, 2004; Wang et al., 2009), and microwave-assisted pasteurization (Zhang, Tang, Liu, Bohnet, & Tang, 2014). M-2 was selected as the most applicable for high tempertaure, short time processes, such as microwave heating, because of the faster reaction rate and first order kinetics (Lau et al., 2003; Pandit et al., 2006). Chemical marker (M-2) and brown color formation in model foods systems were utilized for heating pattern visualization, as well as process and simulation validation of a microwave-assisted thermal sterilization (MATS) process, where product temperatures typically reach over 120 °C (Tang, 2015).

A Microwave Assisted Pasteurization System (MAPS) has been developed at Washington State University to thermally pasteurize food (Tang, 2015). For thermal pasteurization of prepackaged chilled food, the European Chilled Food Federation (ECFF) (2006) and United States Food and Drug Administration (FDA) (2011) recommend an equivalent heat treatment of 70 °C for 2 min for a minimum 6 log reduction in *Listeria monocytogenes* or 90 °C for 10 min for a minimum 6 log reduction in the most heat resistant group of nonproteolytic *Clostridium botulinum* spores, e.g. types B and E. The

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http://dx.doi.org/10.1016/j.lwt.2016.09.020
0023-6438/

MAPS was designed with flexible temperature controls; process schedules can be developed to meet either of these pathogen reduction requirements to achieve pasteurization.

During the development of MAPS, it is essential to be able to visualize the heating pattern and validate computer simulations and proposed process schedules. Similar to validating a MATS process, model food systems with Maillard reaction product formation may be useful for MAPS process development and simulation validation. However, the whey protein gel (Lau et al., 2003) and mashed potato with xanthan gum (Pandit et al., 2006) model food systems used for sterilization are not optimal for pasteurization due to slower Maillard reaction kinetics and high gelation temperatures (80 °C) for whey proteins. There is a need to develop model food systems that are feasible for pasteurization temperatures (70–100 °C) and determine the Maillard reaction kinetics in those systems. In this research, nonproteolytic *C. botulinum* was selected as the target pathogen for pasteurization and therefore, 90 °C was utilized during kinetic studies.

Previous research on M-2 chemical marker formation at pasteurization temperatures is very limited, with one published work by Zhang et al. (2014) on an egg white model food and preliminary tests on a gellan model food (Zhang, 2014). Model food development in all earlier studies for microwave applications was aimed at process lethality determination, not quality optimization. The objectives of this research were to (1) develop model food systems with varying amounts of precursor compounds (ribose and lysine) for use in MAPS process validation and optimization, (2) assess the color and M-2 formation kinetics at 90 °C of the model food systems, and (3) recommend an optimal model food system for future research.

2. Materials and methods

2.1. Sample preparation

Three model foods were selected for analysis: egg white, gellan, and mashed potato with added gellan gum. Four formulas were used for all model food systems with varying amounts of chemical marker precursors (D-ribose and L-lysine): 0 g/100 g D-ribose and 0 g/100 g L-lysine, 1 g/100 g D-ribose and 0.5 g/100 g L-lysine, 1 g/100 g D-ribose and 1 g/100 g L-lysine, and 2 g/100 g D-ribose and 2 g/100 g L-lysine, abbreviated throughout the paper as 0_R, 0_L, 1_R, 0.5_L, 1_R, 1_L, and 2_R, 2_L, respectively. The formula with the lowest amount of added precursors, 1_R, 0.5_L was selected based on Zhang et al. (2014). Formulas with greater amounts of Maillard browning precursors (1_R, 1_L and 2_R, 2_L) were selected based on the hypothesis that these formulas would have faster reaction rates.

Egg white model food was selected due to promising initial results in heating pattern analysis at pasteurization temperatures (75–100 °C) (Zhang et al., 2014). The egg white model food formula was modified from Zhang et al. (2014) and 100 g of the model food contained 25 g stabilized, glucose reduced powdered egg whites (JustWhites®, Deb-El Food, Elizabeth, NJ), 0–2 g D-ribose (Sigma-Aldrich Co. LLC, St. Louis, MO), 0–2 g L-lysine (Sigma-Aldrich Co. LLC, St. Louis, MO), and the remaining amount double deionized (DDI) water (71–75 g). The powdered egg whites were mixed with 35 °C DDI water for 10 min and the mixture was heated at 35 °C for 20 min to further rehydrate the egg whites. Chemical marker precursors (D-ribose and L-lysine) were added and mixed for 30 min. The solution was placed into a custom designed aluminum test cell with a diameter of 18 mm and height of 4 mm (Chung, Birla, & Tang, 2008). The egg white solution inside the test cells was heated for 30 min at 70 °C and cooled in ice water to form a firm gel (Zhang et al., 2014).

Gellan model food (Zhang, 2014; Zhang et al., 2015) showed promising initial results, but the model was translucent, which is a limitation because a translucent model food can obscure color and heating pattern analysis. The gellan model food formula in this study was modified from Zhang (2014) to be opaque by adding titanium dioxide. 100 g of the gellan model food consisted of 1 g low acyl gellan gum (Kelcogel® F Food grade gellan gum, supplied by CP Kelco Inc., Atlanta, GA), 0.5 g titanium dioxide dispersed in glycerin and water (white-white icing color, Wilton Industries Inc., Woodridge, IL), 0.26 g calcium chloride ($CaCl_2 \cdot {}_2H_20$, J.T. Baker, Avantor Performance Materials, Inc., Center Valley, PA), 0–2 g D-ribose, 0–2 g L-lysine, and the remaining amount DDI water (84.24–98.24 g). The titanium dioxide was mixed with 22 °C DDI water for 5 min, followed by the addition of the gellan gum powder, mixed for an additional 5 min. While stirring, the mixture was heated to 90 °C, the calcium chloride was added, and the mixture was held at 90 °C for 1 min. Chemical marker precursors were added once the solution was cooled to 65 °C and were mixed for 3 min. The solution was poured into the custom designed test cells and cooled to 22 °C to form a firm gel.

Mashed potato with added xanthan gum was a successful model in microwave sterilization work (Pandit et al., 2006), but did not form a firm gel at pasteurization temperatures. Mashed potato was selected for this study, but the formula was modified to include gellan gum instead of xanthan gum to obtain a firm gel. Low acyl gellan was selected over alternative gelling agents because it forms a strong, brittle gel in the presence of cations and has a low enough gelation temperature to be used in pasteurization applications (Morris, Nishinari, & Rinaudo, 2012; Tang, Lelievre, Tung, & Zeng, 1994; Tang, Tung, & Zeng, 1997). The mashed potato model food formula was modified from Pandit et al. (2006) and 100 g of the model food contained 15 g instant mashed potato flakes (Oregon Potato Co., Boardman, OR), 0.5 g low acyl gellan gum, 0.13 g calcium chloride, 0–2 g D-ribose, 0–2 g L-lysine, and the remaining amount DDI water (80.37–84.37 g). The gellan gum powder was mixed with 22 °C DDI water for 5 min, followed by the addition of the potato flakes to the solution. Similar to the gellan model, the mashed potato model solution was heated to 90 °C, the calcium chloride was added, and the mixture was held at 90 °C for 1 min. Chemical marker precursors (D-ribose and L-lysine) were added once the solution was cooled to 60 °C and were mixed for 5 min to obtain a uniform distribution of the chemical marker precursors. Mashed potato model food was placed into the test cell and cooled to ambient temperature (22 °C) to form a firm gel.

2.2. Thermal treatment

Model foods were exposed to thermal treatments by heating the samples inside custom designed, cylindrical, aluminum test cells with a diameter of 18 mm and height of 4 mm (Chung et al., 2008) using an ethylene glycol bath (Haake DC 30, Thermo Fisher Scientific Inc., Newington, NH). The average come-up time (CUT), defined as the time for the coldest spot in the sample to reach within 0.5 K of the target, was measured to be 1.75 min using a calibrated type-T thermocouple. All three model foods were heated at 90 °C from 5 to 180 min (excluding CUT), followed by cooling in ice water (0 °C). Kinetic experiments were conducted in triplicates.

2.3. Chemical marker quantification

The average concentration of chemical marker, M-2 (4-hydroxy-5-methyl-3(2H)-furanone) in each sample was determined using an adapted method from Zhang et al. (2014) with high performance liquid chromatography (HPLC). Briefly, sample preparation involved grinding each 0.8 g sample in 8 mL of 10 mmol/L H_2SO_4

extraction buffer, centrifuging, collecting the supernatant, filtering, and sealing the sample in a glass HPLC sample vial. M-2 measurement was performed with an Agilent 1100 HPLC system (Agilent Technology, Santa Clara, CA) equipped with a diode array detector and 100 × 7.8 mm fast acid analysis column (Bio-Rad Laboratories, Hercules, CA) with 10 mmol/L H_2SO_4 mobile phase at 1 mL/min with a detecting wavelength of 285 nm (Zhang et al., 2014). Each sample was analyzed twice using the HPLC automatic injection system with a sample injection volume of 25 μL. M-2 standard curves were developed using solutions of varying concentration levels with commercial M-2 (Sigma-Aldrich Co. LLC, St. Louis, MO). Following the method of Zhang et al. (2014), the standard curve data was used to convert the peak area from the HPLC analysis into M-2 concentration (mg M-2/g sample).

2.4. Color quantification

The color was determined in L*a*b* (CIELAB) color space using a computer vision system. The camera and hardware set-up was described in Pandit, Tang, Liu, and Mikhaylenko (2007), but this study used different camera settings and image analysis. The camera white balance was preset using mode S with a 15 frames per second speed and smooth white paper (Recollections® Signature Smooth Cardstock in white, Michaels Stores Inc., Irving, TX). The camera was set with an F (aperture value) of 11, speed of 15 frames per second, and ISO sensitivity of 200; these camera settings were found to be optimal in order to produce the most realistic picture of a 35 patch reference color card (QPcard 203, QPcard AB, Sweden). During each photography session, the color reference card was photographed and used to correct the color and transform the sample images from RGB to L*a*b* color space by using a quadratic model adapted from Leon, Mery, Pedreschi, and Leon (2006). Image analysis was performed in MATLAB R2013a and consisted of applying the color correction and analyzing the pixel values in a circle containing 37,695 pixels for each sample.

2.5. Statistical analysis

Statistical analysis was performed using SAS® 9.2. Pearson correlation coefficients were determined to look for correlation between the color parameters (L*, a*, and b*) and time. The p-value for significance was less than 0.05.

A modified non-linear regression method described in Lau et al. (2003) was utilized to determine the reaction kinetics for M-2 and color (L* and a*) parameters. Briefly, non-linear regression in SAS® 9.2 was used to fit zero, first, and second order rate equations to the data. For example, the generalized first order equation was (Lau et al., 2003):

$$C = C_\infty - (C_\infty - C_0)\exp(-k\cdot t) \quad (1)$$

where C is the value of the parameter (M-2, L*, or a*), C_∞ is the value of the parameter ($M\text{-}2_\infty$, L^*_∞, or a^*_∞) at saturation, C_0 is the initial value of the parameter ($M\text{-}2_0$, L^*_0, or a^*_0), k is the reaction rate constant (1/min), and t is time (min). For L* value regression, Equation (1) was multiplied by −1 because the L* value decreased with time rather than increased like the other parameters, M-2 and a*. The Newton algorithm for non-linear regression in SAS was used to determine the C_0, C_∞, and k for each parameter (M-2, L*, or a*) at each temperature. Experimental results showed that the initial M-2 concentration was zero for all models and therefore, the value of $M\text{-}2_0$ was assigned as a constant (zero). Coefficient of determination (R^2) values were calculated for each regression and utilized to determine which rate equation (zero, first, or second order) fit the data best.

The model foods' accumulated thermal lethality (F_{90}) for the target pathogen, nonproteolytic *C. botulinum*, was determined by (Toledo, 2007):

$$F_{90} = \int_0^t 10^{(T-90)/z}dt \quad (2)$$

where F_{90} is the equivalent thermal treatment time at 90 °C (min), T is the temperature (°C) at time t (min), and z is the thermal resistance constant with a value of 10 K for the target pathogen mentioned above (FDA, 2011; ECFF, 2006). Cook value (C_{100}) has been used as an indicator of food quality and the model foods' accumulated cook value was determined by (Toledo, 2007):

$$C_{100} = \int_0^t 10^{(T-100)/z}dt \quad (3)$$

where C_{100} is the equivalent thermal treatment time at 100 °C (min), T is the temperature (°C) at time t (min), and z is the thermal resistance constant with a value of 33 K for overall food quality (Toledo, 2007). Pearson correlation coefficients were determined between M-2, L*, a* and F_{90}, C_{100}.

3. Results and discussion

3.1. Chemical marker (M-2) results

All three model food systems without added ribose or lysine had no significant M-2 formation (0 mg M-2/g sample). The pH of the 0_R, 0_L formula at 22 °C was 6.0 for egg white, 5.2 for mashed potato, and 6.1 for gellan model food. In contrast, the pH of the formulas with added precursors at 22 °C ranged from 7.8 to 9.5 for egg white, 8.4–9.5 for mashed potato, and 9.8–9.9 for gellan model food. The higher pH of formulas with added precursors may have contributed to the increased rate of the Maillard reaction and M-2 formation (Van Boekel, 2001). This showed the importance of adding the precursors to adjust the pH and facilitate the Maillard reaction at pasteurization temperatures.

The M-2 concentration in egg white and mashed potato model foods with added precursors increased with increasing time at 90 °C until an apparent $M\text{-}2_\infty$ concentration was achieved (Fig. 1). However, the gellan model foods with added precursors had very small M-2 concentrations (<0.01 mg M-2/g sample); the M-2 concentration was too low to measure accurately and therefore, the results for those model foods were not included in the following analysis. The small M-2 concentration finding agreed with previous work on chemical marker formation at pasteurization temperatures in water with added ribose and lysine (idealized gellan model food) (Zhang, 2014). The near zero M-2 concentration in gellan models could be due to the composition of the model food. The gellan model did not contain significant amounts of carbohydrates or proteins that could participate in the Maillard reaction, aside from the added chemical marker precursors, ribose and lysine. This finding showed the importance of the model having carbohydrate or protein components to facilitate chemical marker formation.

M-2 formation in egg white and mashed potato models followed first order kinetics, as they had the best model fit, with average R^2 values among all treatments of 0.91 for zero order, 0.98 for first order, and 0.76 for second order. First order reaction kinetics for M-2 formation at 90 °C in this study matched previous research on M-2 kinetics at sterilization temperatures (116–131 °C) in whey protein (Lau et al., 2003) and mashed potato (Pandit et al., 2006). However, Zhang et al. (2014) concluded that M-2 formation

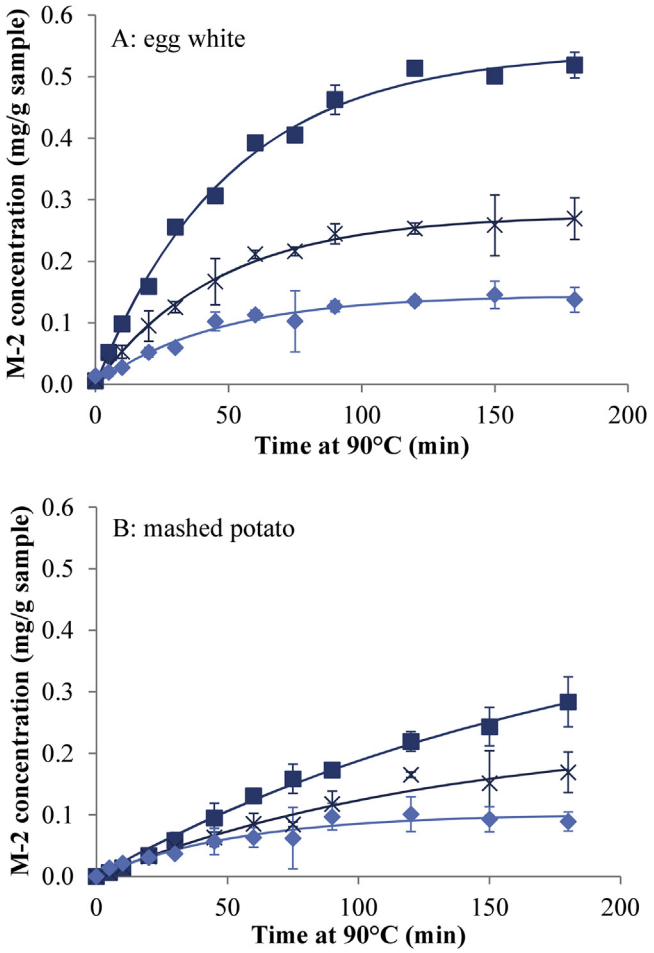

Fig. 1. Experimental chemical marker M-2 concentration (3 replicates) during heating at 90 °C with 95% confidence intervals for egg white (A) and mashed potato (B) with added precursor amounts of 1 g/100 g ribose and 0.5 g/100 g lysine (■), 1 g/100 g ribose and 1 g/100 g lysine (×), and 2 g/100 g ribose and 2 g/100 g lysine (◆). Predicted concentrations using the first order kinetic model are shown for each model food (——). The gellan model was excluded due to low M-2 concentrations.

in egg white model food (1 g/100 g ribose, 0.5 g/100 g lysine added) at pasteurization temperatures (75–100 °C) fit best to zero order reaction kinetics. This seemingly contradictory result could be due to a different data analysis technique (graphical method) and the short total time used in the Zhang et al. (2014) study, where the maximum time the model food was heated was 30 min, which was not enough time for the apparent M-2_∞ value to be reached. A first order reaction may look like a zero order reaction if a short enough time is considered, which could explain the different reaction orders between Zhang et al. (2014) and this study.

Both egg white and mashed potato had similar M-2_∞ values for each level of precursor amount (Table 1). M-2 saturation values (M-2_∞) decreased with increasing amounts of added precursors; this result matched findings from Pandit et al. (2006), who showed decreased M-2 formation at 121 °C in mashed potato models with greater amounts of added lysine. M-2 is an intermediate Maillard reaction product; as the reaction proceeds, furanones, such as M-2, may degrade into other smaller molecular weight color and flavor compounds (O'Brien, 1998). There are many other Maillard reaction pathways that result in brown color formation without M-2 formation. These alternative pathways could be the primary source of brown color in model food systems with greater amounts of precursors, which may explain the lower M-2_∞, but higher amount of brown color formation.

The egg white model had similar reaction rates for all formulas, averaging 21.2 × 10^{-3} 1/min (D-value average 108.8 min), but the reaction rates for mashed potato models increased with increasing precursor amounts, ranging from 5.1 to 18.3 × 10^{-3} 1/min (D-values 125.8–448.8 min) (Table 1). This could be explained by the difference in the composition of the models and limiting factor of the reaction rate. There are four key amino acids that lead to M-2 formation during the Maillard reaction: lysine, arginine, methionine, and histidine (Pandit et al., 2006). In glucose reduced egg white powder reconstituted to a 25 g/100 g solid level (egg white model food), there were approximately 0 g/100 g total sugars, 1.3 g/100 g lysine, 1.2 g/100 g arginine, 0.8 g/100 g methionine, and 0.5 g/100 g histidine (USDA, 2015). In instant mashed potato flakes reconstituted to a 15 g/100 g solid level (mashed potato model food), there were approximately 0.5 g/100 g total sugars, 0.07 g/100 g lysine, 0.06 g/100 g arginine, and 0.02 g/100 g methionine and histidine (USDA, 2015). Egg white may have had a faster reaction rates with lower amounts of added precursors because of the higher amino acid content compared to mashed potatoes, where the amino acid content was the limiting factor in the M-2 formation reaction. In egg white, the reaction rates may have been similar for all formulas because there were excess sugars and amino acids and their concentration did not limit the reaction rate during heating at 90 °C for 180 min. Reaction rates in this study cannot be compared to previous work on egg white model food at pasteurization temperatures by Zhang et al. (2014) because reaction rates are not reported.

3.2. Color results

All model food systems with no added ribose or lysine did not show significant brown color formation (Fig. 2). The lack of brown color formation in the 0 g/100 g ribose, 0 g/100 g lysine formulas matched M-2 formation results and could be attributed to lower pH in these models and insufficient concentration of ribose and lysine to catalyze the reaction. This finding demonstrated the importance of adding the precursors to adjust the pH and facilitate Maillard browning at pasteurization temperatures.

During heating at 90 °C, all model foods with added precursors showed increased brown color formation with increasing time until an apparent saturation was reached, with greater brown color formation for models with a greater amount of added precursors, ribose and lysine (Fig. 2). The mashed potato model with 2 g/100 g ribose, 2 g/100 g lysine had the greatest amount of brown color formation during heating, according to visual inspection and image analysis.

All L* values were significantly correlated to time with negative correlation coefficients ranging from −0.72 to −0.94. a* values were also significantly correlated to time with positive correlation coefficients ranging from 0.71 to 0.95, except the mashed potato 2_R, 2_L sample, which had a non-significant correlation coefficient of −0.17. The poor correlation coefficient between a* and time for the 2_R, 2_L mashed potato samples could be explained by a rapid browning rate; the samples browned so quickly that the a* value saturation occurred after 20–30 min and the correlation coefficient was poor when all the time points up to 180 min of heating were utilized. However, when the data were restricted to 20 min of heating the correlation coefficient between a* and time for the 2_R, 2_L mashed potato samples improved to a significant value of 0.88. For the remainder of the analysis, the mashed potato 2_R, 2_L a* values were modified to include up to 20 min of heating. The b* values' relationship with heating time was less consistent, with correlation coefficients ranging from −0.87 to 0.90; five of the treatment conditions had a significant positive correlation, two had

Table 1
Predicted M-2_∞, L^*_0, L^*_∞, a^*_0, a^*_∞ and k with estimated standard error (3 replicates) for egg white, mashed potato, and gellan model food samples with added precursor amounts of 1 g/100 g ribose and 0.5 g/100 g lysine (1_R, 0.5_L), 1 g/100 g ribose and 1 g/100 g lysine (1_R, 1_L), and 2 g/100 g ribose and 2 g/100 g lysine (2_R, 2_L) during heating at 90 °C. The M-2 data were excluded for the gellan model due to low M-2 concentrations. M-2_0 concentration was assumed zero for all models.

Model food		M-2			L* value				a* value			
		M-2_∞ (mg M-2/g sample)	k (10^{-3} 1/min)	R^2	L^*_0	L^*_∞	k (10^{-3} 1/min)	R^2	a^*_0	a^*_∞	k (10^{-3} 1/min)	R^2
Egg white	1_R, 0.5_L	0.54 ± 0.01	19.9 ± 0.7	0.99	89.4 ± 0.8	59.0 ± 5.8	6.9 ± 2.2	0.91	−2.0 ± 0.4	13.2 ± 0.6	17.5 ± 2.2	0.95
	1_R, 1_L	0.28 ± 0.01	21.7 ± 1.8	0.99	85.3 ± 1.0	54.7 ± 2.6	12.5 ± 2.5	0.93	−0.4 ± 0.7	14.6 ± 0.7	24.3 ± 3.9	0.89
	2_R, 2_L	0.14 ± 0.01	22.0 ± 2.9	0.98	70.3 ± 0.9	38.7 ± 0.6	37.2 ± 3.3	0.97	6.6 ± 1.0	17.0 ± 0.4	67.8 ± 17.6	0.79
Mashed potato	1_R, 0.5_L	0.47 ± 0.06	5.1 ± 0.9	0.99	68.2 ± 1.3	39.5 ± 13.1	6.0 ± 4.3	0.76	1.7 ± 0.6	28.3 ± 5.3	6.5 ± 2.1	0.93
	1_R, 1_L	0.24 ± 0.03	7.4 ± 1.8	0.97	66.1 ± 1.0	35.4 ± 0.9	25.4 ± 2.9	0.95	2.4 ± 0.6	20.7 ± 0.5	28.8 ± 3.0	0.95
	2_R, 2_L	0.10 ± 0.01	18.3 ± 4.1	0.93	62.5 ± 1.2	22.7 ± 0.5	69.3 ± 5.2	0.97	2.7 ± 0.7	19.9 ± 1.0	169.9 ± 28.7	0.97
Gellan	1_R, 0.5_L	–	–	–	90.9 ± 2.1	66.7 ± 2.5	18.7 ± 6.3	0.68	−0.1 ± 0.9	12.0 ± 1.3	17.0 ± 5.7	0.74
	1_R, 1_L	–	–	–	91.5 ± 1.0	59.3 ± 1.0	23.2 ± 2.5	0.96	0.2 ± 0.6	12.8 ± 0.7	21.1 ± 4.0	0.90
	2_R, 2_L	–	–	–	86.4 ± 1.5	43.3 ± 0.8	48.7 ± 4.8	0.96	0.2 ± 1.0	13.8 ± 0.4	99.3 ± 20.2	0.85

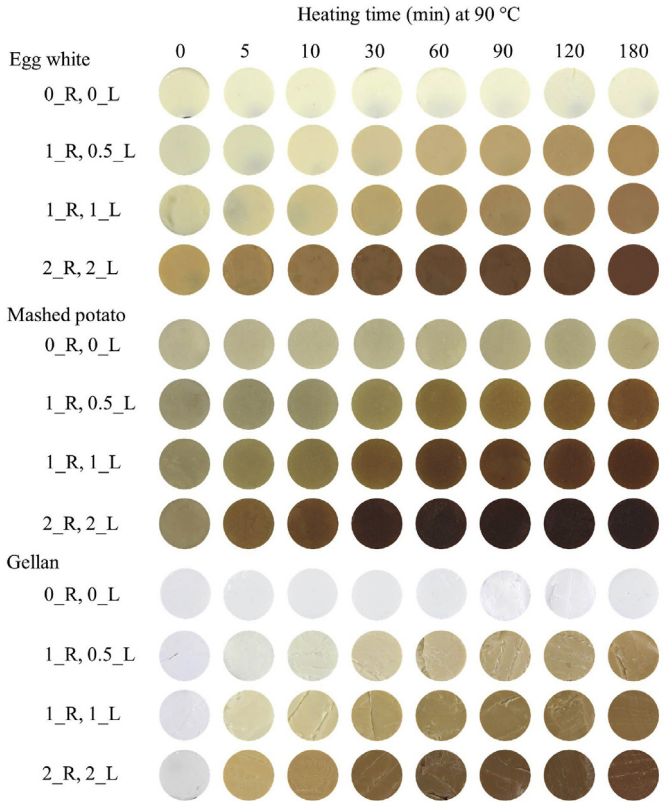

Fig. 2. Color change during heating at 90 °C of egg white, mashed potato, and gellan model food samples with added precursor amounts of 0 g/100 g ribose and 0 g/100 g lysine (0_R, 0_L), 1 g/100 g ribose and 0.5 g/100 g lysine (1_R, 0.5_L), 1 g/100 g ribose and 1 g/100 g lysine (1_R, 1_L), and 2 g/100 g ribose and 2 g/100 g lysine (2_R, 2_L).

a significant negative correlation, and two had no significant correlation. Additionally, four out of nine treatments showed poor correlation, with correlation coefficients between 0.02 and 0.57. For this reason, b* values were excluded from further kinetic analysis and regression was performed for only L* and a* parameters.

Color formation measured by a* value change fit best to first order reaction kinetics, with average R^2 values among all treatments of 0.71 for zero order, 0.89 for first order, and 0.69 for second order. Color formation measured by L* value change fit equally well to both first and second order kinetics, with average R^2 values among all treatments of 0.71 for zero order, 0.89 for first order, and 0.89 for second order. Among nine treatment conditions, six fit equally well to first and second order kinetics, two fit better to first order, and one fit slightly better to second order, with a difference of only 0.01 in the R^2 value. This implied that the color formation (L* value change) from the Maillard reaction is complex and could be explained by both first and second order kinetics. For ease of comparison with a* reaction rates in this study and previous literature containing quality and safety reaction kinetics, many of which are fit to first order, L* value change was modeled with first order kinetics.

For egg white, mashed potato and gellan models, the reaction rate of L* and a* value change increased with increasing amount of precursors in the formula (Table 1). This matched expectations for a first order reaction with a limited amount of reactants; as more precursors were added to the formula, the reaction proceeded at a faster rate. The range of L* value reaction rates among the three formulas was largest for mashed potato (63.3×10^{-3} 1/min), followed by egg white (30.3×10^{-3} 1/min) and gellan models (30.0×10^{-3} 1/min). The range of a* value reaction rates among the three formulas was greater than the L* value reaction rate range and mashed potato also had the largest a* value reaction rate range of 163.4×10^{-3} 1/min, followed by gellan (82.3×10^{-3} 1/min), and egg white models (50.3×10^{-3} 1/min). When selecting model foods for quality optimization, a larger range of reaction rates (i.e. mashed potato model) was preferable because of the greater flexibility in matching safety or quality reaction rates with the model food color formation rates.

3.3. Thermal lethality and cook value correlations

For food safety, the minimum thermal lethality (F_{90}) needed at the coldest spot in the product is 10 min in order to achieve a 6 log reduction in the target food pathogen, nonproteolytic *C. botulinum* (FDA, 2011; ECFF, 2006). During initial tests with the microwave-assisted pasteurization system, the hottest spot in the product may reach a much higher F_{90} (e.g. 50 min). For this reason, the correlation assessment between M-2, L*, and a* values and F_{90} and C_{100} was conducted for times up to 60 min at 90 °C or an F_{90} range of 0 min to approximately 60 min.

M-2 formation was significantly correlated to thermal lethality (F_{90}) and cook value (C_{100}) for egg white and mashed potato model foods (Fig. 3). Correlation coefficients were above 0.92 with an average correlation among all six treatments of 0.97 for egg white and mashed potato models. The correlation coefficients for the gellan model were excluded because the M-2 formation was not significant.

F_{90} and C_{100} were also compared to L* value (Fig. 4) and a* value (Fig. 5). L* value change was significantly correlated to F_{90} and C_{100} for all model foods, with negative correlation coefficients above −0.73 and an average correlation of −0.87, excluding the mashed potato 1_R, 0.5_L sample that had a poor correlation

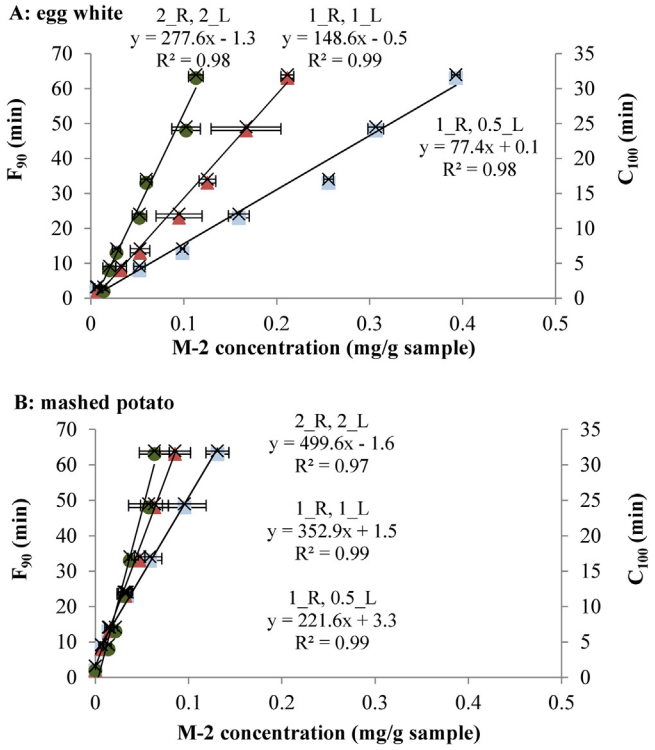

Fig. 3. Thermal lethality, F_{90} (●,▲,■) and cook value, C_{100} (×) with experimental chemical marker M-2 concentration (3 replicates) and 95% confidence intervals during the first 60 min of heating at 90 °C for egg white (A) and mashed potato (B) models with added precursor amounts of 1 g/100 g ribose and 0.5 g/100 g lysine (■), 1 g/100 g ribose and 1 g/100 g lysine (▲), and 2 g/100 g ribose and 2 g/100 g lysine (●). The gellan model was excluded due to low M-2 concentrations.

coefficient (<−0.7). The poor correlation coefficient between L* and F_{90} and C_{100} for 1_R, 0.5_L mashed potato samples could be explained by a slow browning rate. When the data used in the Pearson correlation coefficient calculation were expanded to 90 min of heating, the correlation coefficient improved to −0.93. This suggested that the mashed potato 1_R, 0.5_L L* value may not be a feasible indicator of thermal processing lethality and safety at 90 °C and may be useful at higher temperatures where the rate of browning would be faster. a* value change was significantly correlated to F_{90} and C_{100} for all model foods, where correlation coefficients were above 0.76 and an average correlation of 0.86.

The significant correlations between M-2, L*, and a* values and F_{90} and C_{100} indicated that there was potential for using M-2, L*, and a* values to predict thermal processing severity for both safety and food quality applications. This was a critical finding for this research and demonstrated the relevance of these model foods systems with Maillard reaction products for quality and safety evaluation during 90 °C heating. These results could be used as the basis for quantifying, evaluating, and comparing the safety and quality attributes of various thermal pasteurization methods, including conventional (e.g. hot water) and microwave-assisted pasteurization. In the future, additional processing temperatures in the pasteurization range (70–100 °C) could be considered and combined with the results from this study to create a more complete picture of the temperature sensitivity of these models and potential application at other processing temperatures for various thermal processing methods.

3.4. Selection of optimal model food

Six critical attributes of three model foods (egg white, mashed potato, and gellan) were considered in order to recommend the model food with the most advantageous properties for future research. Critical attributes included ease of cutting (gel firmness), temperature exposure after precursors were added (above this temperature the model would be useful), preparation time, dielectric properties, measurability of M-2 concentration, and range of L* and a* reaction rates at 90 °C. Mashed potato was determined to be the optimal model food because of the ease of cutting, low temperature (60 °C) exposure after precursors were added (model was useful at 60 °C and above), fast preparation time, dielectric properties (Guan, Cheng, Wang, & Tang, 2004) similar to food, measurable amount of M-2, and the largest range of L* and a* reaction rates at 90 °C. The main disadvantages of the egg white model were that the gel was too firm and difficult to cut, high temperature (70 °C) exposure after precursors were added (model was useful at 70 °C and above), long preparation time, and the

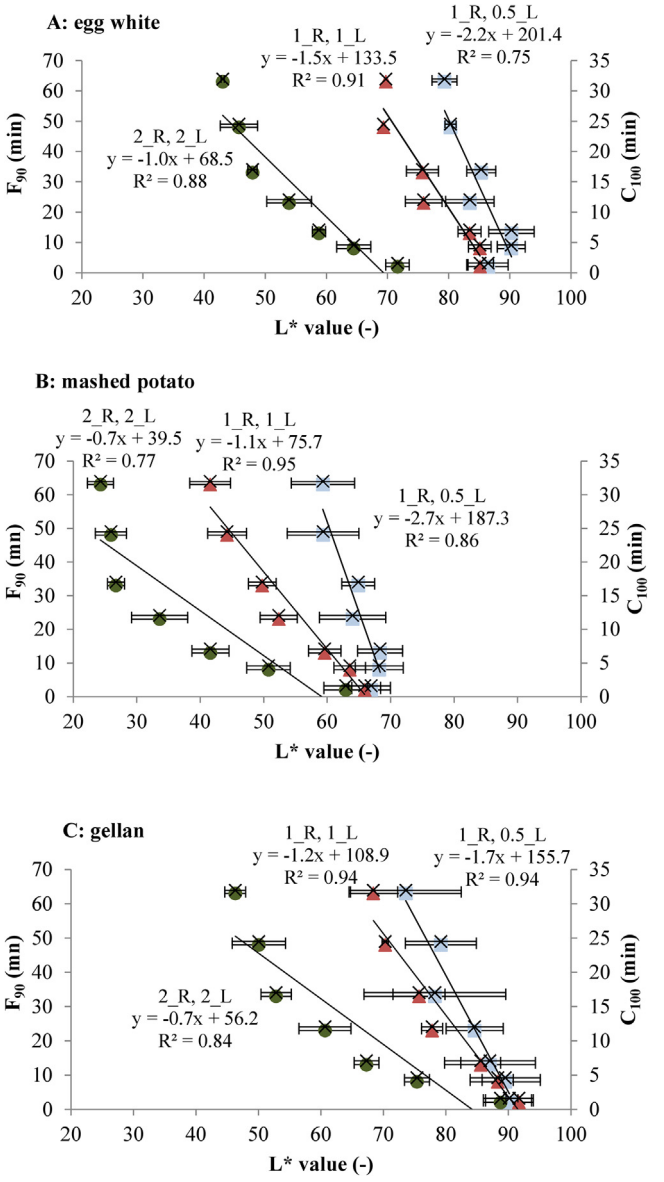

Fig. 4. Thermal lethality, F_{90} (●,▲,■) and cook value, C_{100} (×) with experimental L* value (3 replicates) and 95% confidence intervals during the first 60 min of heating at 90 °C for egg white (A), mashed potato (B), and gellan (C) models with added precursor amounts of 1 g/100 g ribose and 0.5 g/100 g lysine (■), 1 g/100 g ribose and 1 g/100 g lysine (▲), and 2 g/100 g ribose and 2 g/100 g lysine (●).

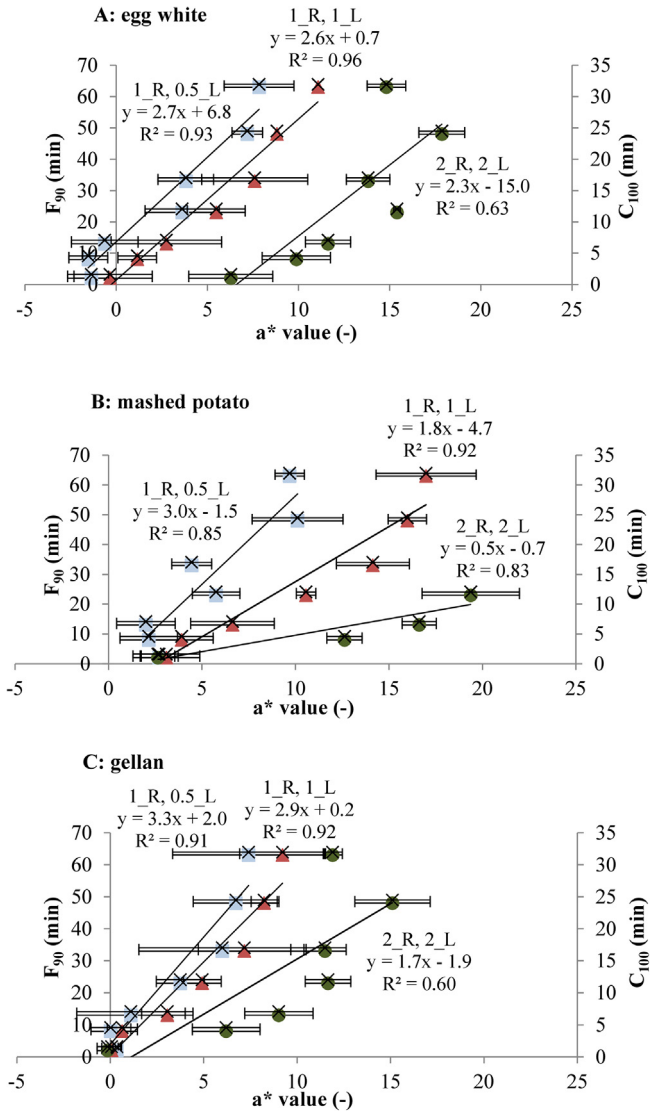

Fig. 5. Thermal lethality, F_{90} (●,▲,■) and cook value, C_{100} (×) with experimental a* value (3 replicates) and 95% confidence intervals during the first 60 min of heating at 90 °C for egg white (A), mashed potato (B), and gellan (C) models with added precursor amounts of 1 g/100 g ribose and 0.5 g/100 g lysine (■), 1 g/100 g ribose and 1 g/100 g lysine (▲), and 2 g/100 g ribose and 2 g/100 g lysine (●).

smallest range of L* and a* reaction rates at 90 °C. The main disadvantages of the gellan model were that the dielectric properties (Zhang et al., 2015) were the least similar to food among the three models, there was a near-zero, not significant amount of M-2 formed, and an intermediate range of L* and a* reaction rates at 90 °C. Thus, mashed potato was the optimal model food for future work in similar processing conditions as in this study.

4. Conclusions

Egg white, mashed potato, and gellan model foods were developed for use in process lethality validation and food quality optimization for thermal pasteurization processes, such as a Microwave Assisted Pasteurization System (MAPS). Chemical marker (M-2) and color (L* and a* values) were significantly correlated to thermal lethality (F_{90}) and cook value (C_{100}). This was an important finding because it suggested that there is potential for using M-2, L*, and a* values to evaluate the thermal processing severity for both safety and food quality applications at 90 °C. Among the three models, mashed potato was determined to be the optimal model food because it was easy to cut, fast to prepare, had a low temperature exposure after precursors were added and had the largest range of L* and a* reaction rates. A greater range of reaction rates was desired for greater flexibility in matching safety and quality reaction rates with the model food color formation rates. Additional pasteurization processing temperatures (70–100 °C) could be considered and combined with the 90 °C results from this research to develop a deeper understanding of the temperature sensitivity of these models and the potential application at other processing temperatures. The model foods developed in this study, especially mashed potato models, could be useful tools in the future for quantifying, evaluating, and comparing the safety and quality attributes of MAPS and conventional thermal pasteurization methods.

Acknowledgments

This research was supported in part by the National Institute of Food and Agriculture, U.S. Department of Agriculture (Grant No. 2011-68003-20096 and 2016-68003-24840). The authors also thank the U.S. Department of Agriculture, National Needs Fellowship grant program (2012-38420-19287) for supporting Ellen Bornhorst's Ph.D. studies at Washington State University.

References

Chung, H. J., Birla, S. L., & Tang, J. (2008). Performance evaluation of aluminum test cell designed for determining the heat resistance of bacterial spores in foods. *LWT- Food Science and Technology, 41*, 1351–1359.
European Chilled Food Federation (ECFF). (2006). *Recommendations for the production of prepackaged chilled food* (2nd ed).
Food and Drug Administration (FDA). (2011). *Fish and fisheries products hazards and control guidance* (4th ed.). U.S. Department of Health and Human Services.
Guan, D., Cheng, M., Wang, Y., & Tang, J. (2004). Dielectric properties of mashed potatoes relevant to microwave and radio-frequency pasteurization and sterilization processes. *Journal of Food Science, 69*, FEP30–FEP37.
Gupta, R., Mikhaylenko, G., Balasubramaniam, V. M., & Tang, J. (2011). Combined pressure-temperature effects on the chemical marker (4-hydroxy-5-methyl-3(2H)-furanone) formation in whey protein gels. *LWT- Food Science and Technology, 44*, 2141–2146.
Kim, H.-J., & Taub, I. A. (1993). Intrinsic chemical markers for aseptic processing of particulate foods. *Food Technology, 47*, 91–99.
Kim, H.-J., Taub, I. A., Choi, Y.-M., & Prakash, A. (1996). Principles and applications of chemical markers of sterility in high-temperature-short-time processing of particulate foods. In T. C. Lee, & H. J. Kim (Eds.), *Chemical markers for processed and stored foods* (pp. 54–69). Washington, D.C.: American Chemical Society.
Lau, M. H., Tang, J., Taub, I. A., Yang, T. C. S., Edwards, C. G., & Mao, R. (2003). Kinetics of chemical marker formation in whey protein gels for studying microwave sterilization. *Journal of Food Engineering, 60*, 397–405.
Leon, K., Mery, D., Pedreschi, F., & Leon, J. (2006). Color measurement in L*a*b* units from RGB digital images. *Food Research International, 39*, 1084–1091.
Morris, E. R., Nishinari, K., & Rinaudo, M. (2012). Gelation of gellan - A review. *Food Hydrocolloids, 28*, 373–411.
O'Brien, J. (1998). *The Maillard reaction in foods and medicine*. Cambridge, UK: Royal Society of Chemistry.
Pandit, R. B., Tang, J., Liu, F., & Mikhaylenko, G. (2007). A computer vision method to locate cold spots in foods in microwave sterilization processes. *Pattern Recognition, 40*, 3667–3676.
Pandit, R. B., Tang, J., Mikhaylenko, G., & Liu, F. (2006). Kinetics of chemical marker M-2 formation in mashed potato - A tool to locate cold spots under microwave sterilization. *Journal of Food Engineering, 76*, 353–361.
Prakash, A., Kim, H.-J., & Taub, I. A. (1997). Assessment of microwave sterilization of foods using intrinsic chemical markers. *Journal of Microwave Power and Electromagnetic Energy, 32*, 50–57.
Ramaswamy, H. S., Awuah, G. B., Kim, H.-J., & Choi, Y.-M. (1996). Evaluation of a chemical marker for process lethality measurement at 110C in a continuous flow holding tube. *Journal of Food Processing and Preservation, 20*, 235–249.
Ross, E. W. (1993). Relation of bacterial destruction to chemical marker formation during processing by thermal pulses. *Journal of Food Process Engineering, 16*, 247–270.
Tang, J. (2015). Unlocking potentials of microwaves for food safety and quality. *Journal of Food Science, 80*, E1776–E1793.
Tang, J., Lelievre, J., Tung, M. A., & Zeng, Y. (1994). Polymer and ion concentration effects on gellan gel strength and strain. *Journal of Food Science, 59*, 216–220.

Tang, J., Tung, M. A., & Zeng, Y. (1997). Gelling properties of gellan solutions containing monovalent and divalent cations. *Journal of Food Science, 62*, 688–692, 712.

Toledo, R. T. (2007). *Fundamentals of food process engineering* (3rd ed.). New York: Springer.

US Department of Agriculture (USDA), Agricultural Research Service, Nutrient Data Laboratory. (2015). *National nutrient database for standard reference, release 28*.

Van Boekel, M. (2001). Kinetic aspects of the Maillard reaction: A critical review. *Nahrung, 45*, 150–159.

Van Loey, A., Hendrickx, M., De Cordt, S., Haentjens, T., & Tobback, P. (1996). Quantitative evaluation of thermal processes using time-temperature integrators. *Trends in Food Science & Technology, 7*, 16–26.

Wang, Y., Lau, M. H., Tang, J., & Mao, R. (2004). Kinetics of chemical marker M-1 formation in whey protein gels for developing sterilization processes based on dielectric heating. *Journal of Food Engineering, 64*, 111–118.

Wang, Y., Tang, J., Rasco, B., Wang, S., Alshami, A. A., & Kong, F. (2009). Using whey protein gel as a model food to study the dielectric heating properties of salmon (*Oncorhynchus gorbuscha*) fillets. *LWT- Food Science and Technology, 42*, 1174–1178.

Wnorowski, A., & Yaylayan, V. A. (2002). Prediction of process lethality through measurement of Maillard-generated chemical markers. *Journal of Food Science, 67*, 2149–2152.

Zhang, W. (2014). *The development of time-temperature indicators for microwave assisted pasteurization processes*. PhD Thesis. Pullman, WA: Washington State University.

Zhang, W., Luan, D., Tang, J., Sablani, S. S., Rasco, B., Lin, H., et al. (2015). Dielectric properties and other physical properties of low-acyl gellan gel as relevant to microwave assisted pasteurization process. *Journal of Food Engineering, 149*, 195–203.

Zhang, W., Tang, J., Liu, F., Bohnet, S., & Tang, Z. (2014). Chemical marker M2 (4-hydroxy-5-methyl-3(2H)-furanone) formation in egg white gel model for heating pattern determination of microwave-assisted pasteurization processing. *Journal of Food Engineering, 125*, 69–76.