THERMAL DEGRADATION KINETICS, HEATING BEHAVIOR AND QUALITY RETENTION IN CANNED VEGETABLES SUBJECTED TO RECIPROCATION AGITATION THERMAL PROCESSING

By

Jia You

Department of Food Science and Agricultural Chemistry

Macdonald Campus, McGill University

Montreal, Canada

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DEDICATED TO MY FAMILY AND MY SUPERVISOR

ABSTRACT

Thermal processing is the most widely used method of destroying pathogenic microorganisms of public health concern and reducing the activity of enzymes and microorganisms that are responsible for their spoilage. However, the severity of heat treatment involved during thermal processing also affects the quality and nutritional attributes. This study was conducted to evaluate the degradation kinetics of quality attributes in vegetables, evaluation of their retention during reciprocation agitation thermal processing. First, the kinetics of thermal degradation of texture and color and antioxidant activity in potato and radish at different temperatures were evaluated. Subsequently, the effect of processing factors (temperature and reciprocation speed) on heat penetration behavior of canned potato and radish was evaluated to establish the appropriate process times for thermal processing. Finally, the effects of these process variables on quality retention in the processed vegetables were compared.

This study is important to identify processing conditions for the maximum retention of quality attributes. Kinetics of texture, color and antioxidant activity degradation was evaluated in a constant temperature water bath at different temperatures by using potato cubes and red globe radishes. Heating behavior of canned potato and radish in 2% salt solution (1% NaCl and 1% $CaCl_2$) were studied under various modes of retort processing conditions. Heating rate index (f_h), lethality (F_o), heating lag factor (j_{ch}) and processing time (Pt) were evaluated and retention of quality of products treated by different processes were assessed. High reciprocation speed resulted in lowering of heating rate index, meaning improving the rate of heat transfer. The lag factor and processing time were also simultaneously reduced with an increase in reciprocation speed. Processing at higher reciprocation speed and higher temperatures had a positive effect on the retention of quality attributes.

RÉSUMÉ

Les traitements thermiques sont les méthodes les plus utilisées pour détruire les microorganismes pathogènes qui représentent des problèmes de santé publique et aussi pour réduire l'activité des enzymes et des microorganismes qui sont responsables pour la détérioration du produit. Cependant, la sévérité du traitement thermique affecte également la qualité et les caractéristiques nutritionnelles. Cette étude a été menée pour évaluer la cinétique de dégradation d'attributs de qualité dans les légumes et l'évaluation de leur rétention pendant les traitements thermiques qui s'employant l'agitation réciprocité. Premièrement, la cinétique de la dégradation thermique de la texture, couleur, et de l'activité antioxydante dans la pomme de terre et le radis ont été évalués dans une gamme de températures. Ensuite, l'effet de facteurs de processus (température et vitesse de déplacement) sur le comportement de pénétration de la chaleur de la pomme de terre et de radis été etudié pour établir les temps de traitement appropriées pour le traitement thermique. Enfin, les effets de ces variables de processus sur le maintien de la qualité dans les légumes traités ont été comparés.

Cette étude était importante pour identifier les conditions de traitement qui donnent la rétention maximale des attributs de qualité. La cinétique dégradation de la texture, couleur, et de l'activité antioxydante ont été évalués dans un bain d'eau à différentes températures en utilisant des cubes de pommes de terre et les radis rouge entière. Le comportement chauffage de la pomme de terre et radis en solution à 2% de sel (1% NaCl et 1% $CaCl_2$) ont été étudiés sous différents modes de traitement à l'autoclave. Indice du taux de chauffage (f_h), létalité (F_o), le facteur de chauffage de latence (de j_{ch}) et le temps de traitement (P_t) ont été évalués et le maintien de la qualité des produits traités par différents procédés ont été évalués. Le déplacement alternatif haute vitesse a entraîné une diminution de l'indice du taux de chauffage, ce qui implique un taux de transfert de chaleur amélioré. Le facteur de retard et le temps de traitement ont également été réduits simultanément avec une augmentation de la vitesse du mouvement. Traitement aux vitesses de déplacement et températures plus élevées a eu un effet positif sur la rétention des attributs de qualité.

CONTRIBUTIONS OF AUTHORS

Some parts of thesis research work have been presented at scientific conferences and manuscripts have been planned for publication. The thesis is written in the manuscript style so that the chapters highlighting the thesis research could be suitably edited for publication. Two authors have been mostly involved in the thesis work and two others have helped in designing of the equipment used for the study and their contributions to the various articles are as follows:

Jia You is the M.Sc. candidate who planned and conducted all the experiments, in consultation with his supervisor, gathered and analyzed the results and drafted the thesis and the manuscripts for scientific presentations and publications.

Dr. Hosahalli S. Ramaswamy is the thesis supervisor, under whose guidance the research was carried out, and who guided and supervised the candidate in planning and conducting the research, as well as in correcting, reviewing and editing of the thesis and the manuscript drafts for publication.

Anubhav Pratap Singh and Anika Singh have designed and developed the reciprocation agitation system for their PhD studies on heat transfer associated with reciprocation agitation thermal processing in model particulate Newtonian and Non-Newtonian fluids.

LIST OF PUBLICATIONS AND PRESENTATIONS

Parts of this thesis have been prepared as manuscripts for publications in refereed scientific journals:

YOU, J and Ramaswamy, H. S., 2015. Thermal destruction kinetics of quality of attributes of potatoes and radishes (***draft prepared***)

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YOU, J and Ramaswamy, H. S., 2015. Enhanced retention of quality parameters in canned potato and radish through reciprocating agitation thermal processing (***draft prepared***).

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Chapter 1

INTRODUCTION

Thermal processing is the oldest and most widely used technique in food industry. The application of heat in thermal processing is to kill the microorganisms causing health and spoilage concerns and to inactive enzymes and spoilage microorganisms in order to obtain a long and stable shelf life. Nicholas Appert, who was the first one to apply this technology in 1809, heated food packed in glass jars to make product shelf stable. The primary concept of thermal processing developed in 1920 by several researchers from different countries: Bigelow, Esty, Underwood, Prescott and Ball. The concept refers to in-container sterilization of food stuff with a hermetic seal to maintain an environment in container to prevent the growth of microorganisms of higher resistance and prevent recontamination.

With the many of the subsequent developments in thermal processing, consumers' demand has moved far beyond just the safety and stability of products. Higher quality retention in thermal processed products has become a major influencing factor with respect to consumers' acceptance of the processed products. It has also been recognized that high temperature and short time can retain the quality attributes better than compared to traditional thermal processing, which usually heat products for a long time to destroy the pathogenic microorganisms (Ball, 1938). This is based on the fact that the relative destruction rates of microorganism and quality parameters are not the same at all temperatures. Higher temperatures yield a more rapid destruction rate for microorganisms than quality parameters, and the relative difference increases at higher temperatures (Stumbo, 1973). So high temperature short time could have rapid heat transfer rate and lower processing time and result in better retention of quality of products. There are three processing types in industry to apply this concept in order to achieve the benefits: 1) aseptic processing, 2) thin profile packing and 3) agitation processing (Ramaswamy and Marcotte, 2006). All these processing methods aim to reduce processing time by achieving a relatively rapid rate of heat transfer potentially facilitating better quality retention in processed products. Aseptic processing is ideal for liquid products which are rapidly processed in heat exchangers and filled and sealed in to pre-sterilized containers in an aseptic environment. Solid foods, which heat very slow due to conduction heating can be best processed in the thin profile mode by keeping the heat transfer path short in thin profile containers. Liquid particulate mixtures benefit from the agitation processing which helps to induce better heat transfer conditions inside the container due rapid mixing of the contents. There are three different modes in which the containers can be agitated during processing: end-over-end, axial and reciprocation agitation. The first two have been explored extensively with respect to heat transfer as well as quality retention in thermally processed foods while the reciprocation agitation processing is receiving attention only recently, albeit the fact that it induces far superior agitation than the two other modes.

The general study objectives are:

1. To study and characterize the thermal destruction kinetics of texture and color and antioxidant activity of potato and radish at various temperatures and establish the kinetic parameters.
2. To evaluate the effect of reciprocation agitation processing factors on the heating behavior of potato and radish, heating rate index and heating lag factor, and establish the required processing times.
3. To investigate the quality retention in canned potato and radish under the reciprocation agitation thermal processing based on the pre-established processing times.

Chapter 2

LITERATURE REVIEW

2.1 Principles of thermal processing

In 1890, the thermal processing was invented by Nicholas Appert and then further developed to be the most widely used technology for producing commercial sterile, safe and shelf stable food products. According to United States Food and Drugs Administration, *Commercial Sterility* of equipment and containers refers to the condition, with the application of heat treatment, which makes the equipment and containers free of microorganisms of public health risk under normal non-refrigerated of distribution and storage (Awuah et al., 2007). The selection of techniques and adequate lethality is depending on the basis of pH of foods. The classification of foods based on pH was presented in Table 2.1.

Table 2.1: Classification of foods based on pH (Ramaswamy and Marcotte, 2006)

Name	pH	Examples
Low Acid Foods	>4.6	Meat and Fish, Vegetables and Soups
Medium Acid Food	3.7-4.6	Fruit jams, Tomato and Fruits
High Acid Foods	<3.7	Fruits Juices, Berries and Pickles

The spoilage of acid and high acid foods mainly results from the vegetative microorganisms, which can be destroyed by mild heat treatment. The spoilage of low acid foods, on the other hand, results from the bacterial spores which are more resistant and destruction of these spores (both the spoilage and pathogenic type) which can grow at room temperature storage conditions are of concern in processing of low acid foods.

Based on the purpose of thermal processing and the severity of the process, the processing can be described either pasteurization or sterilization (Lund, 1975). Pasteurization is a mild heat treatment for destruction of spoilage microorganisms (bacteria, yeast, and molds) and inactivating enzymes. If the pH of the foods were low (acid and high acid foods, pH<4.6), such as fruit juices, fruit jams, tomatoes, it is recommend to apply pasteurization process.

Alternatively, if the pH of foods were high (low acid foods, pH≥4.6), the more severe heat treatments are required. Commercial sterilization need to be applied for destroying pathogenic microorganisms of public health risk. The basic classification of thermal process design is presented in Figure 2.1.

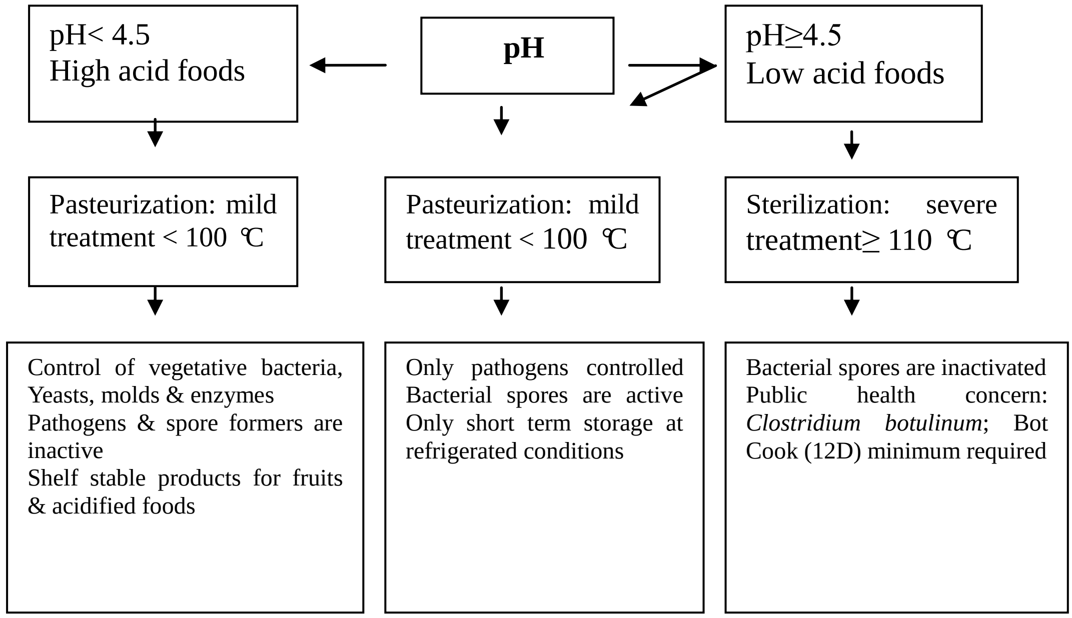


Figure 2.1: A schematic illustrating the principles involved in thermal processing applications (Ramaswamy and Abbatemarco, 1996)

The dividing pH line at 4.6 used to separate acid and low acid foods is based on the ability of *Clostridium botulinum* spores which does not grow at pH < 4.6. *Clostridium botulinum* has a high thermal resistance, but is only able to produce the neurotoxin in an anaerobic environment under mesophilic conditions. Also, *Clostridium botulinum* is a Gram-positive, spore forming bacterium, which has public health concern and cause fatal disease. So it is important to differentiate foods by pH value in order to apply different thermal treatments.

2.2 Microbial activity of food

Survivor curve and D-value

Once the organisms land on food, it might survive due to condition favorable for their growth and activity, and then lead to spoilage and/or produce toxic materials which may be harmful to the public. It is necessary to adjust the severity of heating treatment to destroy those microorganisms in order to keep the product to be a long term safety (Stumbo, 1973). Rahn

(1945) explained that the logarithmic death of bacteria results from the denaturation of a gene which is essential for the reproduction, when subjected to severe heat treatment. When the organism of health concern is evaluated, the kinetics of destruction of microorganism has to be evaluated. Traditionally, inactivation curves of enzymes and microorganism follow the first order reaction kinetics. First order degradation refers to the destruction rate with respect to time which is proportional to the measured concentration of a reacting species. The basic equation for reaction kinetic is given as:

$$-dn/dt = kN^n \qquad (2.1)$$

For the survival curve, N is the number of reacting species at any time t, k is the reaction constant rate and n is order of reaction. Assumed that N_0 represents the initial number of microbes and N stands for the number of surviving microbes after any time t, and n=1, then the Equation 2.1 can be integrated as :

$$\ln(N/N_0) = -kt \qquad (2.2)$$

It also can be presented as

$$\log(N/N_0) = -kt/2.303 \quad \text{or} \quad N = N_0(10)^{-kt/2.303} \qquad (2.3)$$

It can be noted that survivor curve means the logarithmic plot of the number of survivors vs. time. The D-value can be obtained from the plot of the number of surviving microorganisms on a logarithmic scale against time on a linear scale as shown in Figure 2.2. Mathematically, it represents the negative reciprocal slope of the straight line portion of the curve. The D-value represents the time required to kill 90% of the surviving microbial population at a given temperature or alternatively it is the time required for the curve to traverse one log cycle. So when N= 90%*N_0 and t = D-value, the equation can be presented as:

$$D = 2.303/k \qquad (2.4)$$

The general equation to obtain D-value at any time is:

$$\log (N_0/N) = \frac{1}{D}t \quad \text{or } D=-\ \frac{t}{\log N/No} \qquad (2.5)$$

where N is the number of microbes at any time t, N_0 is the initial number of microbes, and t is the processing time and D is the time to destroy 90% of microbial population at a given temperature.

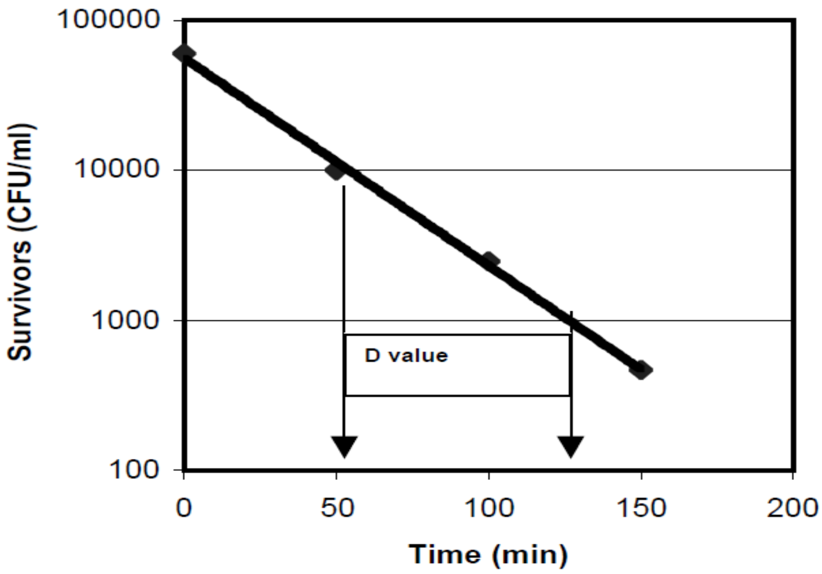


Figure 2.2: Typical D curves (Ramaswamy and Marcotte, 2006)

Thermal destruction time and the z-value

Thermal destruction depends on temperature, which is different from the survivor curve. z-value is the temperature range where D-value passes through one log cycle and is also a temperature sensitivity indicator to evaluate thermal resistance of bacteria (Stumbo, 1973). The equation is:

$$z = \frac{T2-T1}{\log (D1/D2)} \qquad (2.6)$$

where T_2 and T_1 are different temperature, (T_2-T_1) is temperature range and D_1 and D_2 are decimal reduction times at temperature T_1 and T_2 respectively. The curve shows below.

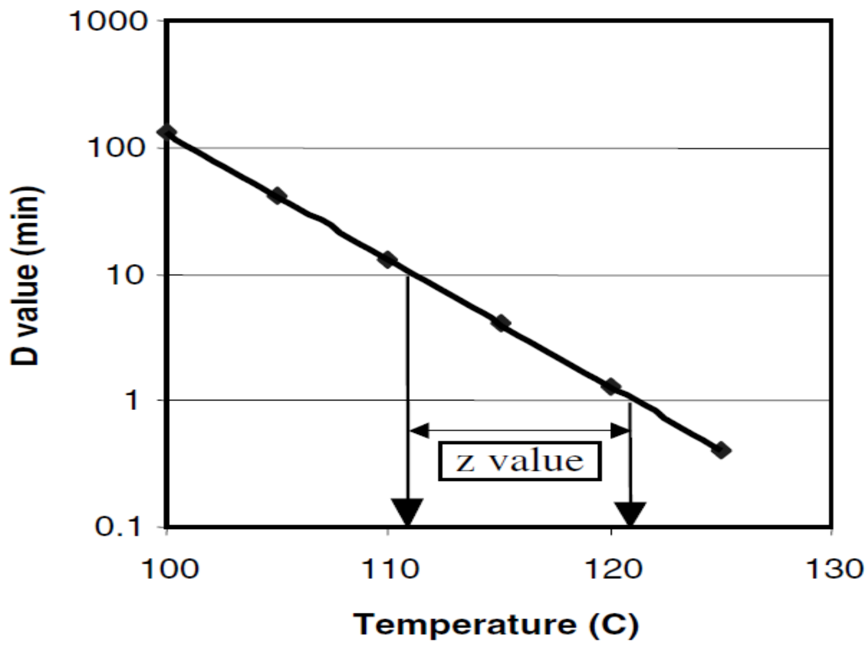


Figure 2.3: Typical z value curves (Ramaswamy and Marcotte, 2006)

2.3 Thermal process evaluations

Process lethality

In real food thermal processing, products are treated at varying temperature for different lengths of time. The whole process need to be integrated to get the process lethality (F_o) since each temperature-time has specific transient lethality. A unit of lethality has been created in order to compare different thermal processing (Stumbo, 1973). Process lethality (F_o) refers to the equivalent heating time at reference temperature of 121.1 ^oC or 250 ^oF. The equation is presented below:

$$F_o = \int 10^{(T-121.1)/10} dt \qquad (2.7)$$

If the lethality at any given temperature is known (like F_o at a reference temperature T_o), the lethality at other temperatures can be calculated if the z value is known:

$$F = F_o \left(10^{[(To-T)/z]}\right) \qquad (2.8)$$

Cook value

Cook value is important to estimate quality losses during processing and to optimize the thermal processing to obtain high quality attributes. The cook value usually is equivalent heating time at 100 ^{o}C with z value of 33 ^{o}C (Eisner and Toska, 1988). It can be calculated, similar to F_o, by the equation below (Ohlsson, 1988):

$$C_o = \int 10^{(T-100)/33} dt \quad (2.9)$$

Heat penetration parameters

Heat penetration curve is a plot of the semi-logarithmic temperature difference between the retort and the product in the can and is represented as shown in Figure 2.4. From the curve, heating rate index (f_h) and heating lag factor (j_{ch}) are obtained. The heating rate index is the time required to the straight line portion of heating curve to pass one log cycle and is equal to the negative reciprocal of the heating curve. The higher value of the heating rate, the faster the products can be heat and lower will be the heating rate index, f_h.

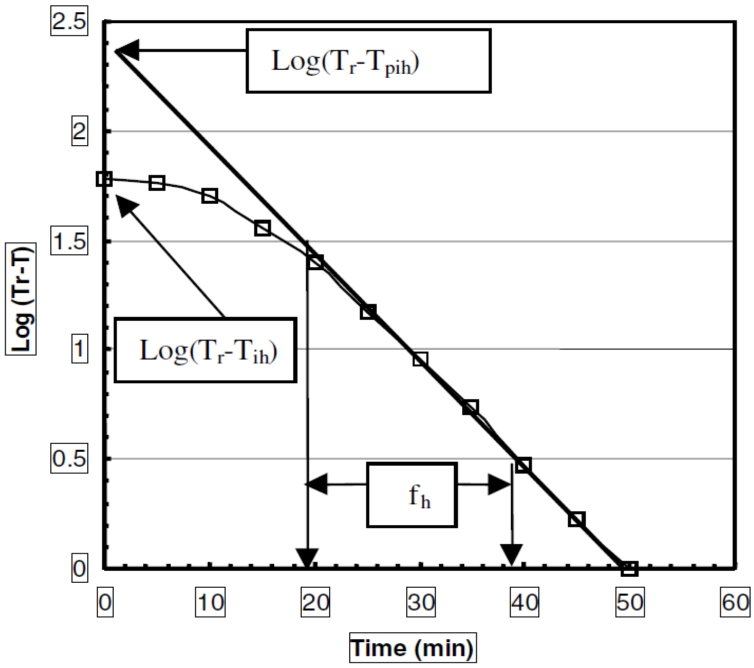


Figure 2.4: Semi-logarithmic heat penetration curve (Ramaswamy and Marcotte, 2006)

The heating lag factor (j_{ch}) represents that the delay in achieving steady phase heating and is obtained by the following equation:

$$j_{ch} = (T_r - T_{pih})/(T_r - T_{ih}) \quad (2.10)$$

T_r represents the retort temperature, and T_{pih} is for pseudo initial sample temperature, and T_{ih} represents initial temperature of sample. T_{pih} can be obtained by the intersection of extrapolated straight line portion and vertical line in heat penetration curve.

2.4 Thermal processing

Blanching

Blanching refers to the inactivation of oxidative enzymes present in food by the treatment in hot water or steam. Blanching also has the functions of lowering of the microbial load on the surfaces of vegetables, cleaning the dirt, and facilitating packing of the prepared vegetable. Blanching is an extremely important processing step for vegetables to be further processed by canning, drying and freezing since enzymes could result in off-flavor, loss of texture and color during handling and distribution and storage. The processing could also retard loss of nutrients and brighten the colors.

Blanching has an impact on enzymes like peroxidase, catalase, lipoxygenase and polyphenol oxidase. Among the oxidative enzymes, peroxidase (PO) has been found to be the most heat resistant enzyme in vegetables and therefore its inactivation is considered as an index of blanching inadequacy. Thermal inactivation of PO is greatly related to the size and nature of vegetables, heat transfer efficiency and temperature-time combination. Some researchers reported that thermal inactivation of PO could be achieved in hot water (99 ℃) in 2 min for fenugreek leaves (Bajaj et al., 1993); while at 95±3 ℃ in 1 min for savoy beet, amaranth, and fenugreek; and at 85 ℃ in 30 seconds or 95 ℃ for 15 sec for spinach (Speek et al., 1988). The Food and Drug Administration (FDA) recommends blanching of vegetables prior to processing in order to reduce quality loss by thermal inactivation of enzymes. Blanching vegetables prior to thermal processing can better preserve the texture of vegetables (Vu et al., 2004).

Pasteurization

Pasteurization is the mild treatment with less impact on product quality. The temperature is usually below 100 ℃. The process aims at inactivation of pathogenic microorganisms and enzymes. Since pasteurization is not severe enough to destroy bacterial spores and *C.*

botulinum, the products, thermally treated by pasteurization, need to be refrigerated immediately following the heat treatment and provides a short term shelf life. *Mycobacterium tuberculosis* and *Listeria monocytogenes* has been considered as target organisms for pasteurization.

Sterilization

Sterilization is a severe process to theoretically inactive all the organisms present in food. However, completed destruction of all microorganisms is not the target of sterilization, but rather achieving commercial sterility. The objective of sterilization is to inactive enzymes and pathogenic microorganisms, especially *C. botulinum* and the mesophilic spores that responsible for the spoilage of foods.

2.5 Quality degradation

Quality attributes of vegetables include that texture, color, taste, smell and flavor. Quality can be described as the composite of various characteristics that can fulfill needs and wants of consumers and determine the degree of their acceptability of products (Kramer and Twigg 1970). Thermal processing has a negative effect on quality attributed of foods. Although the main concern with thermal processing is achieving shelf-stability and assure safety, heat treatments do trigger chemical reactions and changes to the nutritional and sensory attributes, such as texture and color (Awuah et al., 2007). Texture usually regarded as the indicator of overall quality for some particular food products (Hutchings, 1988). During thermal processing, the texture value would be reduced and the products would become soft. The color of product also affects consumer acceptability. Heat treatment would degrade or change the natural occurring pigments in foods. Vitamins and antioxidant compounds are also sensitive to heat.

Texture

Texture is a marketable quality parameter of processed vegetables for the customer. Excessive softening would adversely affect consumer acceptability of food. Texture changes in thermal processing are closely related to cellular degradation, breakdown of cell wall and pectin structure resulting from enzymatic and non-enzymatic reactions in pectin (Anthon et al., 2005; Greve et al., 1994). In research, the characterization of texture can be described by various parameters include hardness, chewiness, gumminess, springiness and fracturability.

Vegetables are characterized as low acid foods. In thermal processing, vegetables are required to be treated at high temperature to inactive enzymes and microorganism of health concern, and thus the safety of canned vegetables can be guaranteed in long storage term. However, texture of processed vegetables is usually damaged to a greater extent, which would have a negative effect on consumers' acceptability of food and possibility of canning processing.

There is continued interested in overcoming the limitation of excessive thermal softening of canned vegetables. It has been observed that hardness of canned potato is of great importance in the acceptability of products. Many studies have been carried out on thermal softening canned potatoes (Abbatemarco and Ramaswamy, 1994; Rattan and Ramaswamy, 2014). By adding calcium chloride into can liquid, firmness of canned potato was increased (Scott and Twigg, 1969; Woodroof et al., 1955). Jen (1989) reported that $CaCl_2$ could interact with pectic substances in cells to improve firmness retention and texture of canned vegetables.

The textural changes of canned vegetables can be assessed by instruments. Texture profile analysis (TPA) has been widely applied to analysis various textural parameters as a universal texturometer in a single or double compression testing (Alvarez et al., 2002). In TPA tests, parameters depend on the nature, size and shape of sample, compression degree, number of bites and the size ratio of compressing probe to sample (Pons and Fiszman, 1996). Textural parameters obtained from compression test can be analyzed by computer assisted texturometers.

Color

Color is a primary quality attribute that directly determines consumers' appeal of processed products. However, during processing, pigment and color losses result from deterioration reactions, which include Millard reactions and enzymatic browning. The heat treatment usually destroys pigments of vegetables and thus results in the leaching of the cooked vegetables (Schwartz and Elbe, 1983). The formation of the olive brown color is undesirable for green vegetables in the heat treatment due to the conversion of chlorophyll to pheophytin based on the magnesium of the chlorophyll (Woolfe, 1979). Color changes in green vegetables have been represented by quantify the conversion of chlorophyll to pheophytin in some studies (Canjura et al., 1991; Steet and Tong, 1996). The color degradations were less in vegetables that mainly contain pigments like carotenoids and anthocyanins as compared to green vegetables (Clydesdale and Ahmed, 1978). It was assumed that carotenoids are associated with protein and liquid which might have protective effect. Anthocyanins are affected by pH and oxygen and the effect become small in anaerobic condition. It is therefore Anthocyanins can be protected and the color changes are small in heat treatment (Clydesdale and Ahmed, 1978).

Many researchers have been done on color degradation of vegetables during thermal processing: potato, carrot and beans (Abbatemarco and Ramaswamy, 1994; Rattan and Ramaswamy, 2014), asparagus (Lau et al., 2000), peas (Steet and Tong, 1996). They concluded that color quality of vegetable is affected by thermal processing and it was necessary to evaluate the color degradation to avoid deterioration.

Color parameters can be described by the Hunter parameters (L. a, and b) and total color difference (ΔE). The L value represents light to dark spectrum; a value and b value represent green to red spectrum and blue to yellow spectrum, respectively.

Antioxidants

It is generally assumed that consumption of fruits and vegetables can reduce the risk of several types of cancer, cardiovascular disease and stroke (Hu 2003; Riboli and Norat 2003). Over 170 epidemiological cancer cases have been studied and concluded that increased consumption of fruits and vegetables are closely related to a lower risk of cancers (Block, 1992). Antioxidants are substances that can delay or inhibit the oxidation reactions to proteins, lipids and nucleic acids caused by reactive oxygen species. Oxidation reactions can produce reactive free radicals, such as superoxide, hydroxyl, peroxyl and non radicals, like hydrogen peroxide, hypochlorous, ect (Lim et al., 2007). Antioxidants can scavenge radicals in various ways include that the quenching superoxide and singlet oxygen, the breakdown of chain propagation and the reduction of hydrogen peroxides (Shi et al., 2001). The content of Vitamin C and polyphenols are higher in fruits, and Vitamins A, B and E and carotenoids are lesser content (Fleuriet and Macheix, 2003). The content of natural antioxidants is assumed to be remarkably higher in the peels and seeds than that in the pulp. For example, in banana, mango and avocado skin, the concentration of phenolic compounds was higher than that of the pulp of these fruits by 4, 29 and 2.6 times, respectively (Ayala-Zavala et al. 2011).

There are some bioactive compounds with antioxidant activity produced by plants, such as phenolic acids, flavonoids and carotenoids. Phenolic acids are naturally occurring in most plants and are associated with their color and taste. The antioxidant activity of phenolic acids has been evaluated by many researches (Egüés et al., 2012; Razali et al., 2012). Flavonoids are widely found in many vegetables and fruits and have positive impact on human health and disease management (Ammar et al. 2009). Enzymes contributed to oxidative reactions can be inhibited by flavonoids, which show their antioxidant activity (Crespo et al. 2008). Carotenoids are characterized by a group of natural pigment occurring in fruits and vegetables and flowers, and present like the orange-red to yellow colors (Ribaya-Mercado et al. 2000). However, in some cases, the antioxidant activity of selected *Allium* vegetables was increased in thermal processing (Roy et al., 2007).

2.6 Origin and importance of potato and radish

Potato

The origin of potato is from South America and belongs to *Solanaceae* family. The potato is a major tuberous, starchy crop in tropical and sub-tropical countries. It can be consumed in various ways after different methods of processing, including cooking, frying, dehydration and canning. The crop has become an important source to provide energy. It is the one of the largest food crops in the word and follows only maize, rice and wheat. Over past few decades, eastern and southern Asia has improved its production rapidly, and China and India contributed to majority potato production.

The potato has been long considered as a staple starch that provides carbohydrate calories to the diet. The assumption of potatoes as a source of energy is mainly depends on their high carbohydrate content, which comprises up to 75% of their dry weight and to 90% of total energy (King and Slavin, 2013). The protein content of potatoes is low, which approximately 1-1.5% of total weight (Camire et al., 2009). The lipid content is also low, averaging 0.1% of fresh weight (Camire et al., 2009). The potato is also a great source of ascorbic acid, pyridoxine and thiamin.

However, potato is easily perishable since it contains high moisture content. It is therefore potatoes have to be processed to extent their shelf life and avoid waste. Moreover, cold storage conditions and careful transportation are also recommended for keeping storage stability and better quality of potatoes.

White potatoes are processed as can food all around the world and are easily available and economical feasibility. The potatoes were selected in this study.

Radish

Radish (*Raphanus sativus L.*) belongs to *Brassicaceae* family and has been in cultivation in Europe in pre-Roman times. Radishes are nutritious root vegetables and usually consumed raw as salad vegetables throughout the world. Radishes have various forms; varying in size, color and crop duration. The flesh of radish is usually white, while the color root skin ranges from red, pink, white, purple and green to black. Mainly radish composes of water, carbohydrate, protein and a trace of fat. Radish contains vitamins and minerals. Radishes are a good source of vitamins A, B_1, B_2 and C. Vitamins A are associated with possible cancer prevention. They are also rich in ascorbic acid, folic acid and potassium (Huang et al., 1994; Potter and Stenmetz, 1995). The red globe radish was selected in this study since it is the most popular variety and its feasibility and globe-type.

Radish also contains high moisture content, hence it is easily perishable. In order to extend the shelf life, radishes have to be processed to decrease water activity and inactivation of enzymes and microorganism.

Potato and radish, two different kinds of vegetables, are selected in this study to be processed as canned vegetables in reciprocating agitation. However, the quality attributes of potato and radish would be affected by thermal processing and hence results in quality and nutrition loss. The study was aimed for maximum retention of quality attributes of can potatoes and radishes.

PREFACE TO CHAPTER 3

Thermal processing is recognized as a success method for food preservation for more than two centuries resulting in safe and shelf stable products. However, texture and color degradation as well as nutrition loss are major disadvantages during thermal processing. Fortunately, the destruction rate of quality attributes is not in the same order of magnitude as that of microorganisms. In order to understand degradation of quality factors during thermal processing, it is always considered essential to determine the destruction kinetics under carefully controlled conditions under laboratory conditions. This chapter is focused on characterizing the thermal destruction kinetics of texture and color parameters and antioxidant activity of potato and radish, and establishing kinetic parameters. Kinetic data obtained in this study could be used for predicting quality attributes loss during thermal processing.

Based on this study, the following manuscript has been prepared for publication.

YOU, J. and Ramaswamy, H. S., 2015. Thermal destruction kinetics of quality of attributes of potatoes and radishes (***draft***).

The experimental work and data analysis were carried out by candidate under the supervision of Dr. H. S. Ramaswamy. Manuscript is awaiting final review for publication.

Chapter 3

KINETICS OF QUALITY OF ATTIBUTES OF POTATO AND RADISH

3.1 Abstract

Thermal degradation kinetics of texture and color properties and antioxidant activity of potatoes and radishes were studied at different temperatures (70 ℃, 80 ℃, 90 ℃ and 95 ℃). Cubes of potato (15 mm x 15 mm x 15 mm) and small and uniform size whole red globe radish (average radius: 15 mm) were heated in a constant temperature water bath. After heating for selected times, samples were removed from water bath, cooled to the room temperature in running water for evaluation of texture, color and antioxidant properties. Changes in color degradation and antioxidant activity of potato and radish obeyed a simple first order reaction kinetics at all temperatures. The rate of thermal softening of these vegetables well fitted the simple first order at lower temperatures (70 ℃ and 80 ℃), while at higher temperatures (90 ℃ and 95 ℃), the softening rate was well described by two simultaneous pseudo first order reaction kinetics. Thermal destruction kinetic the different quality parameters were characterized in terms of decimal reduction time (D value) and temperature sensitivity parameter (z value) for later use in quality loss predictions.

3.2 Introduction

Quality attributes are important for determining consumers' acceptability when they are choosing products. Consumers have the increasing demands for products of fresh-like quality with the guarantee of safety. Food quality includes sensory attributes that are easily perceived by human sense, such as appearance color, texture and flavor and hidden attributes, such as safety and nutrition (Shewfelt, 1999).

Color is perhaps a predominant criterion for consumers to accept or reject thermally processed foods. Generally, color can be objectively expressed as the energy distribution of light, which is reflected by or transmitted through the food. Tristimulus colorimeters are widely used to describe color by Hunter color values (L, a, and b) individually or through several of their combinations, hue or total color difference value (Ahmed and Shivhare, 2006). Among these parameters, L value is expressed as lightness-darkness, a value is for greenness-redness, and b represents blueness- yellowness. The tristimulus color ratios (a/b, La/b) have also been used to represent reaction kinetics of discoloration for vegetables. Shin and Bhowmik (1995) reported that for pea puree, La/b was the optimum combination to describe the total color changes. Thermal processing, a heat-intensive process, has a significant effect on the color degradation. Many researchers have reported that the kinetics of thermal degradation of color and pigments follow the first-order reaction, for example as shown for potatoes (Jobe, 2003), asparagus (Lau et al., 2000), and mango puree (Ahmed et al., 2002). The kinetics of color degradation of mango puree followed first-order reaction when mango puree heated at 50-90 ℃ for 0-20 min (Ahmed et al., 2002). Lau et al. (2000) investigated that asparagus heated at 70-98 ℃ and concluded that the color of asparagus surface turned bright green to olive green and the color degradation was consistent with a simple first order reaction. Canjura et al. (1991) investigated the thermal degradation of chlorophylls and chlorophyllides in spinach puree heated at 80 ℃ to 145 ℃ for different time intervals and reported that chlorophyll a degraded faster than chlorophyll b. The color degradation kinetic of broccoli juice was reported to be consistent with two-step kinetics mechanism: initial degradation step for pheophytinization of total chlorophyll and the subsequent degradation step for decomposition of pheophytin (Gunawan and Barringer, 2000).

Texture of processed vegetables has a significant influence on determining consumers' preference. Therefore, thermally processed products need to have desirable texture attributes. Thermal softening of the tissues occurs in vegetables due to the destruction of the cellular material such as pectin. The cell separation and pectin degradation is associated with leak of depolymerized pectic substances into the water (Vu et al., 2004). Investigation on the kinetics of texture degradation provides valuable information to improve quality, minimize texture losses, and predict possible changes that occur during thermal processing of vegetables. Various texture parameters are describe texture characteristics include hardness, gumminess, adhesiveness and firmness.

The texture degradation kinetics of vegetables is complex, and the different dependable models had been used to predict experimental data of texture degradation during thermal processing. Numerous researches have been done on thermal softening and kinetics of texture degradation of vegetables. Some reports stated that texture degradation followed first-order reaction kinetics (Huang and Bourne, 1983; Rao and Lund, 1986; Rodrigo et al., 1997). However, Huang and Bourne (1983) reported that an alternative method of the two simultaneous first-order kinetics mechanisms could be used to describe thermal softening during a long processing periods. They assumed that there were two substrates degrading in reaction, resulting two kinetics parameters. One was a labile component, and the other one was a resistant component. The labile component degraded in the initial heating step. The texture degradation kinetics has successfully been studied on potato, peas, and beans, through the dual-mechanism first-order kinetics techniques (Alvarez et al., 2001; Huang and Bourne, 1983). However, the mechanisms for texture degradations show difference at different temperature. Thermal degradation of texture in white beans was studies at 90 to 122 ℃ (Loey et al., 1994). Reaction kinetics revealed that a biphasic behavior could describe thermal softening at 90 to 122 ℃, but the initial step of processing was not showed at 110 ℃. Moreover, thermal softening of potato tissue heated in water within the temperature range 50-100 ℃. The kinetics of thermal softening of potato at 50 ℃, 90 ℃ and 100 ℃ well fitted first-order kinetic mechanism, while the kinetics of softening at 70 ℃ and 80 ℃ followed dual-mechanism first-order kinetics. For 70 ℃ and 80 ℃, gelatinization and light cooking might result in the initial step of heating, while the changes of pectin substances and deep cooking probably contribute to the second step of heating (Alvarez et al., 2001).

Some vegetables like kale, potato, carrots, beets, spinach etc., have high antioxidant activities (Cao et al., 1996). The principle function of antioxidants is the quenching of superoxide and singlet oxygen, the breakdown of chain propagation and the reduction of hydrogen peroxides (Shi et al., 2001).There are some bioactive compounds with antioxidant activity produced by plants, such as antioxidant vitamins, phenolic acids and flavonoids.

Thermal processing affects the antioxidant activity of plant products. The antioxidant activities of swamp cabbage, kale and spinach were greatly decreased after thermal processing (Ismail et al., 2004). However, antioxidant activity in tomato and carrot puree were enhanced during thermal treatments (2 min at 70 ℃) (Patras et al., 2009). Similarly, after heat treatment at 88 ℃ for 2, 15 and 30 min, total antioxidant activity was increased despite a decrease in ascorbic acid content in thermally processed tomatoes (Dewanto et al., 2002). The thermal degradation of ascorbic acid has been evaluated in orange juice and raspberry pulp (Lima et al., 1999; Summen and Erge, 2014). These researchers concluded that the degradation of ascorbic acid followed a first order kinetic model. The degradation of total phenolics in raspberry pulp was reported to follow a zero-order kinetic model after heating treatment at 60 to 90 ℃ for 7 h (Summen and Erge, 2014).

3.3 Materials and methods

3.3.1 Sample preparation

Regular yellow potatoes (*Solanum tuberosum*) of Goldrush variety and red globe radishes (*Raphanus sativus L.*) with white flesh were used in this study as samples. Potatoes and radishes were purchased from the local market and then stored at 4 ℃ in refrigerated condition. Potatoes were peeled and cut into uniform cubes (15 mm x 15 mm x 15 mm) by sharp knife, while uniform globe radishes were selected as samples (average radius:15 mm). Prepared samples were kept in cold water until heating treatment.

3.3.2 Thermal treatment

Potato cube weighed approximately 4g each. Twenty potato cubes were placed in a perforated basket, then placed in a constant temperature water bath and heated at various temperatures (70-95 ℃) for selected times (3- 30min). Four potato cubes were removed from the water bath at selected time intervals at each temperature. The time intervals for 70 ℃, 80 ℃, 90 ℃ and 95 ℃ were 10 min, 8 min, 5 min and 3 min, respectively. The maximum cooking time was 30 min for each heating treatment. The maximum temperature variation in the water bath during heating processing was ±1 ℃. After the heat treatment, samples were taken out from water bath and then cooled to the room temperature using cold tap water for further quality tests. Baby radish weighed approximately 25 g each. Eight red radishes were taken in the basket and 5 baskets were prepared for the 5 selected time intervals at each temperature. Radish samples placed in the perforated basket and then put through the same heating procedure as above. Each treated whole radish was chopped by a sharp knife to obtain the middle part and then cut into cubes (15 mm x 15 mm x 15 mm) for further color and texture and antioxidant activity evaluations.

3.3.3 Texture evaluation

Cooked samples were subjected to a two-cycle compression test using TA-XT Plus Texture Analyzer (Texture Technologies Corp., Scarsdale, NY/ Stable Micro Systems, Godalming, Surrey, UK) with a 2 kg load cell and a circular aluminum probe. Pre-test, test and post test speeds were 1.0, 1.5 and 1.5 mm/s respectively. Textural parameters, such as hardness, chewiness and gumminess were obtained by using Texture Exponent 32 software (Texture Technologies Corp., Scarsdale, NY/ Stable Micro Systems, Godalming, Surrey, U)

3.3.4 Color evaluation

The color characteristics were evaluated by using a Minolta Tristimulus Colorimeter (Minolta Corp., Ramsey, NJ, USA). The color parameters L, a, b and total color difference were obtained by software (SpectraMagic, Minolta Corp., Ramsey, NJ, USA). The total color difference was evaluated using Equation 3.1 given below:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{-1/2} \qquad (3.1)$$

3.3.5 Antioxidant estimation

The free radical scavenging activity of sample extract was measured according to the DPPH (1, 1-diphenyl-2-picrylhydrazyl) method (Shimada et al, 1992) with some modifications. A 4g sample was ground by using a pestle and mortar, and placed in centrifuge tube with ethanol solution (85% ethanol, 15% methanol v/v) filled up to 30 ml, and then centrifuged for 40 min at 5000 rpm. An aliquot of 0.5 ml of sample ethanolic extract (supernatant) was added to 1 ml of 0.1nM DPPH in ethanol, and the color formation through DPPH reaction was allowed to proceed for 30 min in the dark. The absorbance was measured by a spectrophotometer at 520 nm. Free radical scavenging activity (FRSA) on DPPH radicals was expressed as percentage (%) from the obtained absorbance for the sample (A_s) and the blank (A_o) using the following equation (3.2):

$$FRSA = \frac{A_0 - A_S}{A_0} \times 100 \qquad (3.2)$$

where,

A_0 is the absorbance at 520nm in absence of sample

A_s is the absorbance at 520nm in presence of sample

3.3.6 Estimation of kinetic parameters

As detailed earlier, kinetic parameters can be estimated based on first order model using residual values of texture, color and antioxidant parameters following the thermal treatment. For the first order model, the D values and z-values define the kinetic data. D value is the time required to destroy 90% of original quality value at any given temperature and can be obtained using the equation below:

$$D = t/\log(N_0/N) \qquad (3.2)$$

where N_o and N are the texture or color parameter values at time zero and t, respectively. It can be obtained from the plot of $\log(N_0/N)$ vs time as the negative reciprocal slope.

z-value is the temperature range between which D-value changes by an order of 10 or the semi-log D value vs temperature plot passes through one log cycle. z-value can be obtained as the negative reciprocal slope of the D value curve using the slope indicator and can be obtained using the equation below:

$$z = \frac{T2 - T1}{\log(D1/D2)} \qquad (3.3)$$

where D_1 and D_2 are decimal reduction times at temperatures T_1 and T_2, respectively.

The fractional conversion model was used when calculating the color changes. Depending on changes between the initial and the maximum color values, a modified first order model was used to calculate the changes in color parameters (Jobe, 2003):

$$k = - [\ln (C_{max} - C_t)/(C_{max} - C_0)] / t \qquad (3.4)$$

where C_{max} is the maximum value of color parameters, C_0 is the initial color parameters, and C_t is the color parameters at any given time. k is the reaction rate constant by calculating the negative slope of the [log $(C_{max} - C_t)/(C_{max} - C_0)$] vs. time (t).

3.4 Results and discussions

3.4.1 Color change kinetics

Potato

Cooked potato cubes were found to gradually lose their original lightness and turned out to be relatively darker/grey shade as compared to raw potato. The semi-logarithmic plot of the changes in L value of potato was presented in Figure 3.1. The color parameters L value decreased with the increase of heating time at each temperature. Further, higher temperature also contributed to a great decrease in L value. Since the L value is a measure of the relative lightness of the sample, it meant that the cooked potato samples lost their brightness/lightness with increasing heat treatment time and cooking temperature. This could result from the collapse of the cellular structure, removal of tissue gasses, and possible interaction of cellular components through non-enzymatic reactions, which can produce pigments in complex forms resulting in imparting darkening shades with cooking (Lozano and Ibarz, 1997; Muneta and Kalbfleisch, 1987; Pritchard and Adam, 1994).

The changes in L value also contributed significantly to the changes in total color difference (ΔE value). The total color different ΔE is also composed of changes in a and b values which represent color changes in the blue-red or green-yellow shades; however, in the present study the changes in a and b value observed were small and inconsistent. Hence they were not used independently in the analysis, but combined with L to get the ΔE values. Semi-logarithmic plot of changes in ΔE value of potato by using the fractional conversion model is presented in Figure 3.2. The total color difference ΔE was found to increase with both cooking time and temperature. The higher temperature with prolonged heating time was the worst case with respect the associated ΔE value resulting in the maximum change in the composite color value. Similar results were observed by Nourian (2003b). For a value and b value, they were relatively stable and no clear trend was established.

So the thermal degradation of L values and ΔE values both followed the simple first order (or the modified fractional conversion) model kinetics. The results were consistent with other researchers (Ahmed et al., 2002; Jobe, 2003; Lau et al., 2000; Nourian and Ramaswamy, 2003b). D value of both L value and ΔE value were obtained from the corresponding semi-logarithmic plots parametric color change vs time (Table 3.1). D values associated with

L and ΔE values decreased with increasing temperature. Hence color degradation in thermal processing is temperature dependent and the higher temperatures would result in more extensive color change of cooked products.

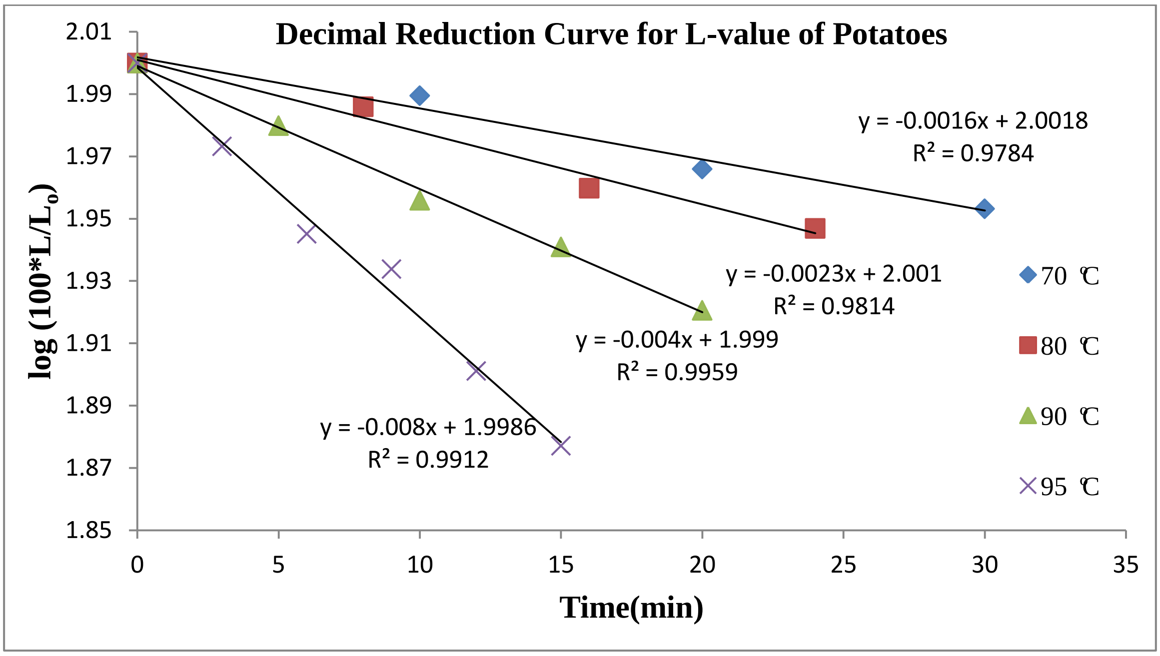


Figure 3.1 Plot of log ratio of L value of potatoes at different temperatures (℃)

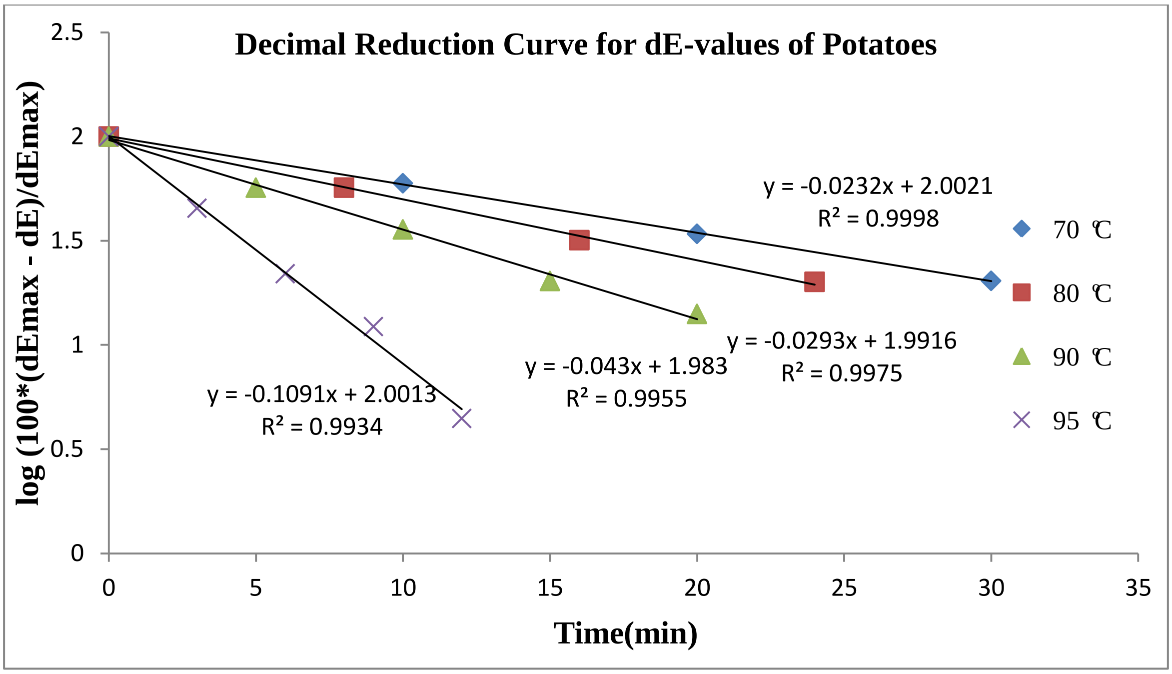


Figure 3.2 Plot of log ratio of ΔE value of potatoes at different temperatures (℃)

Figure 3.3 illustrates the semi-logarithmic plot of log D value against cooking temperature. Similar to the computation of D values, the z-value of associated color change parameters of potato were estimated as the negative reciprocal slope of the semi-logarithmic plot of D values. The z value for L value and ΔE value were 42.7 ℃ and 45.9 ℃, respectively.

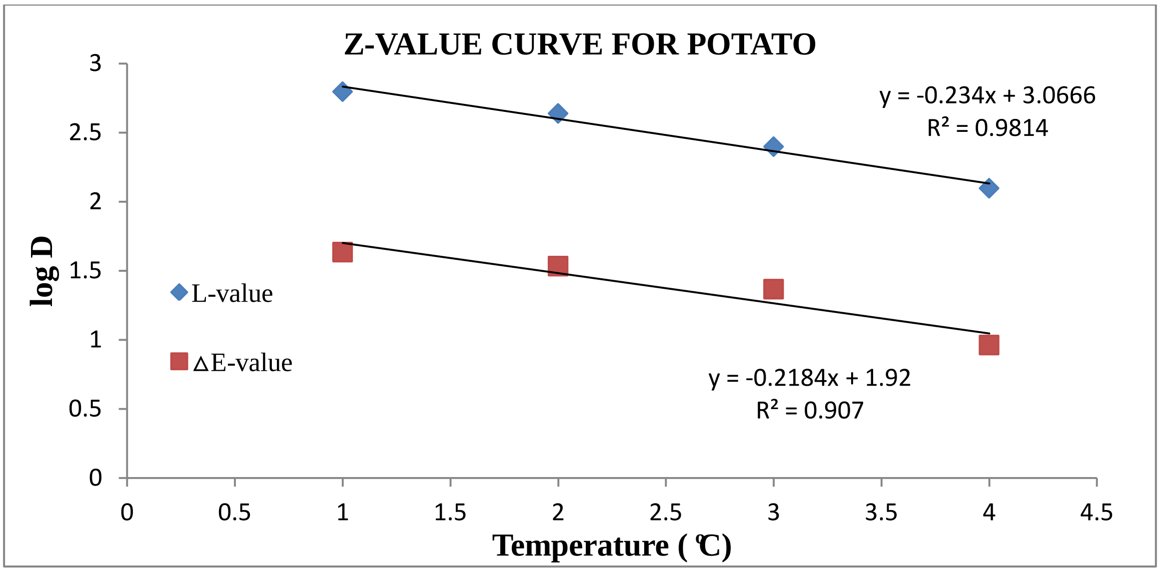


Figure 3.3 Log D value plot of potato vs. temperature

Radish

The semi-logarithmic plot of the changes in L value of radish is presented in Figure 3.4. The semi-logarithmic plot of the changes in ΔE value of radish by using fractional conversion model equation is presented in Figure 3.5. The results of color loss observed in radish samples showed similar trend as that of potato cubes mentioned before. It was found to be a progressively decrease in L value and an increasing in ΔE value with the passage of time at each temperature. The figure trends also followed the simple first order change kinetics. D values of both values decreased with the increasing temperature. So longer heating times at higher temperatures would impart more color changes of radishes. Figure 3.6 illustrates the semi-logarithmic plot of log D value against heating temperature. From the plot, it can be observed that increasing temperature would significantly affect the color changes of radish samples. The z value for L value and ΔE value were 41.5 ℃ and 35.7 ℃, respectively. The various kinetic parameters of color degradation of radishes and potatoes are summarized in Table 3.1.

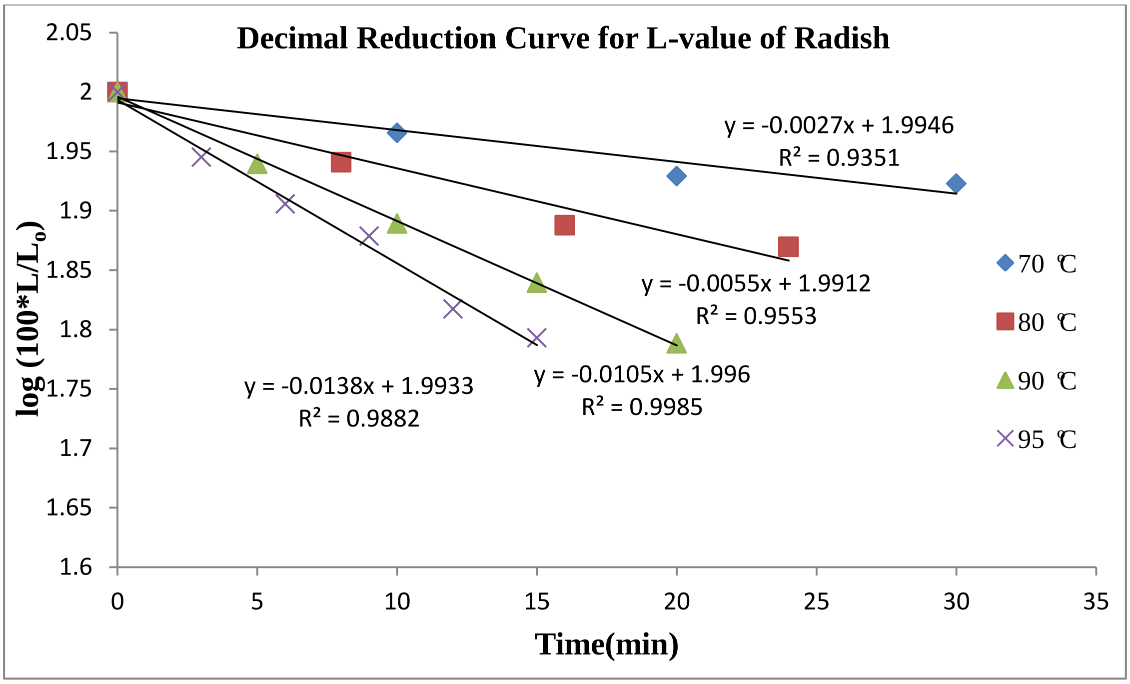


Figure 3.4 Plot of log ratio of L value of radishes at different temperatures (℃)

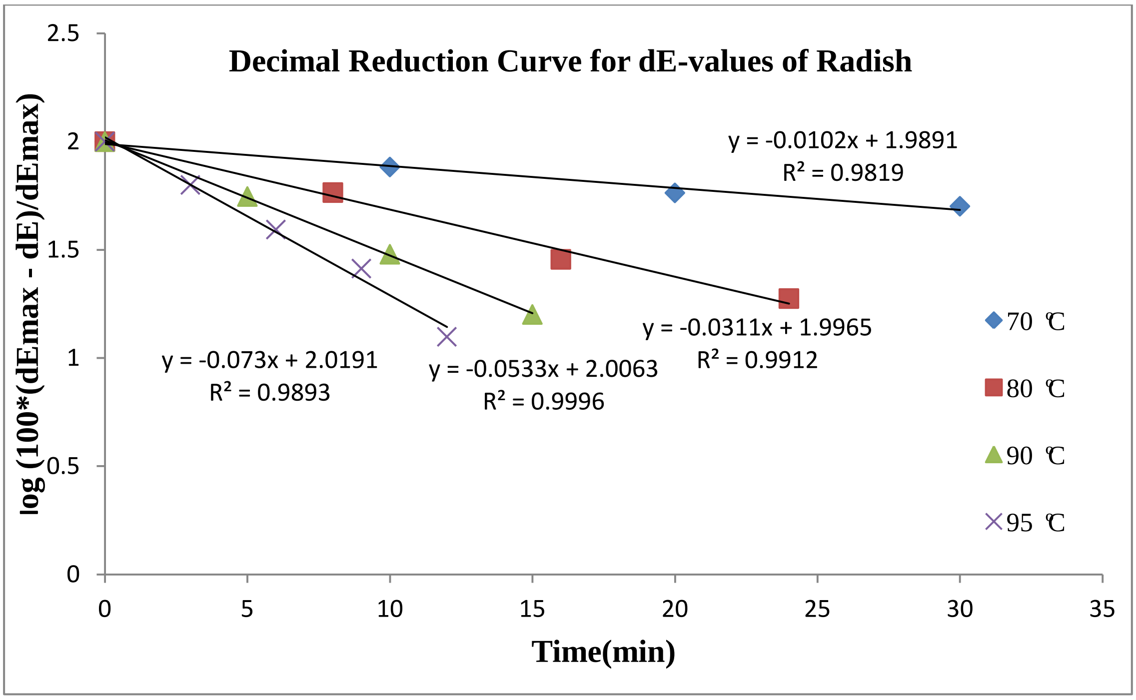


Figure 3.5 Plot of log ratio of ΔE value of radishes at different temperatures (℃)

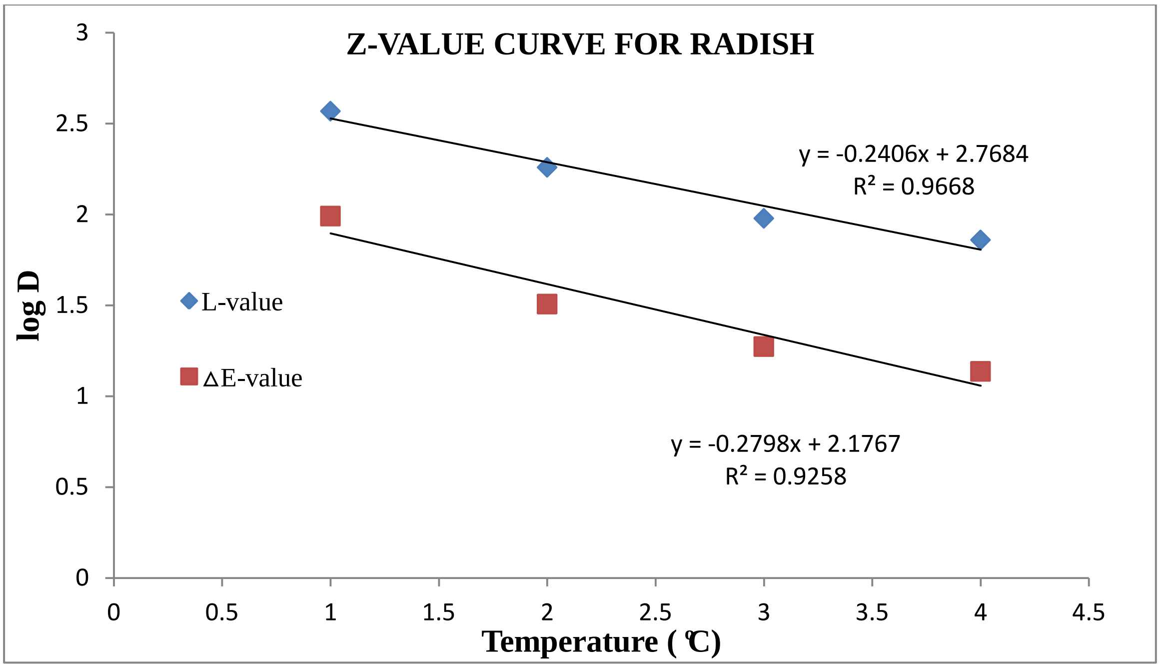


Figure 3.6 Log D plot of color values of radish vs. temperature

Table 3.1 Effects of temperature and time on color of potato and radish

Sample	Temperature (℃)	D value of L value (min)	D value of ΔE value (min)
Potato	70	625	43.1
	80	435	34.1
	90	250	23.3
	95	125	9.20
Z value (℃)		42.7	45.9
Radish	70	370	98.0
	80	182	32.2
	90	95.2	18.8
	95	72.5	13.7
Z value(℃)		41.5	35.7

3.4.2 Texture kinetics

The three major textural parameters (hardness, chewiness and gumminess) of potatoes and radishes were found to be affected by cooking time and temperature. These results are consistent with numerous studies of thermal softening of vegetables (Alvarez et al., 2001; Huang and Bourne, 1983; Nourian and Ramaswamy, 2003a). Thermal softening often renders potatoes and radishes undesirable and unsalable due to the breakdown of pectic substances in cell wall and middle lamella region (Bourne, 1989). Potato has a high content of starch, which is also responsible for softening tissue due to starch gelatinization.

Figures 3.7 to Figure 3.10 show thermal softening kinetics of potatoes for hardness, chewiness and gumminess at 70 ℃, 80 ℃, 90 ℃ and 95 ℃ respectively as plots of logarithmic textural parameters versus heating time. At lower temperatures 70 ℃ and 80 ℃, the associated texture changes in potatoes better described the first order kinetics than the higher temperatures possibly due to differences in the heating profiles associated with heating at higher temperatures. The softening curves indicated that the increasing the treatment time at a given temperature has a considerable effect on the degradation of texture quality. The z value curves of potato textural parameters are presented in Figure 3.11. D values of the three textural parameters of potatoes decreased with an increase in temperature. For hardness parameters of potato samples, D values at the four different temperatures varied from 222 min of 70 ℃ to 14.2 min of 95 ℃ giving a z value of 21.8 ℃.

Figure 3.12 to Figure 3.15 present the D values of the three textural parameters of radishes at different temperatures in the range 70 ℃ to 95 ℃. The softening curves of radishes showed similar trends as that of potato cubes. The z value curves of radish textural parameters are showed in Figure 3.16. The curves indicated that the increased temperature also affected the quality attributes of hardness, gumminess and chewiness and thermal softening was temperature dependence. For hardness parameters of radish samples, the decimal reduction times at four different temperatures varied from 111 min at 70 ℃ to 18.3 min of 95 ℃ giving the z value of 31.1 ℃; for gumminess parameters of radish samples, the D values varied from 172 min at 70 ℃ to 12.6 min at 95 ℃ with a z value of 21.4 ℃ and for chewiness, the associated D values varied from 55.9 min at 70 ℃ to 10.7 min at 95 ℃ giving a z value of 34.0 ℃. The different kinetic parameters of thermal softening of radishes and potatoes are summarized in Table 3.2.

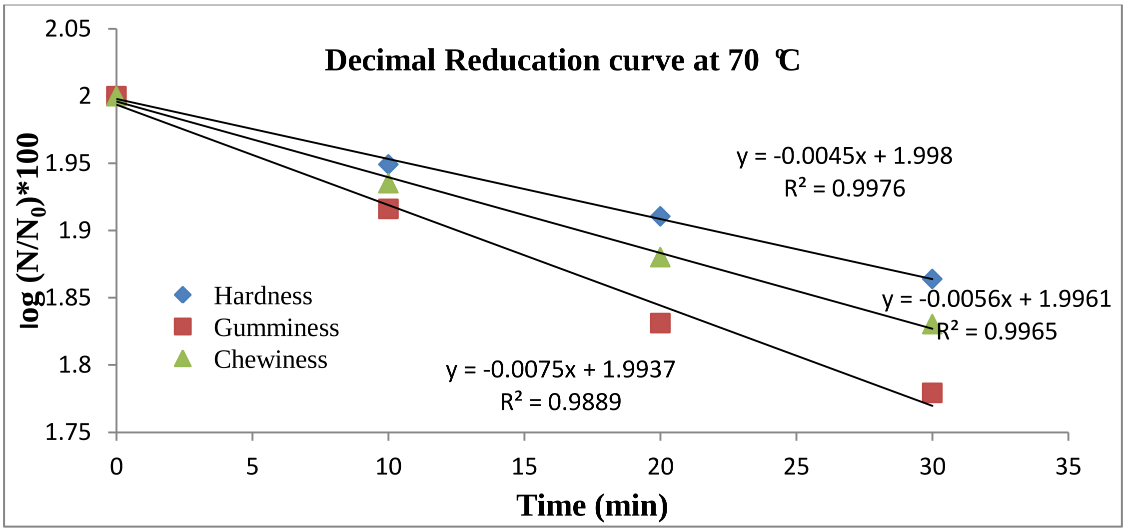


Figure 3.7 Plot of log ratio of texture parameters of potato at 70 ℃

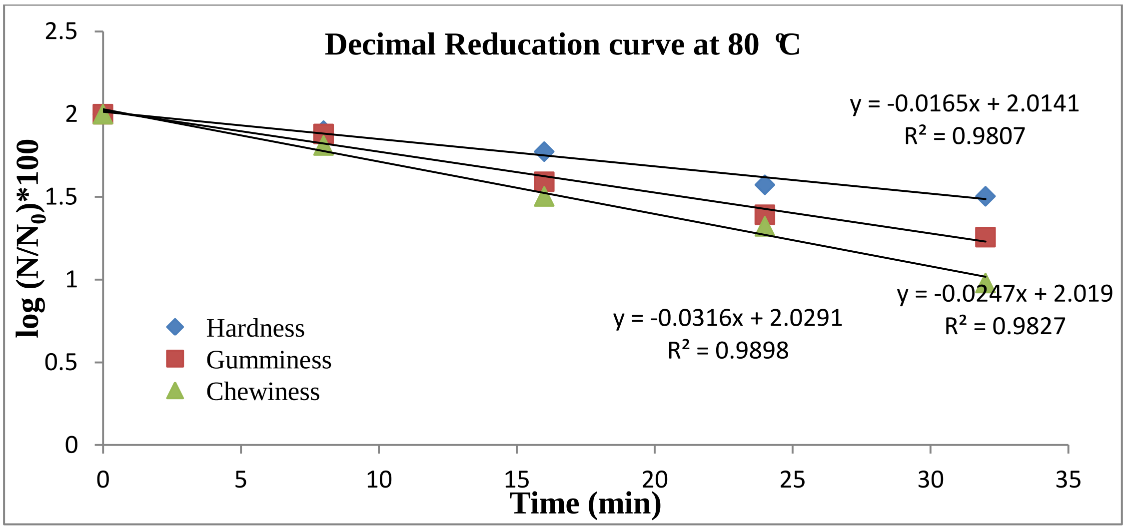


Figure 3.8 Plot of log ratio of texture parameters of potato at 80 ℃

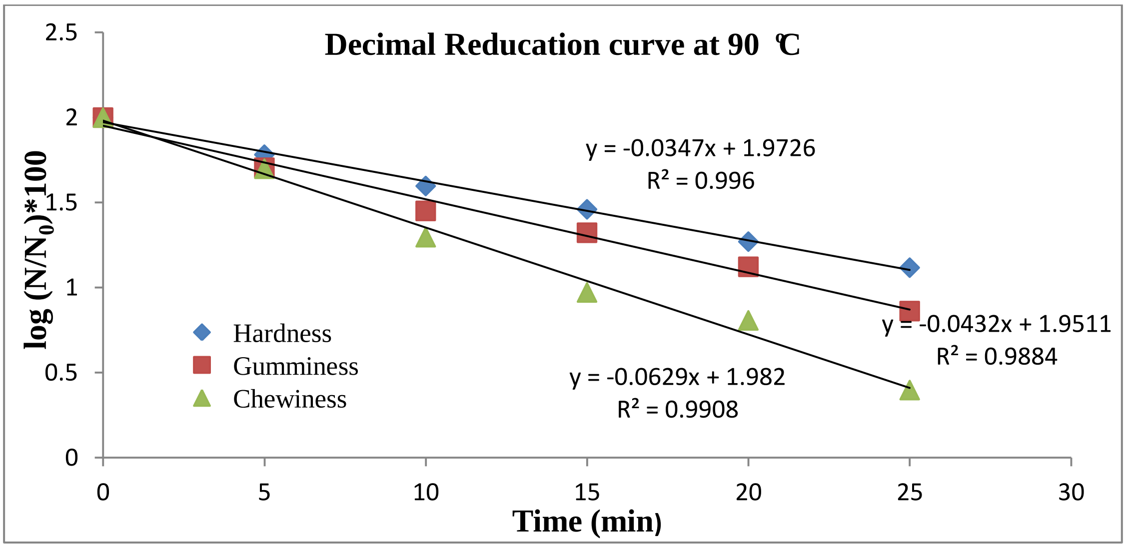


Figure 3.9 Plot of log ratio of texture parameters of potato at 90 ℃

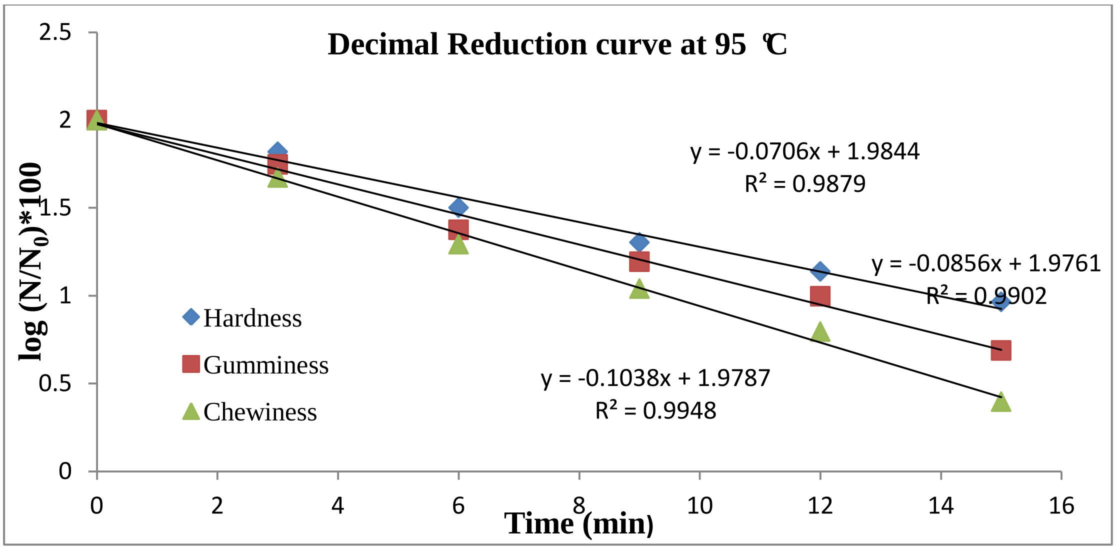


Figure 3.10 Plot of log ratio of texture parameters of potato at 95 ℃

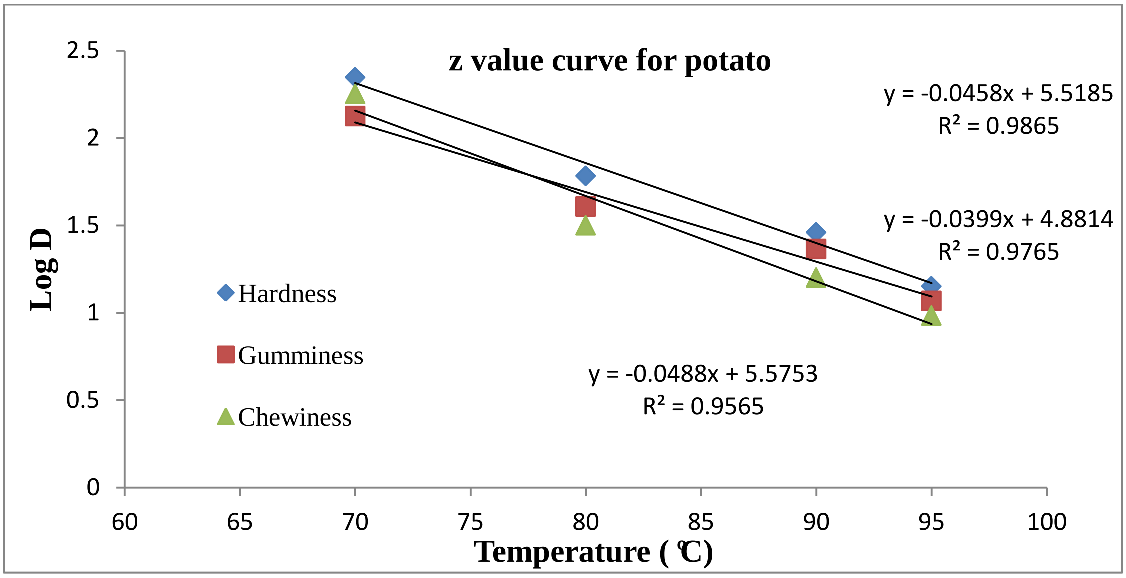


Figure 3.11 Log D plot of texture parameters of potato vs. temperature

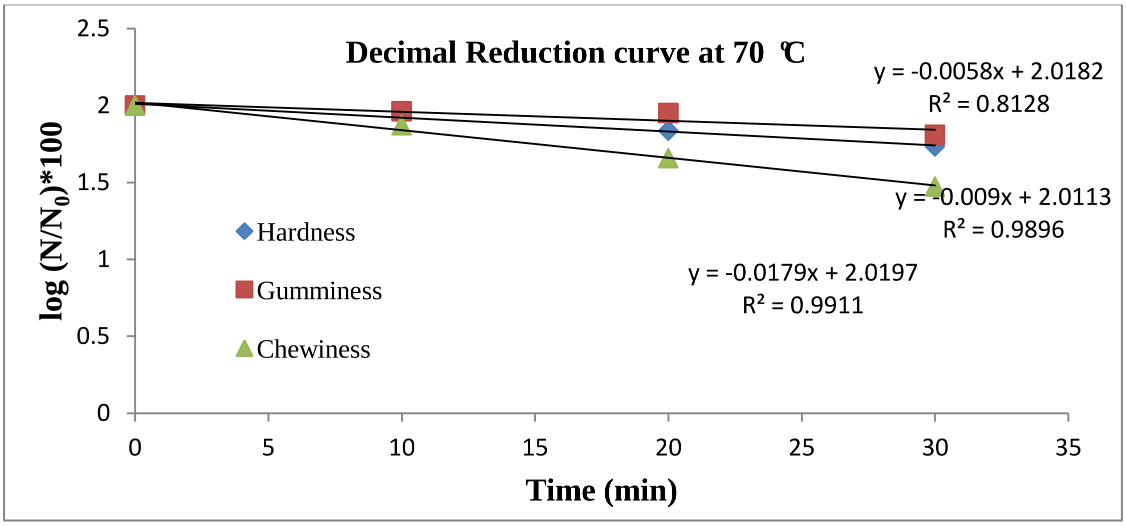


Figure 3.12 Plot of log ratio of texture parameters of radishes at 70 ℃

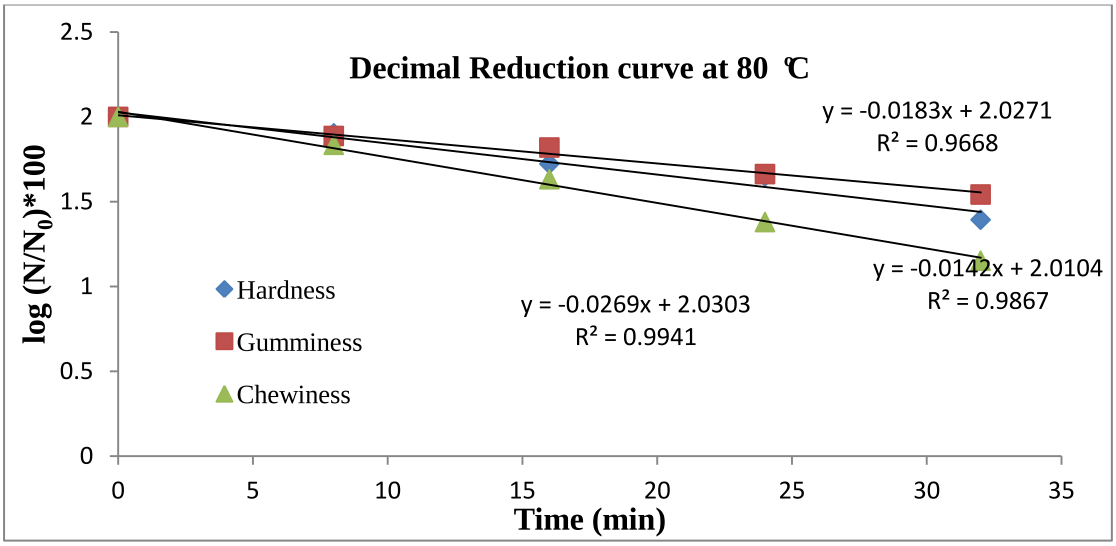


Figure 3.13 Plot of log ratio of texture parameters of radishes at 80 ℃

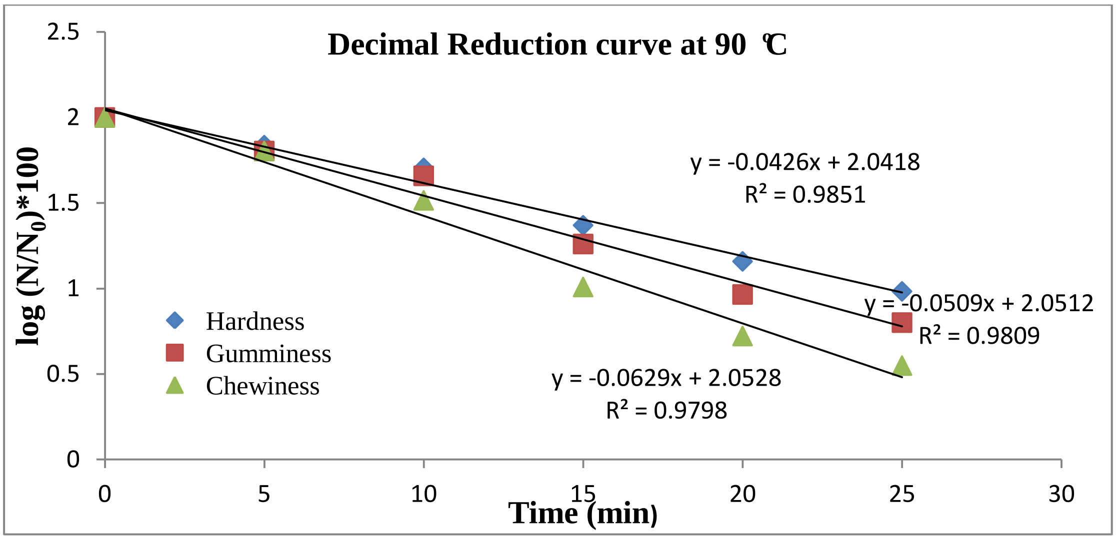


Figure 3.14 Plot of log ratio of texture parameters of radishes at 90 ℃

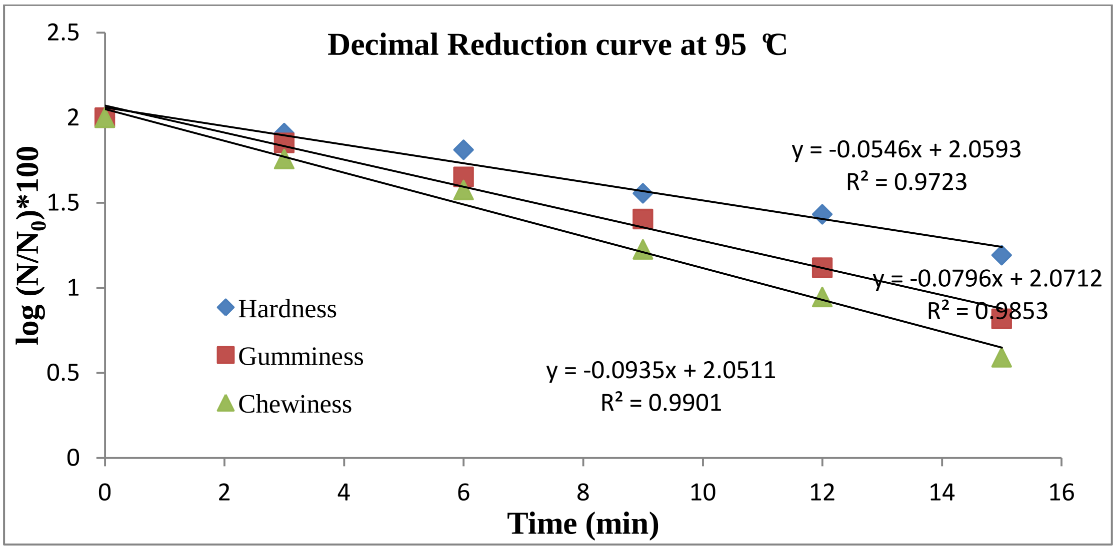


Figure 3.15 Plot of log ratio of texture parameters of radishes at 95 ℃

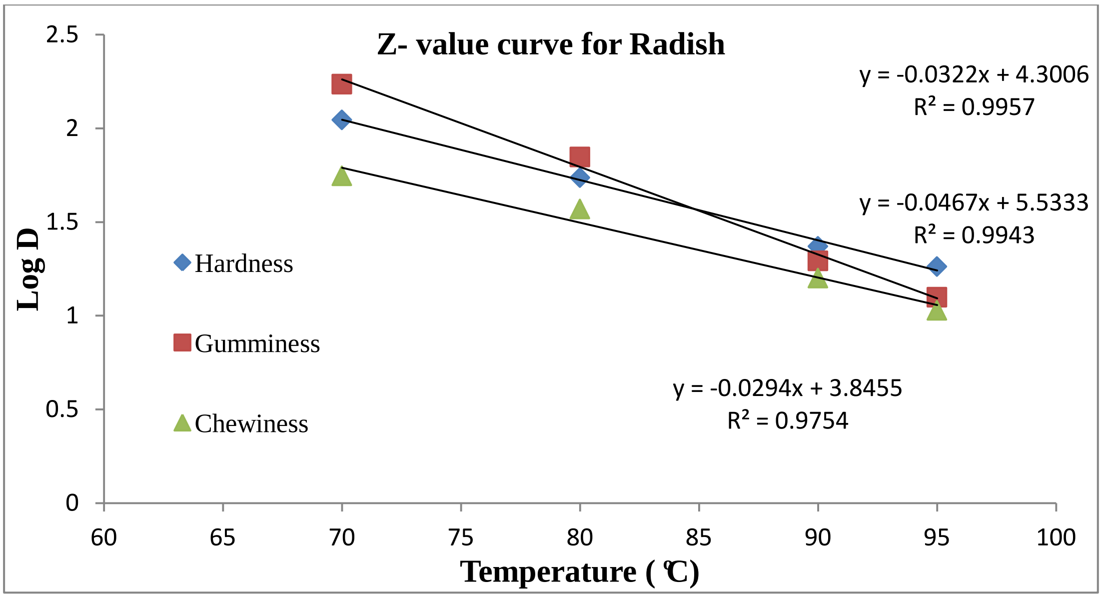


Figure 3.16 Log D plot of texture parameters of radish vs. temperature

Textural parameters degraded at a rapid rate at the beginning of the heating processing and then relatively slower a slow rate as heating increased confirming the first order nature of the degradation kinetics. The common feature in most of these plots that could be observed was that there were two independent first-order softening rates deviating from the simple first order rate at higher times, more clearly observable at higher temperatures. The shapes of curves were characterized by an initial steeper negative slope and a second shallow negative slope that were more obvious at the elevated temperatures. Alvarez (2001) reported that the heating rates of potato tissue in water at 50 ℃ -100 ℃ can be expressed by a pseudo first-order kinetic mechanisms or two pseudo first order mechanisms resulting from the gelatinization of starch and the solubilization of pectic substances. Two mechanisms of softening of potato at 90 ℃ for selected time intervals were showed in Figure 3.17, and softening of radishes characterized by two simultaneous kinetics models at 90 ℃ was showed in Figure 3.18.

Table 3.2 Effects of temperature and time on texture parameters of potato and radish

Sample	Temperature(^{o}C)	D value of Hardness (min)	D value of Gumminess (min)	D value of Chewiness (min)
Potato	70	222	133	179
	80	60.6	40.5	31.6
	90	28.8	23.1	15.9
	95	14.2	11.7	9.60
Zvalue($^{\circ}$C)		21.8	25.1	20.5
Radish	70	111	172	55. 9
	80	54.6	70.4	37.2
	90	23.5	19. 6	15.9
	95	18.3	12.6	10.7
Zvalue($^{\circ}$C)		31.1	21. 4	34.0

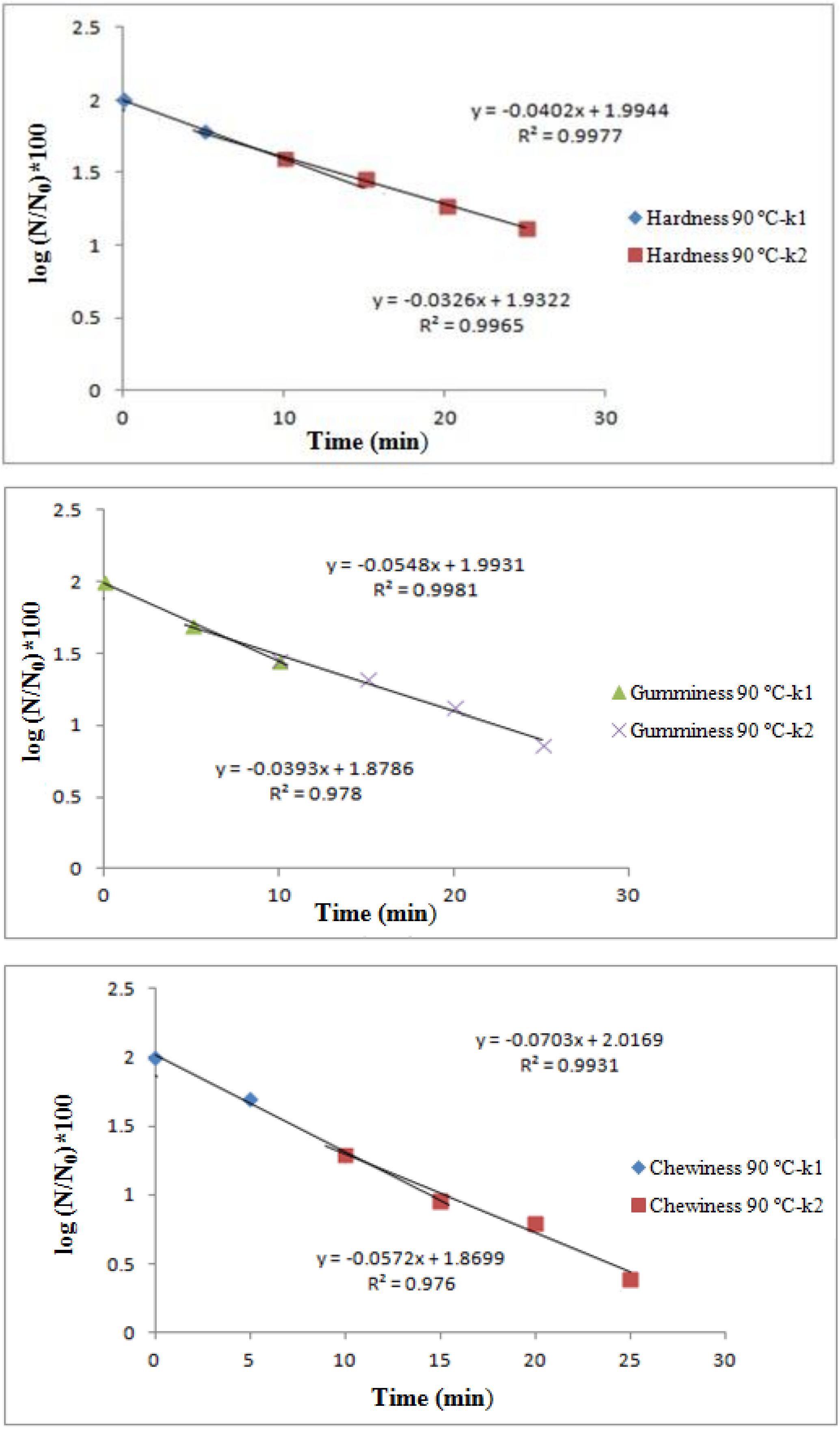


Figure 3.17 Plot showing two mechanisms of textural parameters of potato at 90 ℃

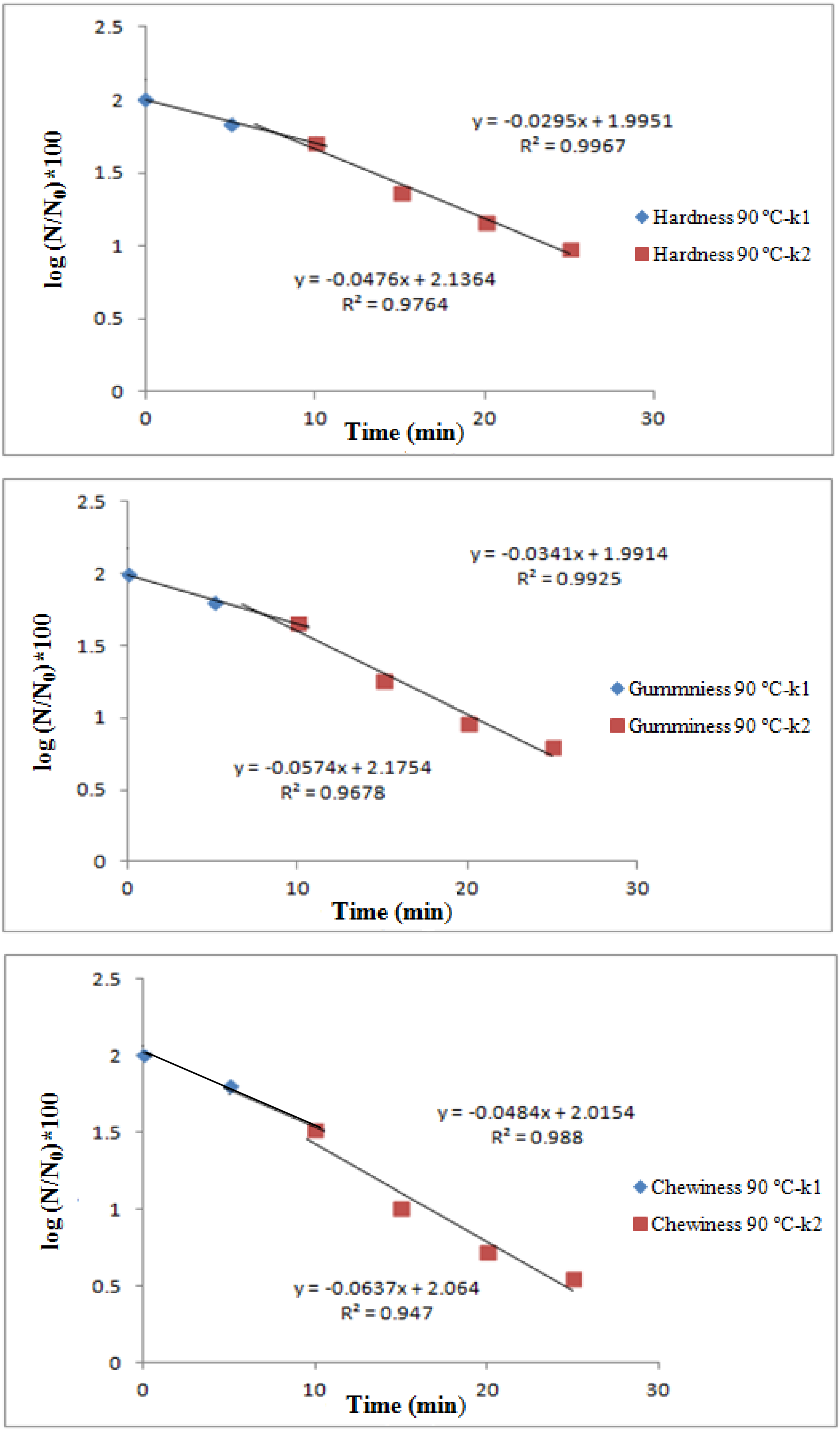


Figure 3.18 Plot showing two mechanisms of textural parameters of radish at 90 ℃

At lower temperature 70 ℃ and 80 ℃, softening curves were characterized by simple first order kinetics since there was probably incomplete gelatinization. At 90 ℃ and 95 ℃, thermal softening probably resulted in breakdown of pectic substances accompanying with gelatinization. Two simultaneous first order kinetic models were suitable to be applied to express softening behavior, which had been confirmed by many researchers (Alvarez et al., 2001; Huang and Bourne, 1983; Nourian and Ramaswamy, 2003a).

Kinetics of textural parameters of potato and radish estimated by using two simultaneous kinetics models are summarized in Table 3.3. For potato, the apparent rate constants (K_a) for mechanisms 1 calculated from hardness, gumminess and chewiness textural parameters were greater than the apparent rate constants (K_b) for mechanisms 2 at 90 ℃ and 95 ℃. The apparent rates were increased with temperature. During heating process, mechanisms 1 might be associated with starch gelatinization and a slight degree of cooking over short treatment times, while mechanisms 2 may reflect the solubilization of the pectic substances in the cell wall and middle lamella and a deep degree of cooking (Alvarez et al., 2001).

For radish, the apparent rates were also found to increase with temperature. The apparent rate constants (K_a) for mechanisms 1 calculated from three parameters were smaller than the apparent rate constants (K_b) for mechanisms 2 in all cases at 90 ℃ and 95 ℃, which were opposite with the results of potato. The reasons might be associated with the size of the radish. The size of globe radish was larger than that of potato cubes and the samples were obtained from the internal parts. Hence, the heating rate was slow at the beginning of the heating and then heating rate became faster in the prolonged heating.

Table 3.3 Kinetics information for textural parameters of potato and radish samples due to thermal treatments

		Mechanisms1 K_1			Mechanisms2 K_2		
Sample	Temperature (℃)	Hardness	Gumminess	Chewiness	Hardness	Gumminess	Chewiness
Potato	90	0.0402	0.0548	0.0703	0.0326	0.0393	0.0572
	95	0.0831	0.104	0.117	0.0591	0.0753	0.0978
Radish	90	0.0295	0.0314	0.0484	0.0476	0.0574	0.0637
	95	0.0314	0.0580	0.0708	0.0661	0.0930	0.108

3.4.3 Antioxidant activity kinetics

The antioxidant activity in potato and radish samples heat treated at each temperature decreased with an increase in treatment time and temperature. The semi-logarithmic plot of change in antioxidant value in potato and radish samples by using the fractional conversion model equation is presented in Figures 3.19 and 3.21. D values for thermal degradation of antioxidant value were obtained from these plots as negative reciprocal slopes. These figures confirm the simple first order trends followed by the kinetics. The z value curves (logarithm of D values vs. temperature) for the antioxidant activity in potato and radish samples are shown in Figures 3.20 and 3.22. The associated D values decreased with an increase in temperature. Therefore, the increasing temperatures would result in more rapid decrease in the antioxidant activity of potato and radish samples.

Kinetic data on thermal degradation of antioxidant activity in radish and potato are summarized in Table 3.4. D values for heat destruction of antioxidant activity in potato were 833 min, 250 min, 217 min and 172 min at 70 ℃, 80 ℃, 90 ℃ and 95 ℃, respectively. The D value reduced by 79% from 70 ℃ to 95 ℃ and z value was 39.4 ℃. D values associated with thermal destruction of antioxidant activity in radish was 135 min, 69.4 min, 57.8 min and 50.5 min at 70 ℃, 80 ℃, 90 ℃ and 95 ℃, respectively. The associated z value was 61.0 ℃. The D value reduced by 63% from 70 ℃ to 95 ℃. For antioxidant degradation in potato is more resistant to thermal degradation than in radish samples with 3-6 times higher D values. However, potato antioxidants are more sensitive to changes in temperature (lower z value).

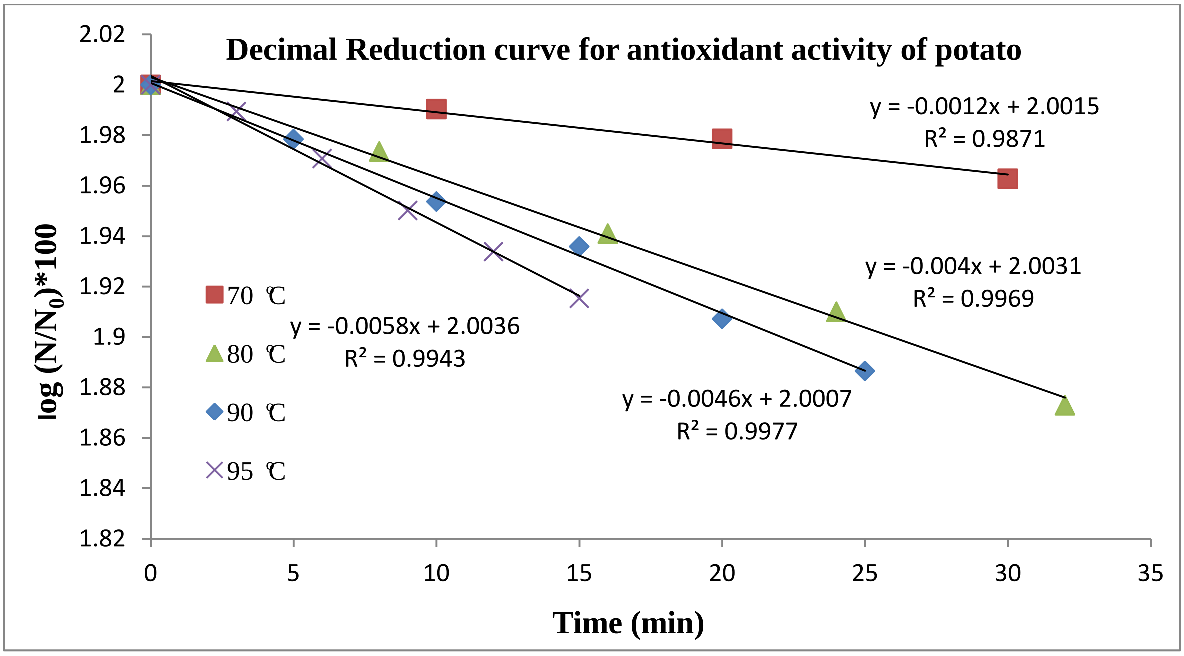


Figure 3.19 Plot of log ratio of antioxidant activity of potatoes at different temperatures (℃)

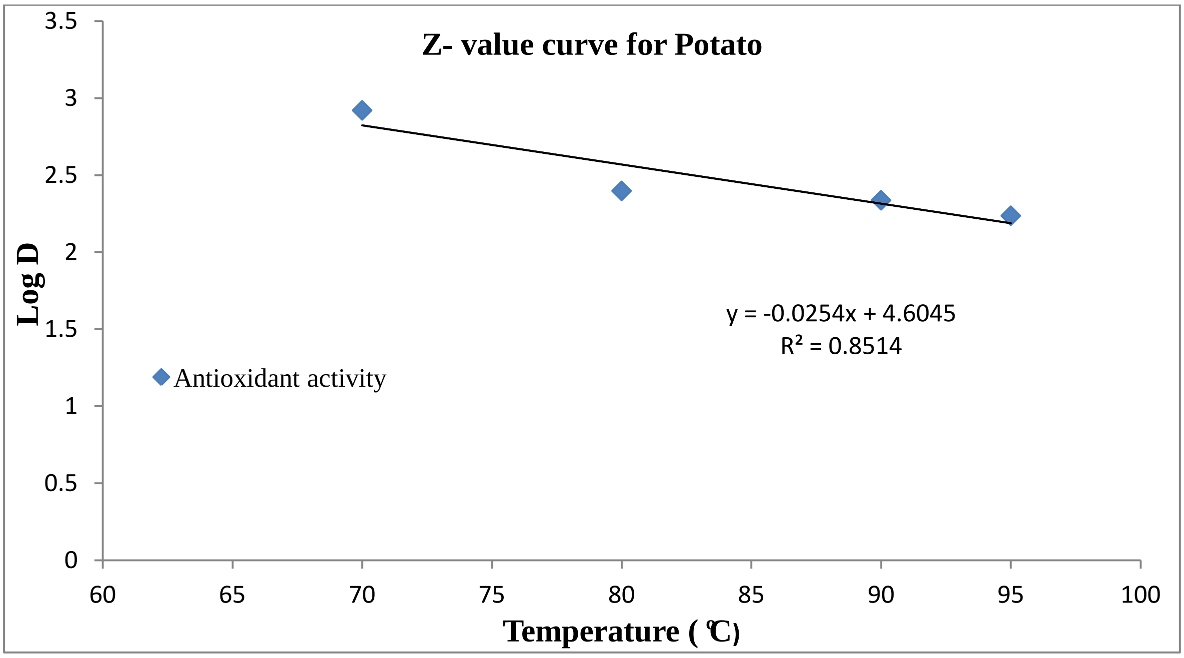


Figure 3.20 Log D plot of antioxidant activity of potato vs. temperature

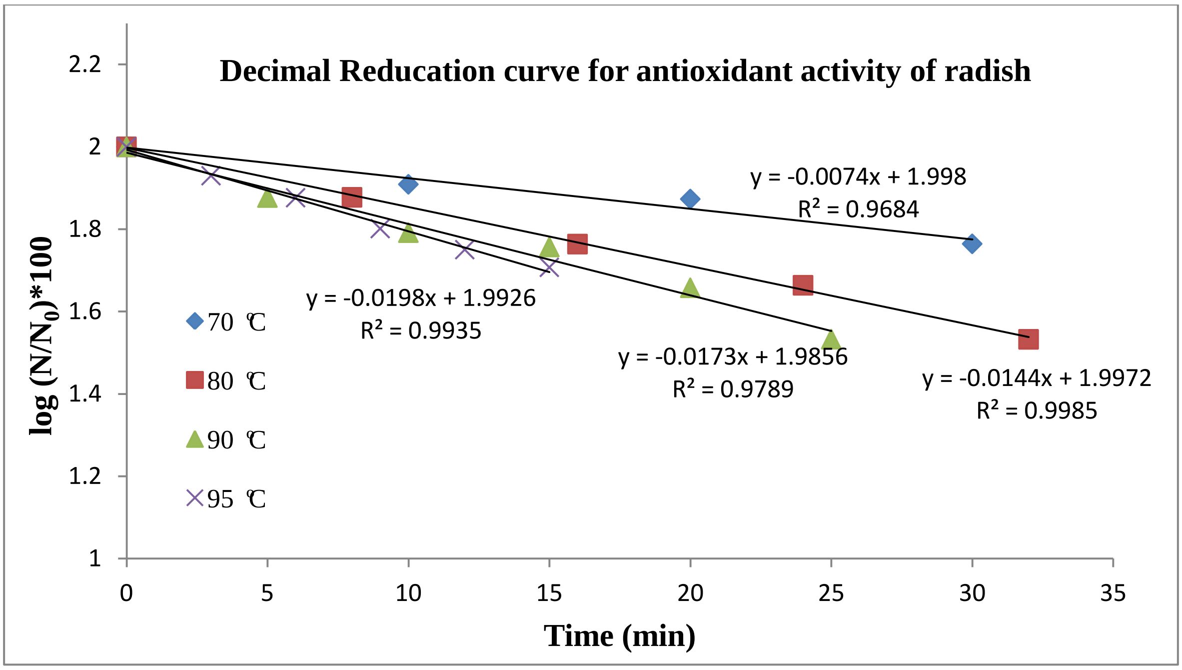


Figure 3.21 Plot of log ratio of antioxidant activity of radishes at different temperatures (℃)

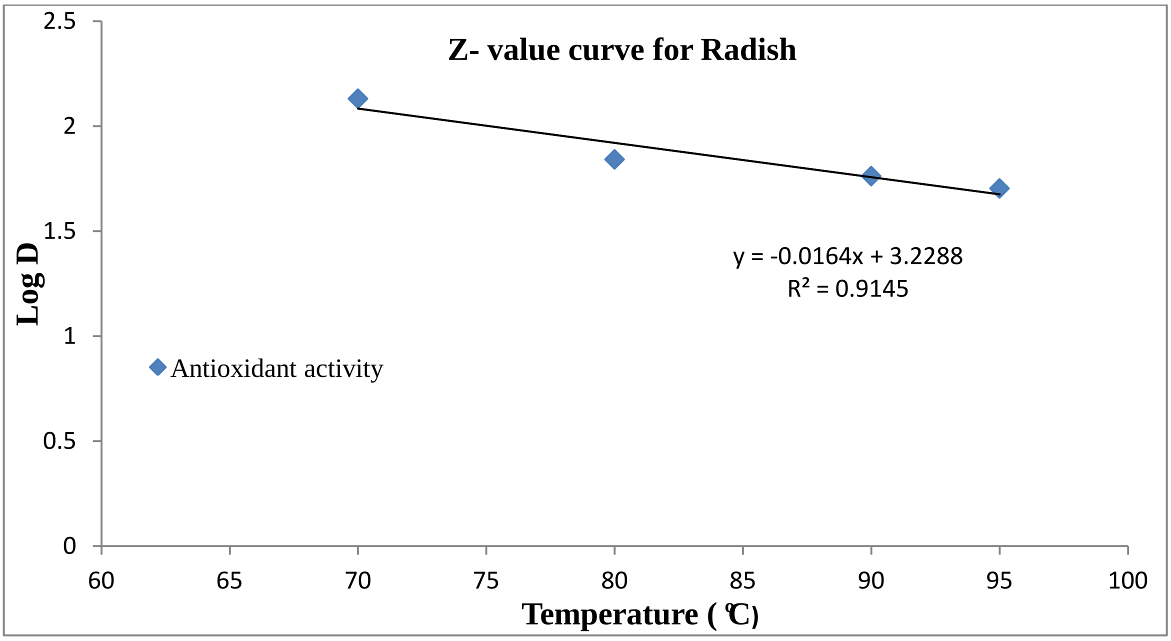


Figure 3.22 Log D plot of antioxidant activity of radish vs. temperature

Table 3.4 Effects of temperature and time on antioxidant activity of potato and radish

Sample	Temperature (℃)	D value of Antioxidant activity (min)
Potato	70	833
	80	250
	90	217
	95	172
Z value (℃)		39.4
Radish	70	135
	80	69.4
	90	57.8
	95	50.5
Z value (℃)		61.0

3.5 Conclusions

The color parameters (L value and ΔE value), texture values (hardness, gumminess and chewiness) and antioxidant activity of potato and radish samples were obtained from the thermal treatment data of test samples at different temperatures. During heating processing, there were considerable changes in color parameters, texture values and antioxidant activity. The degradation of three properties of both potato and radish increased with an increase in temperature and/or an increase in heating time. The rates of thermal softening of potato and radish at 70 ℃ and 80 ℃ followed one pseudo first-order kinetic mechanism, while the rates of thermal softening at higher temperatures followed two simultaneous pseudo first-order kinetic mechanisms. For radish, the apparent rate constant (K_a) for mechanism 1 were less than the apparent rate constant (K_b) for mechanism 2 calculated from three texture parameters. For potato, K_a calculated from hardness, gumminess and chewiness texture parameters were greater than K_b in all cases at 90 ℃ and 95 ℃. The apparent degradation rates increased with temperature for both potato and radish.

The kinetics of changes in color and antioxidant activity attributes followed first order rate. Color parameters a and b values were relatively stable so no kinetics trend were established for these parameters. For potato, z values were 20-25 ℃ for texture parameters, 43 ℃ and 46 ℃ for L value and ΔE value, respectively. For radish, z values were 21-34 ℃ for texture parameters, 42 ℃ and 36 ℃ for L value and ΔE value, respectively. The antioxidant activity of potatoes and radishes heated at each temperature decreased with an increase of time. The D value reduced by 79% and 63% from 70 ℃ to 95 ℃ for potato and radish, respectively. The kinetics results could provide an insight of understanding and predicting thermal quality degradation of vegetables.

PREFACE TO CHAPTER 4

Thermal processing is scientifically established for achieving a selected level of lethality targeting destruction of pathogenic and spoilage microorganisms. In order establish the process one has to know the target process lethality as well as the heating behavior of test products. Processes are developed based on numerical integration of time temperature profile generated under processing conditions with kinetic data (General method) or can be based on Formula methods. Formula methods achieve the integration of heating profile and kinetic data using heat penetration parameters. The purpose of this chapter was to characterize the heat penetration behavior of canned potato and radish under different reciprocal agitation thermal processing from which the processing schedule could be developed using Formula method of process calculations.

A part of this research was presented in 2014 in Research Feeding Industry, Montreal, Canada. The experimental work and data analysis were conducted by candidate under the supervision of Dr. H. S. Ramaswamy. Manuscript for publication has been prepared.

YOU, J and Ramaswamy, H. S., 2015. Effects of processing factors on heat penetration parameters of canned potatoes and radishes under reciprocating agitation thermal processing (***draft***).

Chapter 4

HEAT PENETRATION DATA GATHERING AND PROCESS ESTABLISHMENT FOR CANNED POTATO AND RADISH UNDER RECIPROCATING AGITATION THERMAL PROCESSING

4.1 Abstract

The study was carried out for evaluating heating penetration behavior of canned potato cubes and red globe radish under reciprocating agitation thermal processing in order to establish the appropriate processing schedule. Potato cubes (15 mm x 15 mm x15 mm) and whole red globe radishes (average radius: 15 mm) were separately filled into 307 x 409 cans with a low viscosity covering liquid (1% NaCl and 1% $CaCl_2$ solution). The prepared cans were processed in the pilot-scale reciprocating agitation retort at 120 ℃ with agitation maintained at different reciprocating speeds (0, 0.75, 1.5, 3 Hz). The heat penetration parameters for the canned liquid and particle were obtained from the temperature-time data gathered during the processing. Heating rate index (f_h) and the heating lag factor (j_{ch}), and processing time (Pt) for establishing a target lethality were computed. It was observed that the canned liquid and particles treated under high reciprocation speed had lower f_h, and j_{ch} values which degreased with the speed of agitation. These processing conditions also reduced the required thermal processing time and provided processing opportunity for improving the quality of products.

4.2 Introduction

Thermal processing is widely used to destroy spoilage and pathogenic microorganisms as well as inactive enzymes present in the canned food in order to render them safe and shelf-stable. The fundamental principle of thermal processing the best way to transfer the heat from a heating medium to the can contents to achieve the degree of heat treatment required. Conduction and convection are the two basic mechanisms, which involve the heat transfer into or out of the food contained in the can. In conduction heat transfer mechanism, the heat transfer occurs through solids or viscous stationary fluids, while convection mechanism takes place in liquid foods by using the movement of fluids. The mixture of liquid and particle products packed in cans, such as soups and sauces, will heat by combination of both conduction and convection mechanisms (Ahmed and Shivhare, 2006; Ramaswamy and Marcotte, 2006) and can be improved by induced convection through agitation.

In order to get maximum retention of quality of thermally processed products, high temperature short time processes (HTST) have been applied to heating processing of vegetables in food industry as an alternative approaches to conventional thermal techniques. The benefits of HTST are due to the different destruction rate of microorganisms and quality attributes (Ramaswamy and Marcotte, 2006). Several researchers have shown that the rate of microbial destruction generally is much higher at higher temperatures (z value of 10 to 15 ℃) which are also true for quality destruction (z value of 30 to 35 ℃) (Holdsworth, 1985; Lund, 1977); however, their relative destruction rates differ and drift farther apart at higher temperatures with the destruction rate of microbial spores increasing much more rapidly than that of quality factors (Ramaswamy and Marcotte, 2006).

There are several published reports on heating behaviors of foods in rotary retorts (Berry et al., 1979; Berry and Kohnhorst, 1985).The influences of different processing variables on heat transfer rate have also been studied by several researchers (Dwivedi and Ramaswamy, 2010a,b; Meng and Ramaswamy, 2006, 2007a,b; Rattan and Ramaswamy, 2014; Sablani and Ramaswamy, 1995, 1996). All these studies are unanimous in concluding that heat transfer rate during thermal processing is significantly affected by several major processing variables, including the type of retort, retort temperature, the nature of particle, the size of particle, rotational speed and headspace.

Anantheswaran and Rao (1985) reported that the agitation of container contributes to a rapid heating transfer rate. Therefore the processing time can be reduced and the quality attributes of foods will have a better retention. Agitation processing achieved by novel reciprocating agitation and three types of traditional rotations, includes fixed axial rotation, end-over-end rotation and free axial rotation. Container agitation in retort has many advantages over still retort. Foods heated in container agitation have rapid heat penetration rate, even in particulate or viscous products (Ramaswamy et al., 1993). However, the conventional agitation methods, like continuous retorts with axial agitation and batch retorts with end-over-end agitation, face the limitations that the force resulting the mixing of product within the container are the balance between centrifugal force and gravity. The processing time is reduced with the increasing rotation speed until the optimum is reached. If the rotation speed increases further, the processing time would increase until the speed reaches sufficiently high. At that point, the processing under agitation processing has no difference with a static processing (Walden and Emanuel, 2010; Sablani and Ramaswamy, 1996). Hence, food industry is seeking for a new processing that can reduce the processing time significantly which results in producing foods with better retention of nutrition.

The reciprocating agitation is the new method that exploits the reciprocal agitation in addition to gravity. The reciprocal forces cause greater movement of products within in can, which can increase heat transfer rate and thus reduce the processing time. As compared to conventional static agitation, reciprocating agitation provided a faster heat transfer rate had a 10-fold reduction in processing time (Singh et al., 2015; Walden et al., 2010).

This study aimed to evaluate the effect of reciprocation agitation processing factors on the heating behavior of potato and radish, to compute the heating rate index and heating lag factor, and finally to establish processing times to accomplish a designated process lethality using the formula method of process calculations.

4.3 Method and materials

4.3.1 Preparation of products and cans

Potatoes (*Solanum tuberosum*) of Goldrush variety and red globe radishes (*Raphanus sativus L.*) with white flesh were purchased from the local market and then stored at 4 ℃. Potatoes were cut as uniform cubes (15 mm x 15 mm x 15 mm) with a sharp knife, and uniform globe radishes were selected with a radius close to 15 mm. After blanching samples in 100 ℃ for 1 min to inactive peroxidase enzyme, the prepared potato cubes and radish were filled in separate 307 x 409 size cans with a covering liquid solution (1% NaCl and 1% $CaCl_2$) by keeping 10 mm headspace. Thermocouples were inserted into centers of potato and radish samples and located at the geometrical center of the can in order to obtain temperature-time data in different agitation processing. For each can, two samples were equipped with flexible thermocouples, which were also used to gather the temperature of can liquid during processing. Cans were sealed in the manual double seaming machine (Home Canning Co., Montreal, QC).

4.3.2 Processing experimental setup

A pilot scale, single cage and vertical static reciprocating retort (Loveless Manufacturing Co., Tulsa, OK) was used. The reciprocating retort was based on converting a static retort to a reciprocation agitation device. The internal diameter and depth of this steam retort were 62 cm and 100 cm, respectively. The principle of reciprocating drive method position of a crank and slider mechanism that drives a basket back and forth through a drive shaft entering the retort. Steam is used as the heating medium while cold water is used as the cooling medium. The come up time to reach operating temperature was approximately 3 to 4 min depending on the load and target temperature.

There are three major parts in the modified retort includes that the reciprocating cage, a crank and slider, and a magnet motor (Singh et al., 2015). Retort cage is supported by stainless steel rails with the slip rings to hold the cans. Cage was designed to hold four 307 X 409 mm cans each time. The cage was designed to have length 35 cm, width 12 cm and height 17 cm. The crank and slider assembly had a steel rotating shaft and a crank. In order to make the movement of reciprocating cage, the crank had to be attached to rotating shaft. By varying the position of the crank in the rotating shaft, the amplitude of reciprocating could be changed. Thus, the pivoted end of the crank moves circularly through the rotating shaft, while the reciprocating cage moves linearly through the constricted end of the crank. The magnetic motor determined the reciprocating speed by a voltage controller. The speed can be read through a hand-held tachometer and therefore can be adjusted to the required speed. Rotating shaft is moving circularly once, while the reciprocating cage is moving linearly once.

4.3.3 Temperature measurements

Temperature data of can liquid and samples and retort was gathered during processing in order to obtain temperature-time profile of reciprocating agitation retort. The junction of flexible copper-constantan thermocouple wires (diameter = 0.0762 mm, Omega Engineering Corp, Stamford, CT, USA) were placed at the approximately geometrical center of sample and can in order to monitor temperature of sample and can liquid, respectively. The male connectors of thermocouples for liquid and particles were connected to the female connectors fixed in agitation retort. The thermocouple signals were recorded by data logger unit (HP34970A, Hewlett Packard, Loveland, CO, USA) at regular intervals of one second.

4.3.4 Thermal processing

The heat penetration tests were designed to conduct runs at different reciprocating speed ranging between 0 Hz to 3 Hz at 120 ℃ for each sample. During processing, duplicate experimental cans were placed vertically in the reciprocating cage with dummy cans filling the remaining space. Dummy cans were used to preventing the experimental can from moving during reciprocating process. After thermal processing, the cans and retort were cooled to 30 ℃ by cold water immediately.

4.3.5 Calculation of heat penetration parameters and processing time

From the heat penetration curve which is the semi-logarithmic plot of temperature difference (heating medium minus can liquid or particle), heating rate index (f_h) and heating lag factor (j_{ch}) were obtained. The heat rate index was determined as the negative reciprocal of the heating penetration curve. In other words, the time required for the straight line portion of heating curve to pass one log cycle is the heating rate index. Low f_h value means high heat transfer rate. The heating lag factor (j_{ch}) was obtained by the following equation:

$$j_{ch} = (T_r - T_{pih})/(T_r - T_{ih}) \qquad (4.1)$$

where T_r represented the retort temperature, and T_{pih} the pseudo initial sample temperature, and T_{ih} the initial temperature of sample. T_{pih} was obtained by the intersection of extrapolated straight line portion and vertical line in heat penetration curve. j_{ch} represents that the delay in uniform heating processing. Low j_{ch} value represent high heat transfer rate.

In thermal processing, processing time refers to the time that product was required to be heated in the retort in order to achieve commercial sterilization. In this study, processing time is calculated to achieve a conventional process lethality (F_o) of 5 min. Based on f_h and j_{ch} values, processing time can be calculated according to formula methods (Ball, 1923) as expressed as below:

$$B = f_h \log(j_{ch} I_h/g) \qquad (4.3)$$

I_h represents the temperature difference between retort and initial temperature of products, while g is for temperature difference between retort and temperature of product at the end of the cook which was obtained from Ball tables which relate a factor f_h/U to g. U is obtained as a product of F_o and F_i where F_o is the target lethality (5 min in this case), and F_i is the time equivalent at retort temperature to 1 min at 250 ℉ (121.1 ℃).

4.4 Results and discussions

4.4.1 Heating behavior during reciprocating retort processing

Figure 4.1 and Figure 4.2 show the heating profiles recorded in still, 0.75 Hz and 1.5 Hz and 3 Hz agitation cooking at 120 ℃ in the reciprocating retort. The heating profile of potato cubes and radish in salt solution (1% NaCl and 2% $CaCl_2$) were evaluated under different agitation reciprocating speeds to achieve the target lethality value of 5 min. The come up time of retort was approximately 3-4 min, which was similar to previous researches (Meng and Ramaswamy 2006; Singh et al., 2015). Retort temperature (T_R), liquid temperature (T_L) and potato particle center temperature (T_{pc}) were recorded using a data logger with the input from different thermocouples attached to cans. First, the heat flow occurs from the retort medium to can liquid by getting through the can wall. Then the heat is transferred from the can liquid to the surface of particles. At last, the heat transfers from the surface to the center of particles. Hence, the heating rate of can liquid and particle center lags behind that of heating medium due to the heat transfer resistance between the can liquid and steam (Dwivedi and Ramaswamy, 2010a).

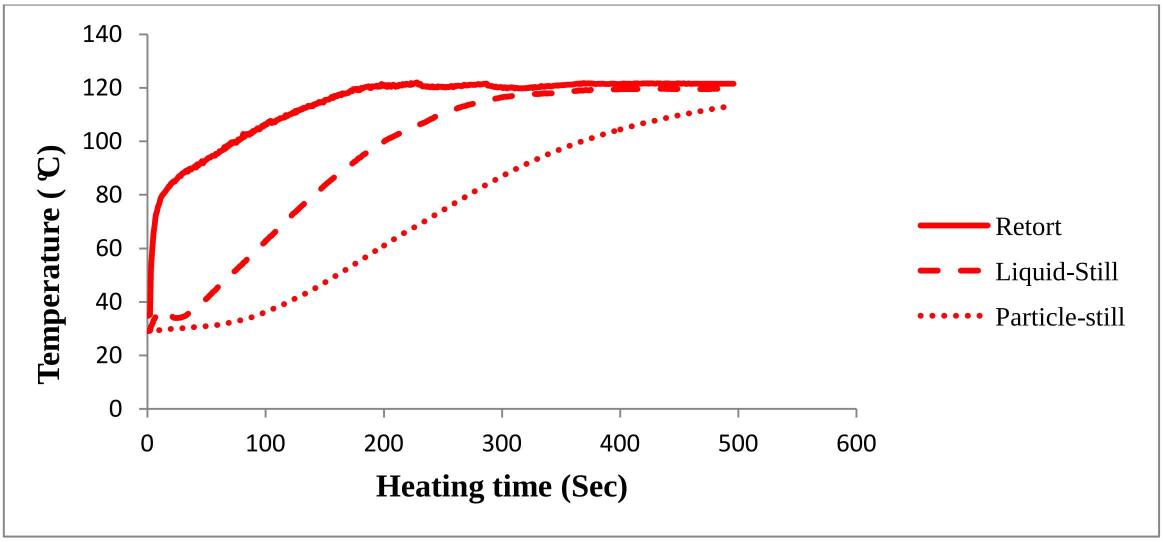


Figure 4.1 Heating profiles of retort, can liquid and particle center of potatoes under still mode at 120 ℃

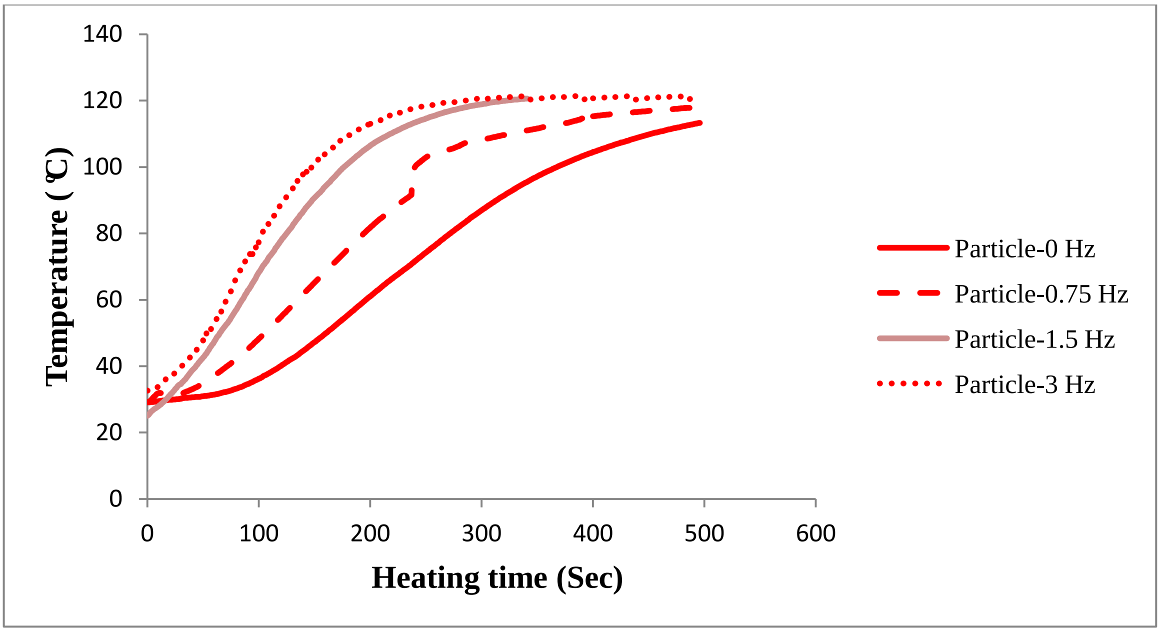


Figure 4.2 Potato particle heating profiles at 120 ℃

It can also be observed that the temperature-time profile of particle under still mode lags behind that of can liquid and retort. This was because of the conductive resistance between the surface of particle and the center of particle (Dwivedi and Ramaswamy, 2010a). The temperature profiles of particle under still mode lags behind that of reciprocating modes at 0.75 Hz and 1.5 Hz and 3 Hz. Particles at 3 Hz reciprocating retort took less time to reach 120 ℃ and which was approximately 280 s. Particles at 1.5 Hz took approximately 300 s and at 0.75 Hz 500 s to reach 120 ℃. The time taken at 3 Hz was reduced by 44% in comparison with that of 0.75 Hz. Particles in still mode took longest time to reach target temperature. The time taken from initial to the target temperature was reduced with the increase in reciprocation speed. This implied that high reciprocating speeds had faster heat penetration rate resulting in reduced process time which could potentially lead to achieving better quality of final products. Similar results were also obtained by Singh et al., (2015) in their study which was conducted with a simulating food heating model (Nylon particle) in glycerin under various reciprocating agitation operating conditions.

Meng and Ramawamy (2007b) explained that the natural convection was mainly responsible heat transfer mode in non-agitated processing, whereas forced convention mode occurred in agitation processing. Hence, the temperature difference between particle surface and particle center was not able to be removed in still mode. Also, the better uniformity of temperature distribution in reciprocating agitation retort was observed by Singh et al., (2015).

4.4.2 Heating rate index f_h

Heating rate index (f_h) is an indicator of the rate of heat transfer, and not a direct measure of the heating rate. The lower value of heat rate index is, the faster heat transfer is. Heating rate index can be obtained by plotting the logarithm of (T_R-T_L) and (T_R-T_{PC}) against heating time. The four reciprocation speeds were selected (0, 0.75, 1.5, 3 Hz) and reciprocation speed was found to have a considerable effect on heating rate index.

Figure 4.3 shows that the graphical representation of f_h values of potato and radish particles obtained from the time-temperature data in different reciprocating speeds. For both potato and radish, f_h values were found to decrease with the increasing reciprocating speeds. The highest value of potato particle was 345 s which was in the slowest mode of heating which is the still mode (0 Hz), while the lowest value was 140 s in agitation mode at 3 Hz. The highest value of radish particle was 769 s in still mode (0 Hz), while the lowest value was 215 s in agitation mode at 3 Hz. The lower heating rate index value demonstrated the higher heat transfer rates at higher reciprocating agitation speeds, resulting from better mixing of can liquid and particles. The results were in consistent with previous literature studies, which reported that higher heating rate index values at lower rotational speeds (Dwivedi and Ramaswamy, 2010b; Singh et al., 2015). Singh et al., (2005) reported f_h values average from 6.5 to 3.1 min with agitation thermal processing at different reciprocating frequencies and it was approximately 13.9 min in non-agitated mode. Dwivedi and Ramaswamy (2010b) studied heat transfer rate of canned Newtonian fluids in various modes of rotation and noted that f_h varied from 11.0 to 7.19 min for fixed axial mode; 10.9-6.15 min for end-over-end mode and 9.21-4.18 min for free axial mode.

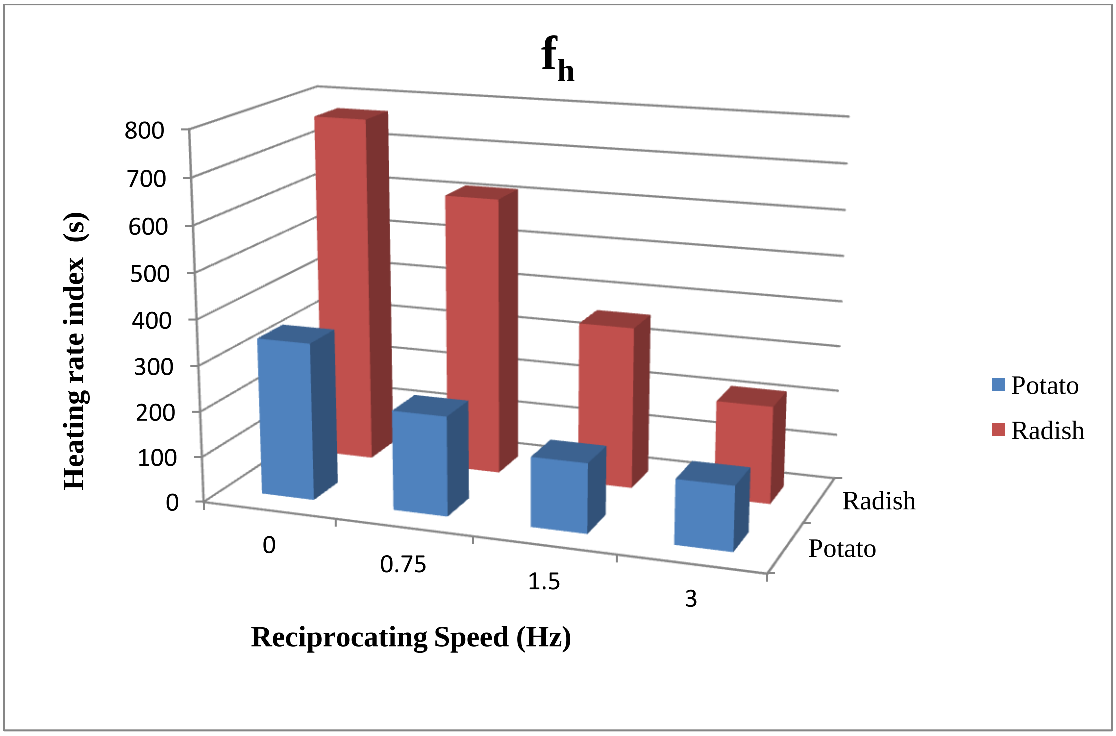


Figure 4.3 Heating rate index under different modes

The f_h values of radishes were higher than that of potato cubes at each reciprocating speed. It obviously indicated that heat transfer rate was also affected by the nature of particle and the shape and size of particle. Radishes used in this study were approximately spherical particle and had a relatively larger size than potato cubes. Hence, its f_h values were higher than that of potato cubes, indicating heating rate was slower. Ramaswamy and Sablani (1997a) found that spherical particles (19.05 diameter) had higher f_h values than that of cube shaped particles (19.05 mm length) in terms to multiple particles (30% particle concentration) in cans under end-over-end rotation. Also they explained that the effect of particle shape on heat transfer rate was determined by the degree of void spaces between particles and the packability of particles. One can filled with the cylindrical and cube particles probably had the thicker boundary layer, whereas a can filled with spherical particles would have the narrow and uniform spaces contributing to high liquid velocity. Moreover, cubes could contact each other through plane heat transfer surface, resulting in reducing f_h values.

From Figure 4.3, processing of potato particle at 120 ℃ in 0.75 Hz, 1.5 Hz and 3 Hz, the f_h values obtained were approximately 37%, 56% and 60% lower than in still mode. It was observed that reciprocating speed did not lower the f_h values much at 3 Hz. Similar finding was found by Singh et al., (2015) that heat transfer rate became slower in high reciprocating speed. Ramaswamy and Sablani (1997b) confirmed that that the increase of heat transfer rate would be inhibited after a certain agitation speed. Radish particle processed at 120 ℃ in 0.75 Hz, 1.5 Hz and 3 Hz, the f_h values obtained were approximately 20%, 54% and 72% lower than at still mode. The influence of reciprocating speed was more pronounced with radishes. It was assumed that radishes were relatively larger and heat transfer rate was lower, and therefore 3 Hz was not beyond a certain agitation speed that would inhibit an increase of heat transfer rate.

4.4.3 Heating lag factor (j_{ch}) and Processing time (Pt)

The main objective of thermal processing is to preserve the product and to give it a long shelf time. It is also used to improve the quality attributed and reduce the loss of texture and color and other quality attributes. The heating lag factor was obtained from the extrapolated intercept portion of the straight-line portion of the heat penetration curve as: $(T_r-T_{pih})/(T_r-T_{ih})$, where T_r is the temperature of reciprocating retort and T_{pih} is the temperature of the pseudo-initial (at the intercept) and T_{ih} is the initial temperature. Figures 4.4 shows the j_{ch} values obtained from corresponding time-temperature data as a function of processing conditions. The j_{ch} values were reduced by increasing reciprocating speed.

For potato, the highest j_{ch} value was 1.9 in still mode (0 Hz), while the lowest value was 1.4 in agitation mode at 3 Hz. Processing at 120 ℃ in 0.75 Hz, 1.5 Hz and 3 Hz, the j_{ch} values obtained were approximately 11%, 25% and 27% lower than in the still mode. For radish, the highest j_{ch} value was 1.4 in still mode (0 Hz), while the lowest value was 1.2 in agitation mode at 3 Hz. Processing of radish particles at 120 ℃ in 0.75 Hz, 1.5 Hz and 3 Hz, the j_{ch} values obtained were approximately 6%, 14% and 16% lower than at still mode. From Figure 4.4, it can be observed that reciprocating speed had a pronounced influence on j_{ch} values of potato cubes more than that of radishes. The j_{ch} values of both samples decreased slightly at higher speed. Similar trends were found in f_h values. Lower heating lag factor values stand for lower lag to heat transfer rate which results from better mixing in rapid reciprocating agitation speed.

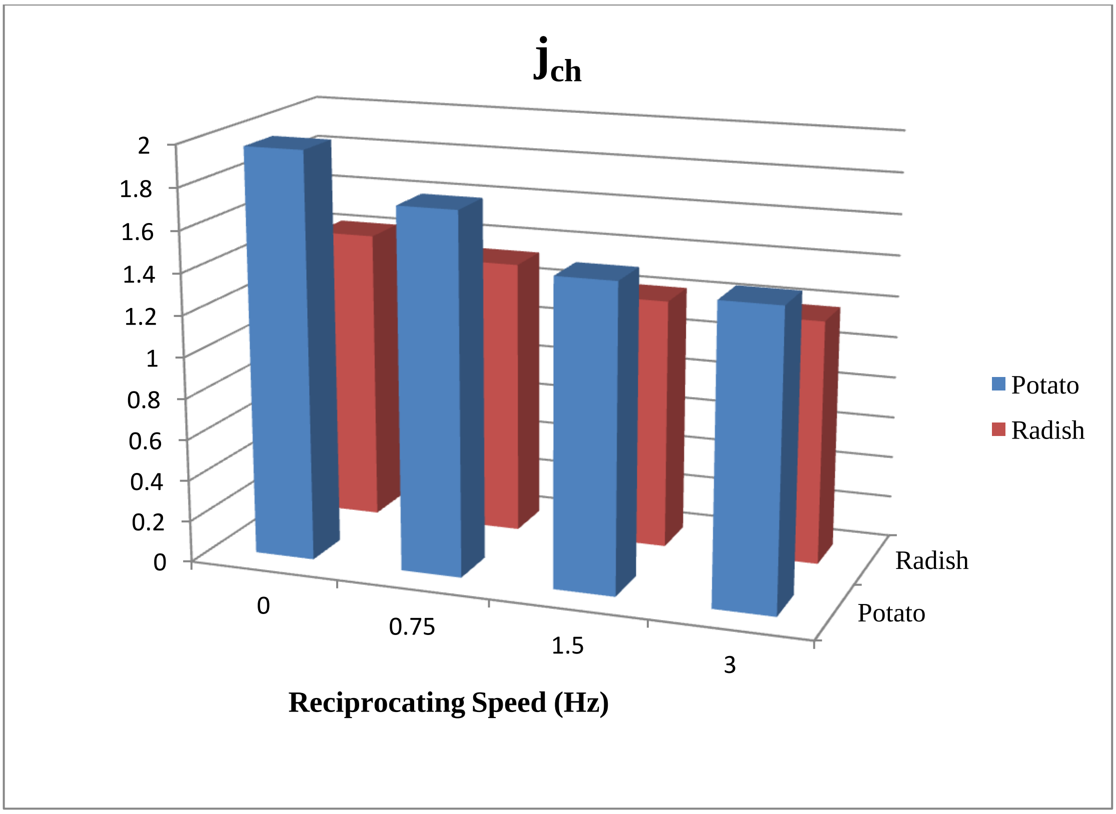


Figure 4.4 The heating lag factors at different modes

Based on the f_h and j_{ch} values obtained from time-temperature profiles, processing times under different experimental conditions could be calculated using Ball formula method and the results are presented in Table 4.1 and Figure 4.5. Processing time is affected by temperature and reciprocating speed. Higher temperature and higher reciprocating speeds result in lower processing times. For potato, the longest processing time was 77 min at 110 ℃ in the still mode, while the lowest processing time was 4.5 min at 130 ℃ and 3 Hz which reduced it by 94% as compared to at 110 ℃ in still mode. In addition, at 130 ℃, processing with agitation at 0.75, 1.5 and 3 Hz resulted in reducing the process time by 43%, 57%, and 68% as compared to the still mode.

For radish, the longest processing time was 84 min at 110 ℃ in still mode, while the shortest was 7 min at 130 ℃ with 3 Hz resulting in 92% lower value as compared to at 110 ℃ still mode. Again at 130 ℃, processing time at 0.75 Hz, 1.5 Hz, and 3 Hz were reduced by 24%, 52%, and 67% as compared to the still mode. Processing time for potato was lower than that of radish since it depends on nature of vegetables and size. Less time was required to achieve a lethality of 5 min at higher temperatures, which was consistent with high temperature short time (HTST) concept in thermal processing. Overall, high temperature and high reciprocating speed has better mixing of particles and high heat transfer rate. It inferred that products heated at 130 ℃ in 3 Hz would have optimal quality due to the least processing time among all conditions. The similar results were found in study by Singh et al. (2015). The processing time was found to decrease from 136 to 11 min with an increase of temperature range from 110 ℃ to 130 ℃.

4.5 Conclusions

In steam heating medium, reciprocation speed has a great impact on heating rate index (f_h) and heating lag factor (j_{ch}) and processing time (Pt). Under high reciprocation speeds, the associated heating rate index was lower, which meant the heat transfer was faster. Values of j_{ch} and processing time were also reduced with the increasing reciprocation speed. High reciprocation speed would have a positive effect on the quality attributes as the processing times were reduced. The optimal quality of products could be expected at 130 ℃ in 3 Hz since it has lowest processing time and fastest heating rate with lowest heating lag for both potato and radish products.

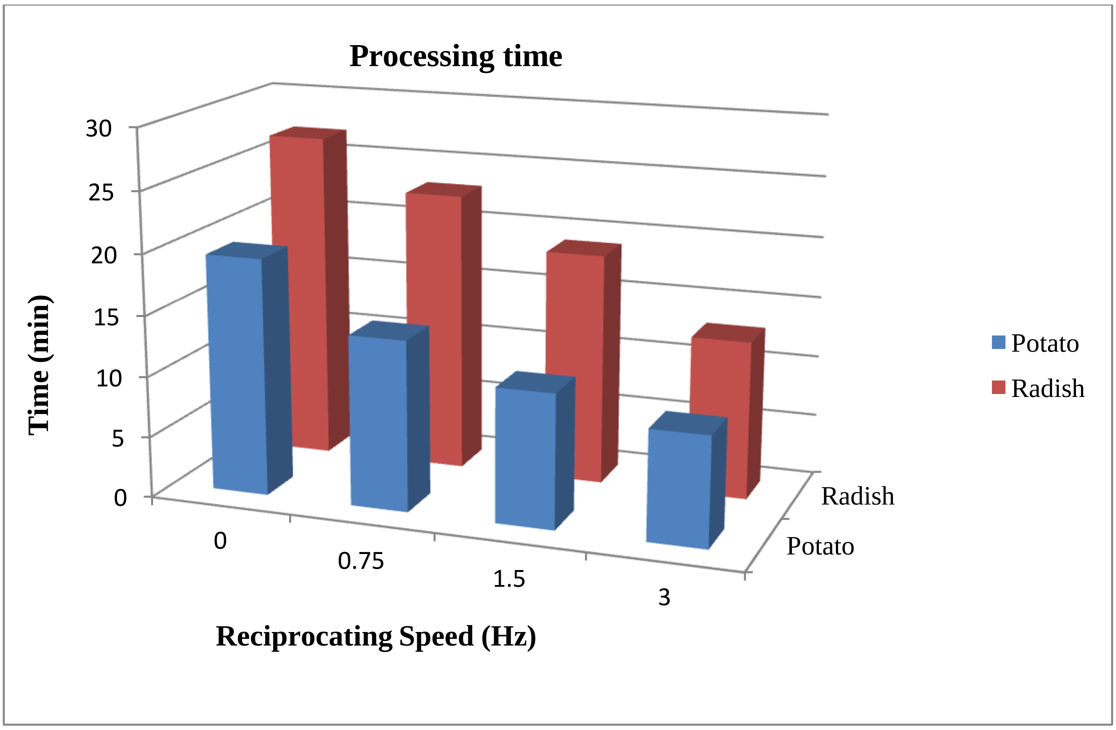


Figure 4.5 The processing time at different modes

Table 4.1 The processing time at different modes

Potato	Speed (Hz)	110 ℃ (min)	120 ℃ (min)	130 ℃ (min)
	0	77	19.5	14
	0.75	72	14	8
	1.5	67	11	6
	3	64	9	4.5
Radish	0	84	27	21
	0.75	79	23	16
	1.5	72	17	10
	3	70	13	7

PREFACE TO CHAPTER 5

The previous chapter was focused on heat penetration parameters associated with potato cubes and radish at various reciprocating frequencies, and establishment of thermal processing conditions for a target lethality of 5.0 min at different reciprocation speeds and retort temperatures. The focus of this chapter was to evaluate the quality retention under these processing conditions and identify the ones that offer better retention of product quality. The product quality parameters tested included the appearance factor (color parameters) and texture attributes (hardness, gumminess and chewiness) as well as retention of antioxidant properties (nutritional).

A part of this research was included in the 2014 presentation in Research Feeding Industry, Montreal, Canada. The experimental work and data analysis were conducted by candidate under the supervision of Dr. H. S. Ramaswamy. A more detailed manuscript is prepared for publication.

YOU, J and Ramaswamy, H. S., 2015. Enhanced retention of quality parameters in canned potato and radish through reciprocating agitation thermal processing (***draft***).

Chapter 5

RECIPROCATION AGITATION THERMAL PROCESSING FOR IMPROVING RETENTION OF QUALITY ATTRIBUTES OF CANNED POTATO AND RADISH

5.1 Abstract

The study was carried out to evaluate the influence of reciprocation agitation thermal processing factors with the purpose of achieving better retention of quality attributes of canned potato and radish. The quality attributes studied were color and texture parameters and antioxidant activity under different processing conditions (retort temperature 110-130 ℃, and agitation speeds (0, 0.75, 1.5, 3 Hz). Potato samples were prepared as cubes of 1.5x1.5x1.5 cm while whole radishes were selected in a uniform size (average radius: 1.5 cm). The samples were filled into 307 x409 size cans with 1% NaCl and 1% $CaCl_2$ as the covering liquid. A pilot scale steam retort modified to accommodate reciprocation agitation was used for processing. The color and texture parameters, and antioxidant activity as well as the integration of solid particles were evaluated for each processing condition. The study indicated a significant influence of process variables on the evaluated quality parameters and provided processing opportunities for better retention of product quality.

5.2 Introduction

Fresh vegetables are perishable since they contain high moisture content. Hence, industries are facing difficulties in their transportation and storage. With the application of heat, fresh vegetables can be processed into canned foods that meet the commercial sterility requirements. Canned vegetable are widely consumed through the world since they are convenience foods and have the stable shelf life at room temperature. A wide range of temperature and time combinations have been applied to process vegetables in order to destroy microorganisms of public health and spoilage concern. However, many quality attributes are also susceptible to heat and would be lost to some extent, including texture, color, antioxidant compounds and vitamins. Therefore, the food industry is seeking efficient methods that impart a rapid and uniform heating treatment and minimize the quality deterioration and destruction of nutrients; however, without compromising on the safety guarantee. Moreover, rapid heating processing can reduce the required processing time by improving heating efficiency, saving energy and also increasing production output (Dwivedi and Ramaswamy, 2010a).

Thermal texture softening occurs during processing. For some vegetables, such as dry peas and beans, texture softening is an advantage of thermal processing that can reduce cooking time and be consumed easily. However, texture changes in most fresh vegetables are undesirable and affect consumer acceptance. Thermal processing of vegetables degrades the pectic substances present in cell wall and inter-lamellar region and results in tissue softening. Texture changes have been studied in many reports (Alvarez et al., 2001; Lau et al., 2000, Rattan and Ramaswamy, 2014).

Color is a primary factor that influences consumers' buying behavior. Heat treatment destroys pigments present in vegetables, such as chlorophyll, xanthophyll, carotenoids, and lycopene. Green vegetables turn bright green to olive brown depending on the severity of heat treatment due the conversion of chlorophyll through a series of reactions (Woolfe, 1979). Color degradation studies have also been conducted by many researchers (Abbatemarco and Ramaswamy, 1994; Nourian and Ramaswamy, 2003b; Rattan and Ramaswamy, 2014; Shin and Bhowmik, 1995).

Antioxidants present in vegetables are, glutathione, ascorbic acid, β-carotene, a-tocopherol, and other flavonoids (Jones et al., 1992; Larson, 1988). Oxidative reactions in the body can lead to the initiation of cancer. The consumption of antioxidant compounds has been implicated in preventing the onset of cancers. Antioxidant compounds are also susceptible to heat, although few studies have showed some beneficial effect of heat treatment (Dewanto et al., 2002; Roy et al., 2007).

Quality changes of canned vegetables in thermal processing have been evaluated in different retort processing situations: static retorts, or end-over-end rotary retorts, or free axial agitation retort. Abbatemarco and Ramaswamy (1994) studied on quality changes in canned potatoes in various agitating modes of rotation. They demonstrated that potatoes processed in free axial had faster heat transfer rate and most effective heating conditions as compared to fixed axial, end-over-end and static thermal processing methods.

A rapid and uniform heating method can strike a balance between the safety requirements (with no compromise) and quality retention. Reciprocating agitation is a novel thermal processing, which can provide rapid and uniform heating condition to increase heat transfer rate and reduce processing time by shaking containers back and forth while they are heat processed. This study was aimed at investigating the evaluation of the influence of different reciprocating agitation processing on quality of canned potato and radish with the purpose of identifying conditions that allow better retention of quality parameters.

5.3 Material and methods

5.3.1 Processing conditions

The processing time for each experimental condition were calculated from the heat transfer studies conducted in Chapter 4 and are detailed in Table 4.1. For both potato and radish, experiments were performed at three temperature (110-130 ℃) and 4 agitation speeds (0, 0.75, 1.5, 3 Hz) in reciprocating agitation retort.

5.3.2 Sample preparation

Potatoes (*Solanum tuberosum*) of Goldrush variety and red globe radishes (*Raphanus sativus L.*) with white flesh were purchased from the local market and then stored at 4 ℃. Potatoes were cut as uniform cubes (15 mm x 15 mm x 15 mm) by sharp knife, and uniform globe radishes were selected in the whole form with an average radius is 15 mm. After blanching samples in 100 ℃ for 1 min to inactive peroxidase enzyme, the prepared potato cubes and radish were filled into 307x409 size cans with a covering liquid of water containing 1% NaCl and 1% $CaCl_2$ by keeping 10 mm headspace. Cans were sealed in the manual double seaming machine (Home Canning Co., Montreal, QC).

5.3.3 Experiments setup

A pilot scale, single cage and vertical static reciprocating retort was used. Retort basket is supported by stainless steel to hold the cans. Basket can hold four 307 X 409 mm cans each time. The magnet motor determined the reciprocating speed by a voltage controller. The speed can be read through a hand-held tachometer and therefore can be adjusted to the required speed. Rotating shaft is moving circularly once, while the reciprocating cage is moving linearly once.

5.3.4 Quality analysis

5.3.4.1 Texture measurement

Cooked samples were subjected to a two-cycle compression test using TA-XT Plus Texture Analyzer (Texture Technologies Corp., Scarsdale, NY/ Stable Micro Systems, Godalming, Surrey, UK) with a 2 kg load cell and a circular aluminum probe. Pre-test, test and post test speeds were 1.0, 1.5 and 1.5 mm/s respectively. Textural parameters, such as hardness, chewiness and gumminess were obtained by using Texture Exponent 32 software (Texture Technologies Corp., Scarsdale, NY/ Stable Micro Systems, Godalming, Surrey, UK)

5.3.4.2 Color measurement

The color characteristics were evaluated by using a Minolta Tristimulus Colorimeter (Minolta Corp., Ramsey, NJ, USA). The color parameters L, a, b and total color difference were obtained by software (SpectraMagic, Minolta Corp., Ramsey, NJ, USA). The total color difference was evaluated using Equation 5.1 given below:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{-1/2} \qquad (5.1)$$

5.3.4.3 Antioxidant measurement of samples

4 g potato and 2 g radish were prepared separately. A sample was ground by using a pestle and mortar, and placed in centrifuge tube with ethanol solution (85% ethanol, 15% methanol v/v) filled up to 30 ml, and then centrifuged for 40 min at 5000 rpm. An aliquot of 0.5 ml of sample ethanolic extract (supernatant) was added to 1 ml of 0.1nM DPPH in ethanol, and the

color formation through DPPH reaction was allowed to proceed for 30 min in the dark. The absorbance was measured by a spectrophotometer at 520 nm. Free radical scavenging activity (FRSA) on DPPH radicals was expressed as percentage (%) from the obtained absorbance for the sample (A_s) and the blank (A_o) using the following equation (5.2)

$$FRSA = \frac{A_0 - A_S}{A_0} \times 100 \qquad (5.2)$$

where,

A_0 is the absorbance at 520nm in absence of sample

A_s is the absorbance at 520nm in presence of sample

5.3.4.4 Weight of solid measurement

After thermal processing, the can liquid was well mixed and then was transferred to 50 ml tube. The solid was separated out by using filter paper and then the weight of solid was be obtained by weighing after drying.

5.4 Results and discussions

5.4.1 The visual appearance of treated potato and radish

The pictures of prepared raw and treated samples are shown in Figures 5.1 and 5.2, for potato and radish, respectively. It is obvious that potato samples treated in 3 Hz at 110 ℃ become totally disintegrated because of the long treatment time and high reciprocating speed resulted in the breakdown of potato particles. At same speed at 130 ℃, there was no disintegration however the influence on particle shape was evident with the cubes turning out more in to somewhat spherical shape. At the other speeds, the particle shape was maintained. Also, the color of potato cubes became much lighter and less yellow in the treated samples as compared to raw and blanched potato when treated at lower temperatures. All 130 ℃ processed samples at speeds 1.5 Hz and lower had light white attractive color, much better than those processed at 110 ℃.

From the pictures of whole globe radishes and the cubes cut from those whole globe radishes, it can clearly seen that radish samples were also totally destroyed and become mushy at the highest reciprocating speed and low temperature combination. The reason was again the mechanical damage to the samples during the high reciprocating agitation going for long duration. As compared to raw radishes, heated radishes lost their original red skin color, and at 3 Hz and 130 ℃ the skin was totally removed. The color of radish cubes prepared from the internal flesh was much lighter at high reciprocating speed and high temperature as compared to raw and radish samples heated at lower temperature in all modes. Radish processed at 130 ℃ and 1.5 Hz had the best light and white color.

5.4.2 Texture changes

Texture of food greatly influences its palatability and is usually modified in order to enhance shelf life of food (Huang and Bourne, 1983). The texture attributes of vegetables changes taking place during thermal processing are therefore considered to be indicator of food quality. Hardness is the one of the most important parameters to verify texture changes and is defined as the maximum force required compressing the food.

Figure 5.1 Potatoes treated in reciprocating agitaion at 110 ℃ and 130 ℃ in different reciprocating speeds

Figure 5.2 Radishes treated in reciprocating agitaion at 110 ℃ and 130 ℃ in different reciprocating speeds

Consumers prefer that textural changes introduced for white fleshed potatoes and radish are minimal. Therefore thermal processing conditions resulting in drastic changes in hardness, gumminess and chewiness values are undesirable. However, the heat damage of texture in thermal processing is unavoidable since degradation of pectin substances and starch gelatinization (Alvarez et al., 2001); Hence, the aim of process improvement is always to minimize texture changes during processing.

Potato

Figure 5.3 shows bar graphs of changes in texture parameters of potato cubes as affected by different processing factors on texture. All three texture parameters were investigated in this study, namely hardness, gumminess and chewiness, were found to be influenced by both processing factors (temperature and reciprocating speed). The results confirmed the expectations discussed in Chapter 4. The retention of the three texture parameters were retained considerably at higher temperatures and reciprocation speeds which required shorter processing times than at lower agitation speed and temperature. The effect of temperature was more pronounced at high reciprocating speed. For instance, for potato cubes processed in 3 Hz at temperatures 130 ℃, the mean hardness, gumminess and chewiness values increased approximately 135%, 141% and 149%, respectively, as compared with processing at 120 ℃; similarly at 1.5 Hz the mean values were found be increased by 33.0%, 77.0% and 91.0%, respectively. The three parameters also showed better texture retention at increased reciprocating speeds. For example, potato cubes processed at 130 ℃, hardness values under reciprocation agitation conditions (3 to 0.75 Hz) were 269%, 66.2% and 11.5% higher as compared to processing under the still mode (0 Hz). Similar trends in gumminess and chewiness values were observed. Overall, the highest of the three values among of all conditions were obtained at 130 ℃ in 3 Hz and this obviously results from the lowest processing time associated due to the turbulence created by the reciprocation agitation. The results are similar to those reported by Abbatemarco and Ramaswamy (1994) who studied the effect of temperature and rotation speed on quality of canned vegetables in end-over-end retort processing, and found that there was better retention of textural values of potato and carrot at higher temperature and firmness was better retained at higher rotation speed.

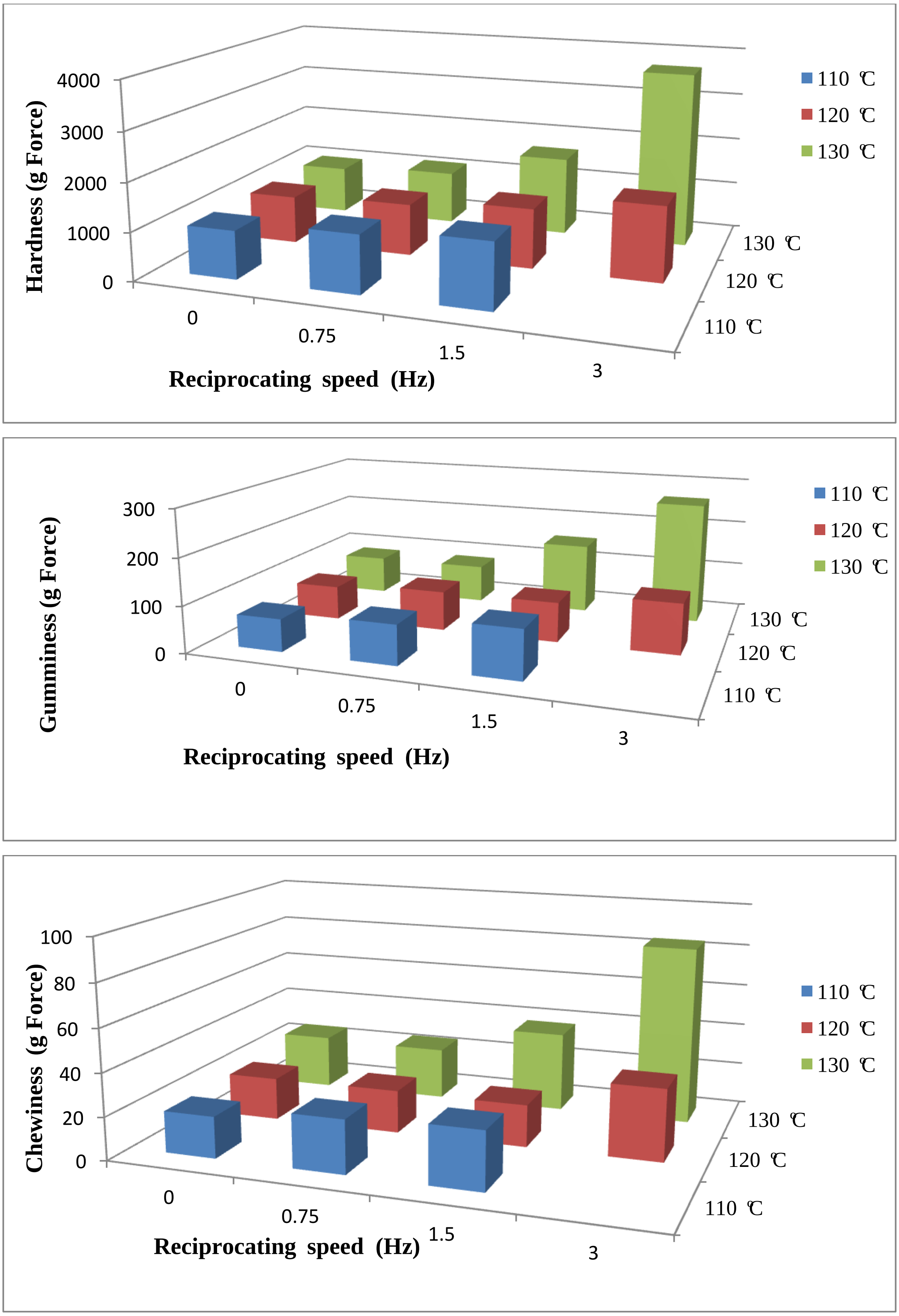


Figure 5.3 Effect of processing factors on Texture of potato cubes

Radish

Figure 5.4 shows bar graphs of changes in texture parameters of radishes as affected by different processing factors on texture. Again, as with potato samples, all three texture parameters were investigated in this study, namely hardness, gumminess and chewiness, were found to be influenced by both processing factors (temperature and reciprocating speed). The retention of the three texture parameters were retained considerably better at higher temperatures and reciprocation speeds which required shorter processing times than at lower agitation speed and temperature. The effect of temperature was also more pronounced at high reciprocating speed. For instance, for cube samples of radish prepared after processing at 3 Hz at temperatures 130 ℃, the mean hardness, gumminess and chewiness values increased approximately 41.2%, 37.3% and 64.1%, respectively, as compared with processing at 120 ℃. There was also better texture retention at increased reciprocating speeds. For example, for radish cubes from 130 ℃, hardness values under reciprocation agitation conditions (3 Hz) was 490% as compared to processing under the still mode (0 Hz). Similar trends in gumminess and chewiness values were also observed. Again, overall, the highest of the three values among of all conditions were obtained at 130 ℃ in 3 Hz which results from the lowest processing time associated because of better mixing.

5.4.3 Color changes

Potato

Figure 5.5 shows that the graphical representation of processing factors on L values and a values of potato cubes. At lower temperature 110 ℃, The L values decreased slightly with reciprocating speed, whereas at higher temperatures (120 ℃ and 130 ℃), L values increased with increasing reciprocating speed. It was in consistent with kinetics of color degradation that L values increased with reduction in cooking time. However, potato cubes at 3 Hz mode did not follow the trend since high reciprocating speed imparted severe surface damage to color. The a values of processed potato cubes were negative and was not highly affected by temperature and reciprocating speed. The b values of potato cubes at 130 ℃ decreased with increasing speed.

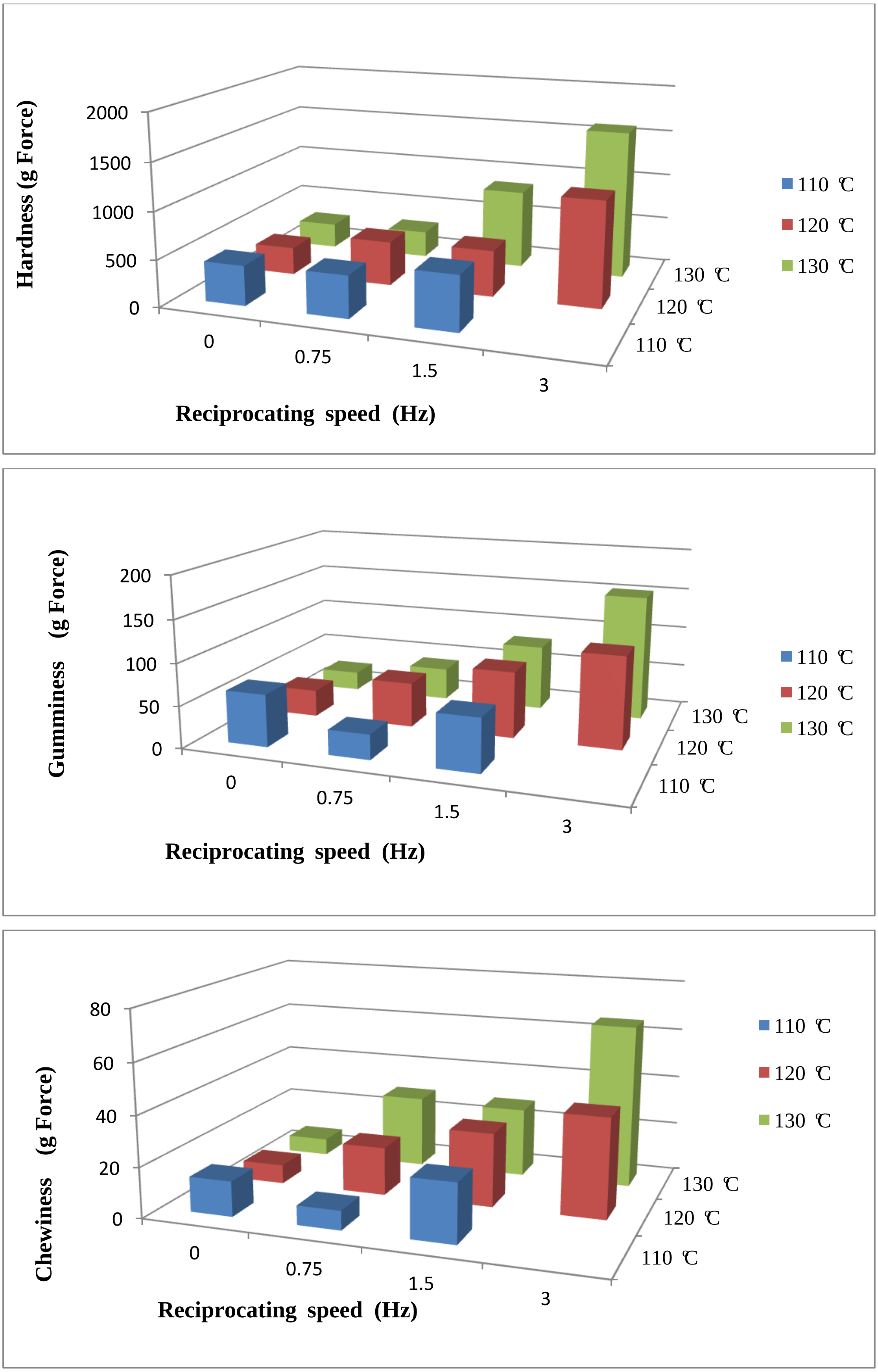
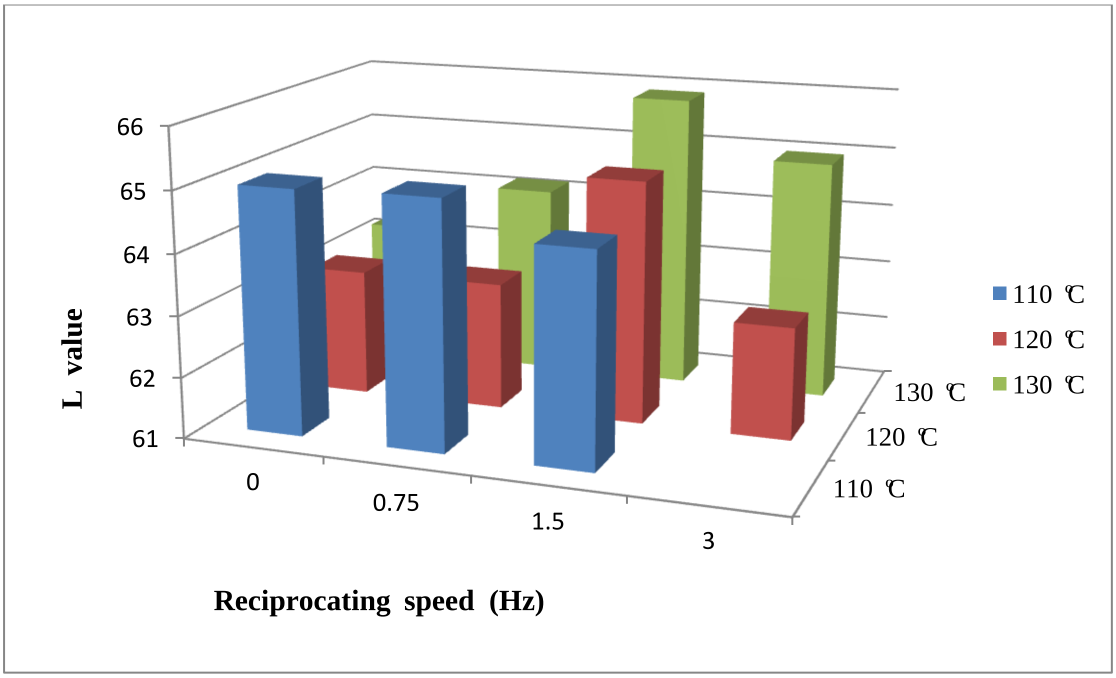


Figure 5.4 Effect of processing factors on texture of radishes



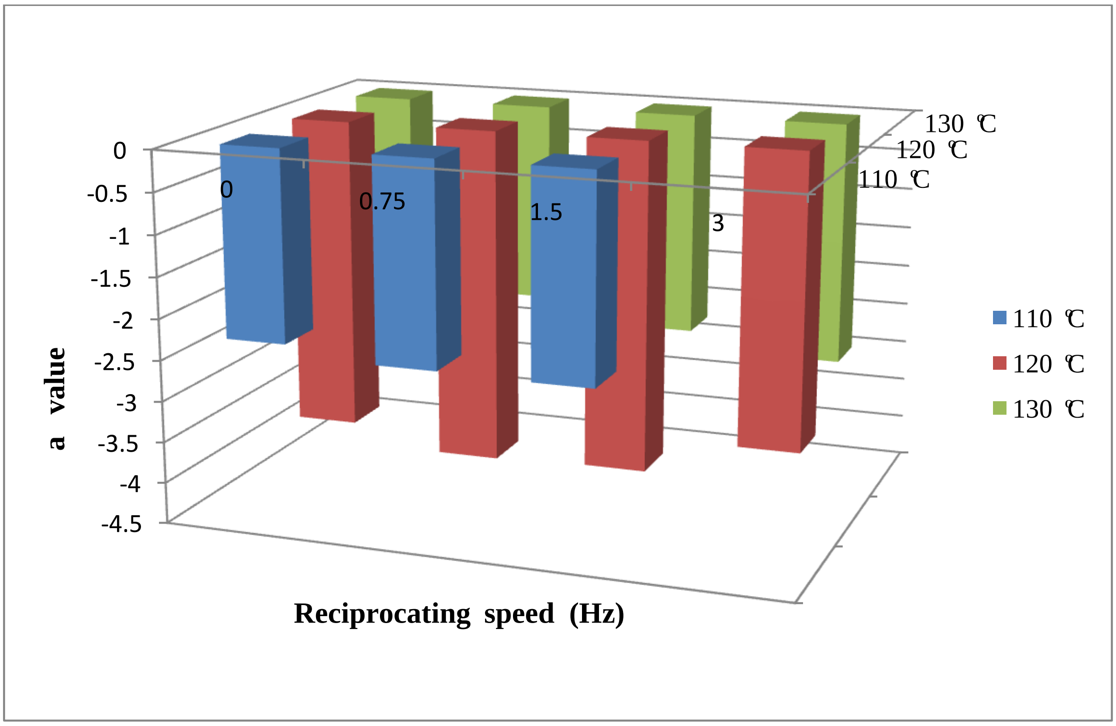
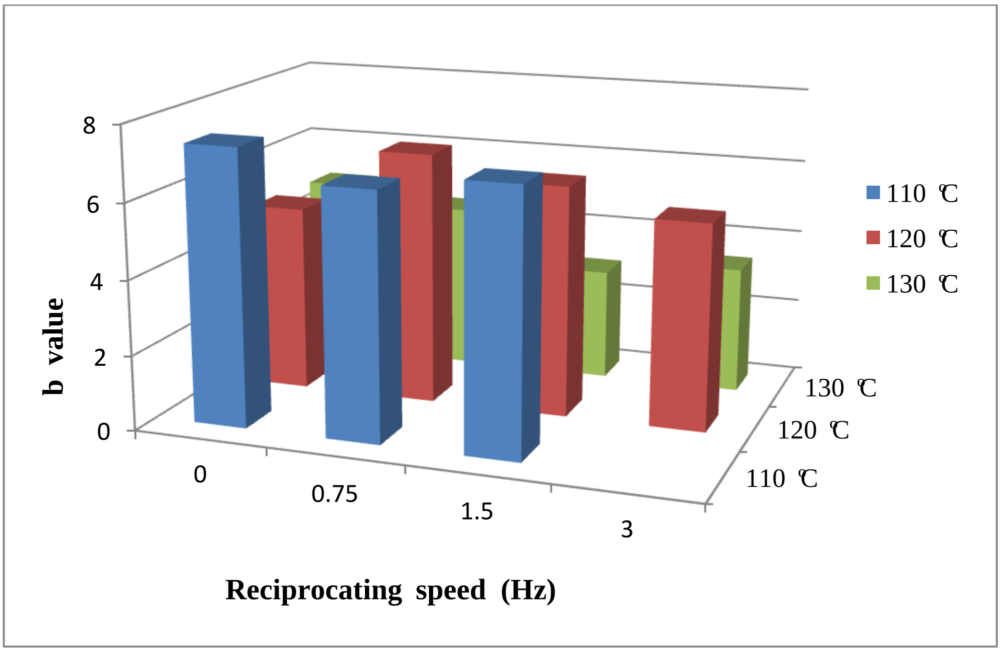


Figure 5.5 Effect of processing factors on L values and a values of potato cubes

Figure 5.6 shows the graphical representation of processing factors on b values and total color changes of potato cubes. The b values of potato cubes processed at 130 ℃ were relatively lower in comparison with samples heated at 110 ℃ and 120 ℃. The lowest b values were samples treated at 130 ℃ in 3 Hz, which was found to be that high temperature affected the yellowness of potato cubes. The total color difference for samples in 110 ℃ was increased with increasing speed, however, total color difference of samples in 120 ℃ were decreased with increasing speed except in 3 Hz mode. Among of the samples, potato cubes treated at 130 ℃ had lowest ΔE.



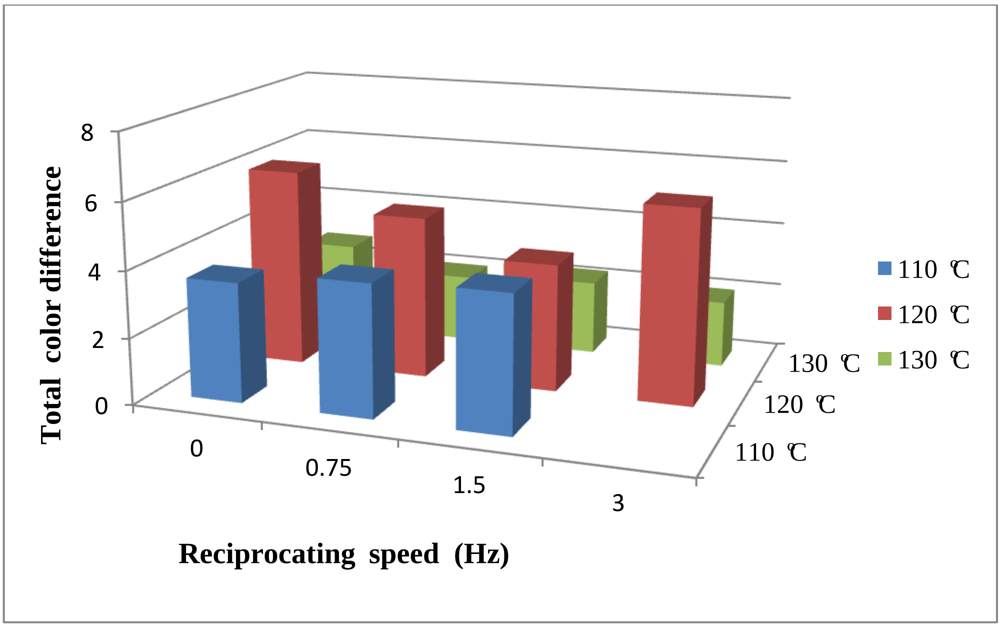


Figure 5.6 Effect of processing factors on b values and total color changes of potato cubes

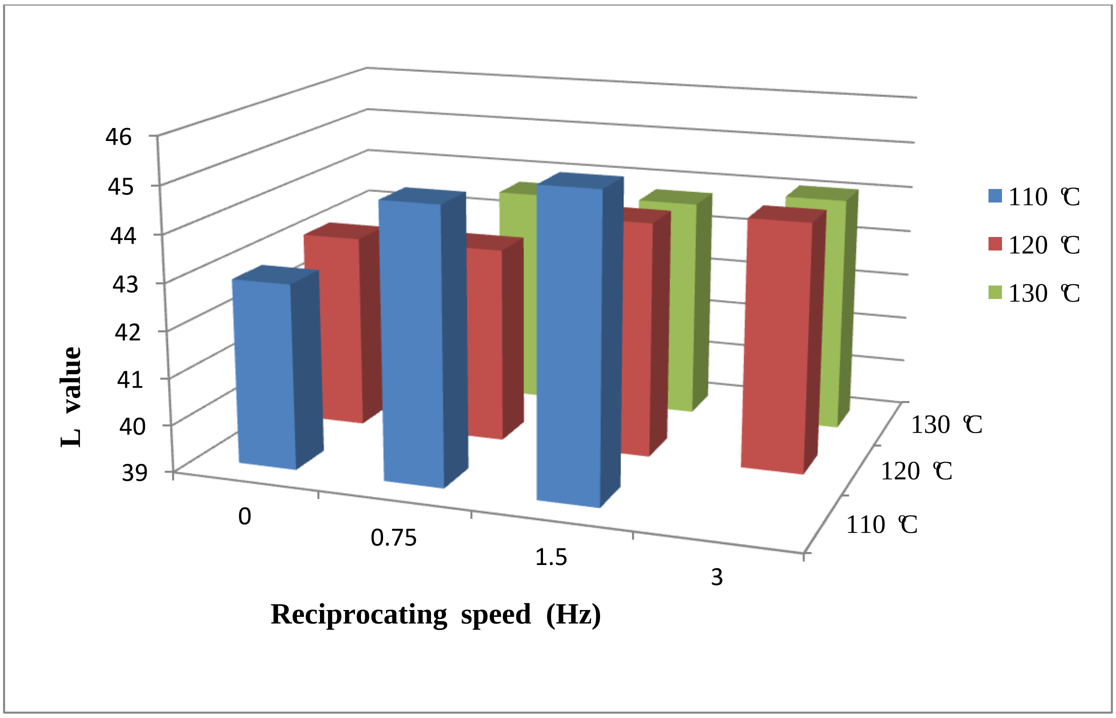
Radish

Figure 5.7 shows that the graphical representation of processing factors on L values and a values of radishes. The L values increased with increasing reciprocating speed for all temperature, which in consistent with results in chapter 3 that less cooking time resulting less L value degradation. The a and b values decreased along with increasing speed from 0 Hz to 1.5 Hz for all temperature. For radishes heated in 3 Hz at 120 ℃ and 130 ℃ did not follow the trend, however, the values were decreased as compared to 0 Hz at corresponding temperature. Figure 5.8 shows that the graphical representation of processing factors on b values and total color changes of radishes. The lowest total color difference was samples treated in 1.5 Hz at 110 ℃. ΔE value of radishes heated in 3 Hz was decreased as compared to 0 Hz, 0.75 Hz and 1.5 Hz at 130 ℃.

5.4.4 Antioxidant activity

Figure 5.9 shows that the graphical representation of processing factors on antioxidant activity of potato cubes. The highest value of antioxidant activity was potato cubes processed at 130 ℃ in 3 Hz. High temperature and high reciprocating speed had better retention of the antioxidant activity of potatoes. Among the different agitation speeds, at 130 ℃, the retention values increased with an increase of reciprocating speed.

Figure 5.10 shows that the graphical representation of processing factors on antioxidant activity of radishes. The similar trends were found in studies of antioxidant activity of radish. Radishes treated at 130 ℃ had relatively higher antioxidant activity than 110 ℃ and 120 ℃ at corresponding reciprocating speed. Again, the highest antioxidant value was radishes processed at 130 ℃ in 3 Hz.



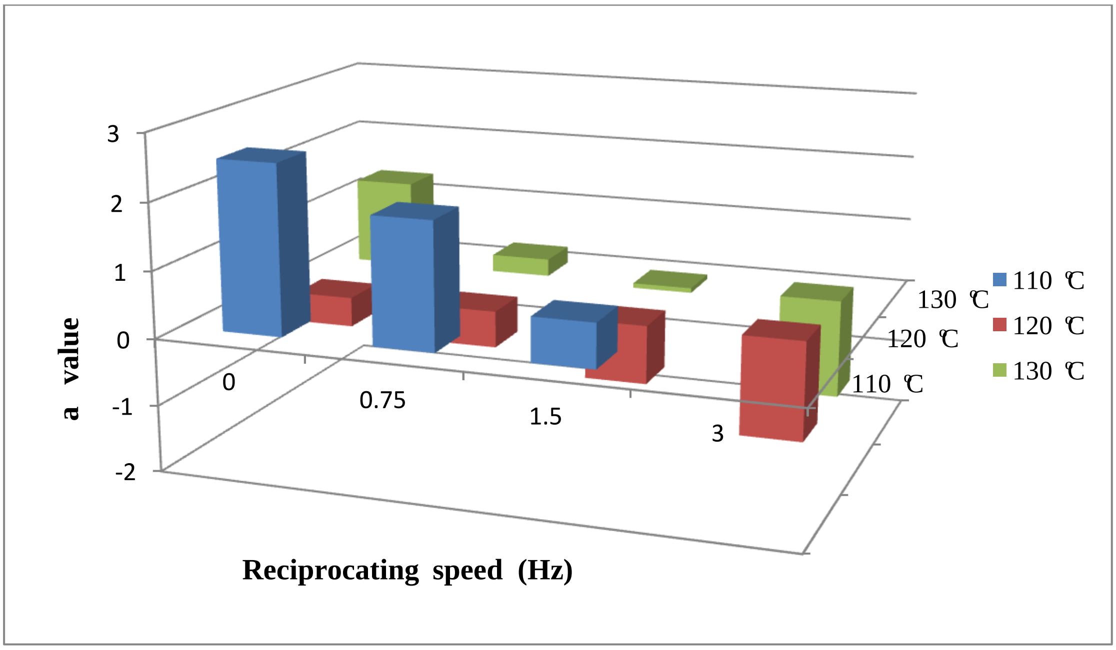
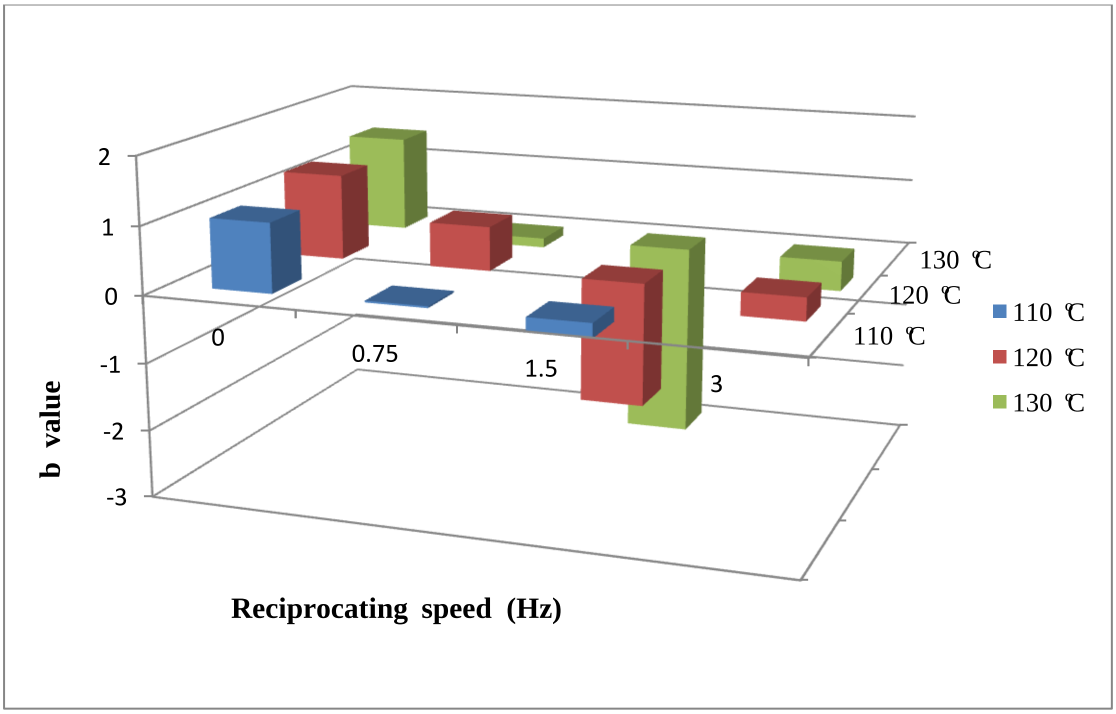


Figure 5.7 Effect of processing factors on L values and a values of radish



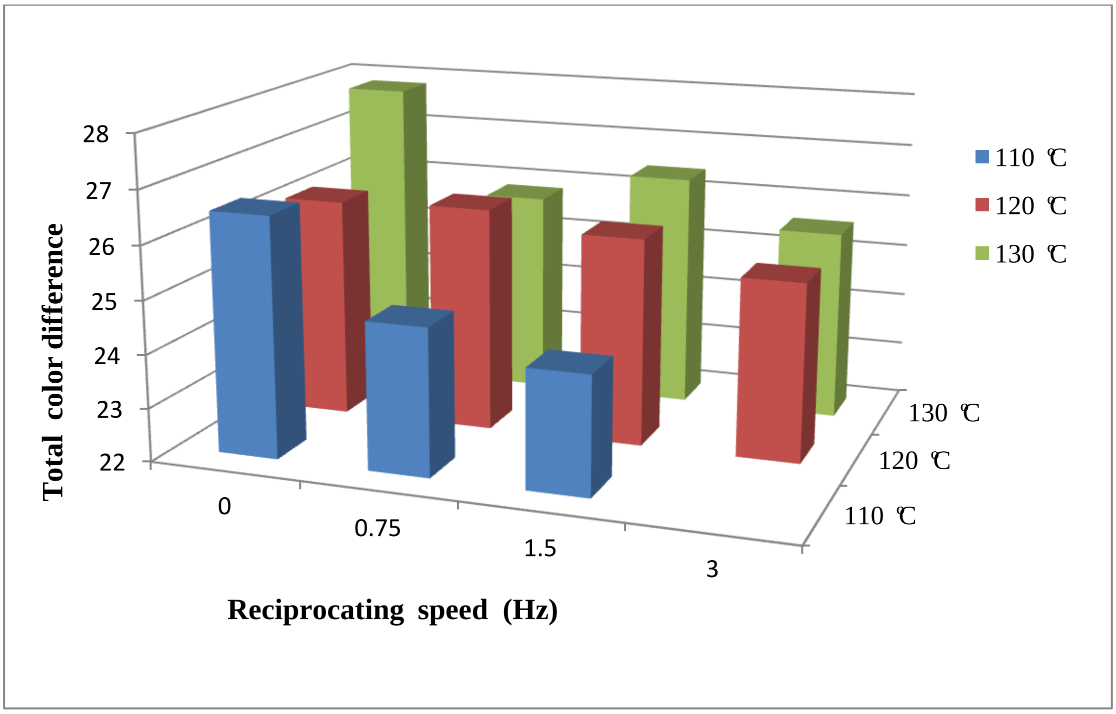


Figure 5.8 Effect of processing factors on b values and total color changes of radishes

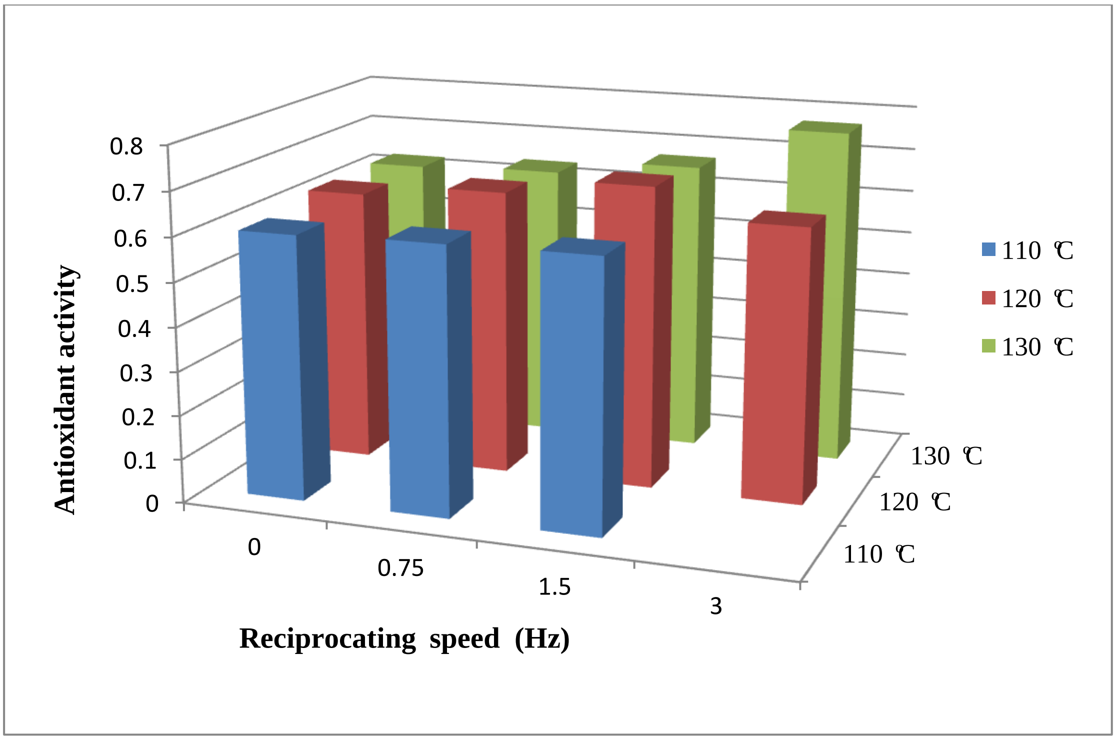


Figure 5.9 Effect of processing factors on antioxidant activity of potato cubes

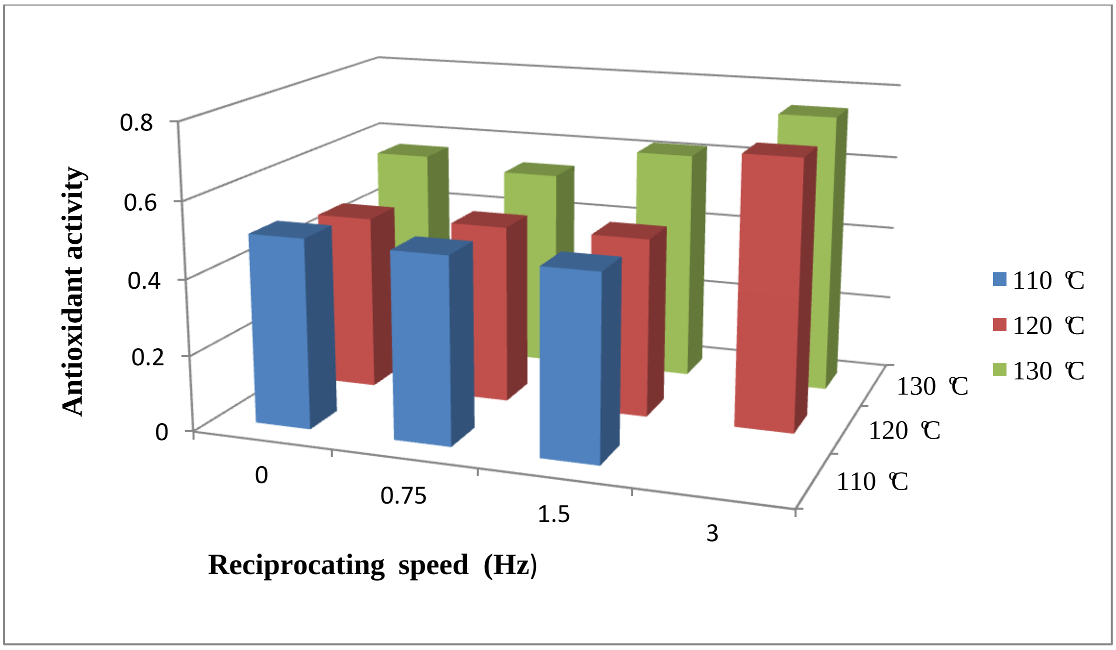


Figure 5.10 Effect of processing factors on antioxidant activity of radishes

5.4.5 The weight of residual solid

Table 5.1 shows that weight of solids leached in to the canned liquid covering potato cubes and radish under different processing conditions. The highest amount of leaching values was found with potato processed at 110 ℃ and 3 Hz since the product suffered significant damage losing the integrity of the particles during the long process time. The samples subjected to 3 Hz reciprocation agitation had highest solids loss at all temperature. The lowest value was found at 130 ℃ and 1.5 Hz, the processing condition that resulted in best quality. At 130 ℃ in 3 Hz, the value was 0.064g, still yielding product that was of acceptable quality.

The solid leaching in canned radishes was lower at 120 ℃ as compared to those radish treated at 110 ℃ and 130 ℃, the specific reason is not clear and it could have been part of experimental variability. The highest loss was also found to be with sample treated at 110 ℃ in 3 Hz and the lowest was with samples heated in 120 ℃ in 0 Hz. The processing at 0 Hz (static mode) presents the least agitated system, with liquid movement resulting from natural convection; hence the leaching was lower, despite resulting in excessive softening. At 130 ℃ in 3 Hz, the value was 0.16 g, and the quality was still acceptable. The pictures of can liquid with residual solid particles of potato and radish after thermal processing at 130 ℃ are presented in Figure 5.11, Figure 5.12 and Figure 5.13.

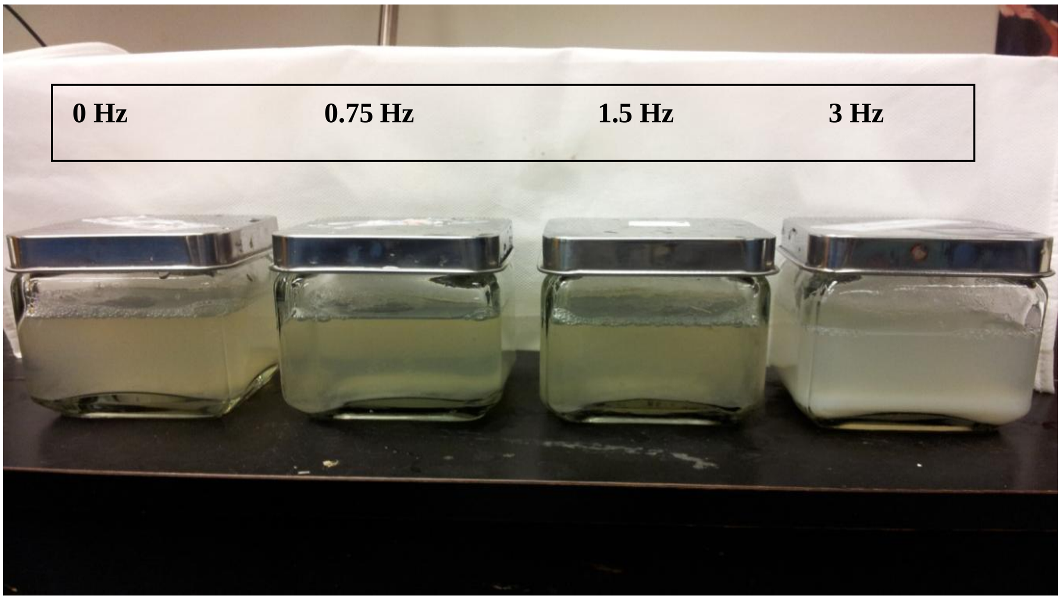


Figure 5.11 The can liquid with leached potato solids after reciprocating agitation processing at 130 ℃ in different modes

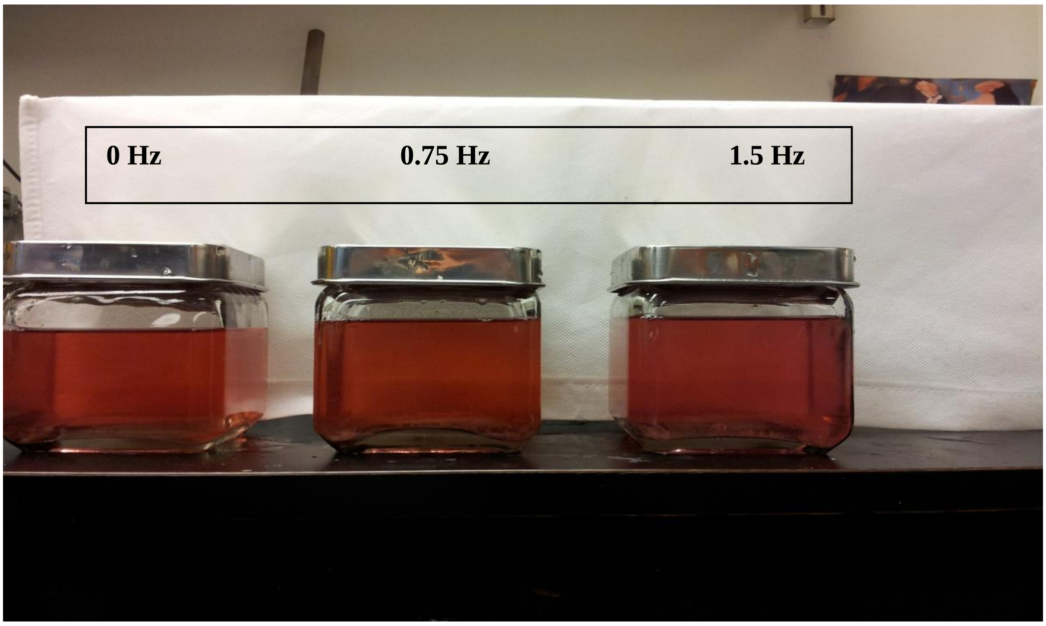


Figure 5.12 The can liquid with leached radish solids after reciprocating agitation processing at 130 ℃ in different modes

Figure 5.13 The can liquid with leached radish solids after reciprocating agitation processing at 130 ℃ in 3 Hz mode

Table 5.1 Weight of solids leached out of vegetable particles

Potato	Speed (Hz)	110 ℃ (g)	120 ℃ (g)	130 ℃ (g)
	0	0.215	0.076	0.095
	0.75	1.86	0.358	0.078
	1.5	0.224	0.156	0.064
	3	12.4	3.58	1.26
Radish	0	0.062	0.018	0.078
	0.75	0.085	0.026	0.093
	1.5	0.216	0.067	0.075
	3	7.25	0.066	0.16

5.5 Conclusions

For potatoes and radish, samples processed at 130 ℃ and 3 Hz can better retain the quality attributes of texture, color, antioxidant activity, and also has relatively lower leaching of solids to the can liquid. Higher temperature and high reciprocating speed shows the positive effect on retention of quality of canned vegetables in reciprocating agitation retort due to faster heat transfer rate and less processing time, which also confirmed the expectation in Chapter 4. Nevertheless, excessive agitation can result in particle breaking, solids leaching and loss in product quality.

6 General conclusion

Thermal processing aims to preserve food for a long shelf life. However, the heat treatment would affect the quality attributes of vegetables like potato and radish.

Kinetics of potato cubes and radish were evaluated at different temperatures by heat treating them in a water bath maintained at selected constant temperatures. The kinetics were modeled by simple pseudo or two simultaneous first order rate model or the modified fractional conversion model. Conventional rate parameters and their temperature dependency were characterized by the decimal reduction time and z value. Textural parameters (hardness, gumminess and chewiness) and L values would decreased and total color difference increase with increasing temperature and heating time. The study indicated that the kinetic rate constants of texture and color values were significantly influenced by temperature. The evaluated kinetic parameters, D and z, are useful in predicting quality loss in these vegetables during thermal processing.

In order to establish processing conditions under reciprocation agitation retort processing, the heating behavior of potato and radish samples were evaluated. For this purpose, potato cubes and radishes were filled into 307 x 409 size cans with a covering liquid of 2% salt solution (1% NaCl and 1% $CaCl_2$). Data obtained from the temperature-time profile were used to compute the heating rate index and lag factors which were found to depend on the reciprocation speed. Higher reciprocation speed resulted in lower heating rate index, which means enhanced heat transfer leading to lowering of process times. Moreover, the lag factor j_{ch} and processing time were reduced with the increasing reciprocation speed due to the better mixing.

Finally, the cans filled with potato and radish samples were processed at different temperatures and reciprocation velocities for the predetermined process times, each designed to give a target lethality of 5 min. Higher reciprocation speeds yielded a positive effect on the retention of quality attributes. Canned potatoes and radishes processed in 3 Hz at 130 ℃ were found to have better quality retention such as texture, color and antioxidant activity with minimal leaching of solids in to the covering liquid. Overall, high temperature and high agitation speed processing leading to short time processing time had the least damage to the quality of canned vegetables in reciprocating agitation retort.

Further studies are suggested to use the kinetic data for predicting the quality loss under the various processing conditions and compare them with experimental values. Also develop procedures for optimizing the processing conditions for maximizing quality retention in potato and radish products using reciprocation agitation thermal processing. Evaluation of the influence of other process variables such as headspace, reciprocation amplitudes, fluid viscosity etc. Detailed sensory and microstructure analysis can be incorporated in the further studies to provide a thorough insight into quality loss during reciprocation agitation thermal processing.

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