EVALUATION OF MAILLARD REACTION-BASED TIME-TEMPERATURE INTEGRATOR FOR THE ASSESSMENT OF THERMAL IMPACT ON QUALITY CHANGES OF THERMALLY PROCESSED FOODS

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by

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LIST OF ABBREVIATIONS / SYMBOLS

Abbreviations / Symbols	**Caption**
BSA	Bovine serum albumin
SPI	Soy protein isolate
AA	L-ascorbic acid
DHAA	L-dehydroascorbic acid
DKGA	2,3-diketogulonic acid
DCIP	2,6–dichlorophenol-indophenol
M-1	2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one
M-2	4-hydroxy-5-methyl-3(2H)-furanone
M-3	5-hydroxymethylfurfura
TTI	Time-temperature integrator
TDT	Thermal death time
t	Time (min)
T	Temperature (°C or K)
T_{ref}	Reference temperature (°C or K)
T_H	Heating temperature (°C or K)
n	Apparent reaction order
k	Rate constant (min^{-1})
k_{ref}	Rate constant at reference temperature (min^{-1})
Ea	Activation energy (kJ/mol)
Ea_{TTI}	Activation energy for TTI (kJ/mol)
Ea_{target}	Activation energy for target attribute (kJ/mol)
z	*z*-value (°C)
z_{TTI}	*z*-value for TTI (°C)
z_{target}	*z*-value for target attribute (°C)
z_c	*z*-value for quality target attribute (°C)

D	Decimal reduction time (min)
D_{ref}	Decimal reduction time at reference temperature (min)
R	Universal gas constant (8.314 J $mol^{-1}K^{-1}$)
C_0	Cooking-value of z_c = 33°C and T_{ref} = 100°C (min)
C_{max}	Maximum cooking-value (min)
F	Processing value (min); indicates the intensity of a thermal process on quality attributes
F_0	Sterility of a process (min); indicates the intensity of a thermal process on safety attributes (microbial load)
F_{target}	Processing value calculated based on the changes in a quality target attribute (min)
F_{TTI}	Processing value read form the changes of TTI response (min)
L	Destruction rate
A	Quality attribute
A_0	Initial state of quality attribute
C_i	Composition factors
E_j	Environmental factors
pH/pH_o	Relative pH changes in TTI
AA/AA_0	AA retention
H/H_0	Relative hardness of potatoes
n	Number of samples
R^2	Coefficient of determination
CV	Coefficient of variation

PENILAIAN INTEGRATOR MASA-SUHU MENGGUNAKAN TINDAK BALAS MAILLARD UNTUK MENGKAJI IMPAK TERMAL TERHADAP PERUBAHAN KUALITI MAKANAN TERPROSES TERMAL

ABSTRAK

Fenomenon kejatuhan nilai pH yang didorong oleh tindak balas Maillard sebagai asas pembinaan integrator masa-suhu (TTI) telah dikajisiasat. Melalui rawatan pada suhu tetap dalam lingkungan suhu 80°C sehingga 100°C, sifat-sifat kinetik TTI telah dikaji untuk kedua-dua sistem Maillard: 3%(w/v)BSA+3%(w/v)Xylose dan 3%(w/v)BSA+5%(w/v)Xylose. Kejatuhan nilai pH didapati mengikut tindak balas tertib pertama dan tenaga pengaktifan (*Ea*) untuk 3%BSA+3%Xylose dan 3%BSA+5%Xylose masing-masing adalah 111.89 kJ/mol dan 93.65 kJ/mol. Seterusnya, TTI ini telah disahkan dalam pemprosesan termal melalui uji kaji hubung-kait dengan penyusutan kualiti makanan seperti kehilangan kualiti secara keseluruhan, penahanan asid askorbik (AA) dan penyusutan kekerasan ubi kentang. Tahap impak termal semasa pemprosesan telah dijangkakan dengan menggunakan TTI yang nilai *Ea*-nya dekat dengan sifat sasaran dan kemudiannya, dibandingkan dengan nilai yang diperoleh daripada eksperimen. Untuk mengurangkan ralat ramalan, graf penentu-ukuran telah digunakan untuk menghubungkaitkan nilai pemprosesan yang dibaca daripada TTI dengan nilai pemprosesan yang berdasarkan profil masa-suhu. Selain itu, hubungkait juga dilakukan antara perubahan nilai relatif pH dengan perubahan nilai sifat sasaran. Kehilangan kualiti secara keseluruhan adalah diwakili oleh nilai-*C* di mana nilai *Ea* adalah 76.17 kJ/mol dan suhu rujukan (T_{ref}) adalah 100°C. Manakala, nilai *Ea* untuk penahanan AA dan penyusutan kekerasan ubi kentang masing-masing adalah 69.05 kJ/mol dan 170.20 kJ/mol. Semua hubung-kait yang dilakukan antara TTI dengan sifat-sifat sasaran menunjuk persetujuan yang baik (R^2 > 0.9). Selain daripada nilai pengukuran TTI yang konsisten dan jitu (CV = 0.49%), TTI ini adalah senang disedia dan mudah diguna. Prestasi dan sifat-sifat TTI ini telah mencadangkan bahawa TTI ini merupakan satu alat yang berkesan dan cekap dalam pengesahan proses termal.

EVALUATION OF MAILLARD REACTION-BASED TIME-TEMPERATURE INTEGRATOR FOR THE ASSESSMENT OF THERMAL IMPACT ON QUALITY CHANGES OF THERMALLY PROCESSED FOODS

ABSTRACT

The Maillard reaction-induced pH decrease as the basis of a time-temperature integrator (TTI) development was investigated. The kinetic behaviours of two Maillard-systems of 3%(w/v)BSA+3%(w/v)Xylose and 3%(w/v)BSA+5%(w/v)Xylose were obtained through isothermal treatments in the range form 80°C to 100°C. The pH decrease followed first-order reaction and the *Ea*-values of 3%BSA+3%Xylose and 3%BSA+5%Xylose were 111.89 kJ/mol and 93.65 kJ/mol, respectively. These TTIs were then validated through correlation studies with respective food quality degradations (overall quality loss, ascorbic acid (AA) retention and hardness degradation in potatoes) during thermal processing. The intensity of thermal impact was predicted with the TTI with closer *Ea*-value with the target attribute and then compared with the obtained experimental values. In order to reduce error in prediction, calibration graphs were used for the correlations between processing values read from TTI with processing values based on time-temperature profiles; and for the mere correlation between relative pH change with the changes of target attributes. The overall quality loss was assigned as *C*-value with the *Ea*-values of 76.17 kJ/mol and T_{ref} = 100°C. The *Ea*-values for AA retention and hardness degradation in potatoes were 69.05 kJ/mol and 170.20 kJ/mol, respectively. All the correlations showed good agreements (R^2 > 0.9) between TTI and target attributes. The good performances of these TTIs with high reproducibility of measurements (CV = 0.49%) as well as its ease of preparation and use; suggest that the Maillard-based TTIs can be a very promising tool for thermal process validation.

CHAPTER 1
INTRODUCTION

1.1 Background

Over the years, thermal processing persists as the most widely used method of preserving and extending the useful shelf-life of foods. In addition, it has gained a vibrant market place relying on the impressive record of food safety. Traditionally, the heating process is set to achieve specific lethality to ensure that the target food-borne pathogen has been destroyed to an acceptable level. On the contrary, this has led to a common practice where foods are over-processed and hence brought detrimental effects on product quality by altering the nutritional as well as the organoleptic properties.

Nowadays, the demand for processed foods goes beyond the basic requirements, despite safety and shelf life-stability, consumers now expect varieties of value-added foods with higher quality and more convenient end use (Awuah *et al.*, 2006). On the other hand, in conjunction with the globalization of food trade, the national or international legislatures recommend and/or enforce performance standards or methods for achieving safety and quality assurance through the scientific rationale (Awuah *et al.*, 2006). This phenomenon can be observed through the evolving shift from a command-and-control paradigm, which relies on the scheduled process where the specific endpoint temperature is held for predetermined time intervals; to lethality performance standards, where newly developed or altered thermal processes must be validated by "scientific supportable means" (Marks, 2001).

Besides, the introduction of new thermal technologies in the industry requires regulatory approval. From this point of view, a scientific basis to assess quantitatively the impact of thermal process is indispensable (Claeys *et al.*, 2003). It is of key importance for food companies to measure accurately the impact of heat processes in terms of food safety and quality. Failing to accurately verify a process increases legal liability (Awuah *et al.*, 2006).

Unfortunately, the current state-of-knowledge is insufficient for reliable lethality predictions in commercial processes. Therefore, 'scientifically supportable means' do not currently exist for reliable and robust predictions of thermal process lethality in food industry. The continued development of new products and processes (and the ongoing regulatory changes) necessitate a proactive stance in ensuring proper evaluation of thermal process lethality (Marks, 2001).

This has inspired researchers and the food industry to explore alternative methods as replacement for the traditional processing methods. The food industry is poised to adopt new concepts and technologies that offer competitive advantages over the conventional systems. Each of these alternatives has to be challenged in terms of microbiological capabilities, safety, efficiency and overall quality for acceptance as a mainstream technology (Awuah *et al.*, 2006).

For the time being, there are two well-documented techniques which have long been used in the industry to evaluate thermal impact on food safety and quality. They are: (1) the *in-situ* method, which measures a selected target attribute of the food before and after the process; and (2) the physical-mathematical method, which thermal impact is calculated based on the interpretation of time-temperature history of the product combined with the knowledge of priori determined kinetic parameters for the selected target attribute (VanLoey *et al.*, 1996a, VanLoey *et al.*, 1999).

Nevertheless, these two methods have serious limitations with regard to modern heating processes. For the former method, it is too laborious, time- and cost-consuming. As for the latter, under certain circumstances it is impractical to incorporate a temperature logger to register the time-temperature history of the product. Limitations of both methods have promoted the development of time-temperature integrators (TTIs) as alternative tool in process design to measure the thermal impact of heat processes in terms of food safety and quality (VanLoey *et al.*, 1996a, VanLoey *et al.*, 1996b, Stoforos and Taoukis, 1998, VanLoey *et al.*, 1999).

The use of TTI involves the measurement of a response status before and after processing. The TTI response refers to a change in the concentration of a heat sensitive substance or device, either present in the product itself or introduced into the food samples, as to mimic the thermal degradation of the target attribute of interest. The TTI response should be an easily measurable, irreversible and time-temperature dependent change that can be attributed to a biological, chemical or physical phenomenon (Stoforos and Taoukis, 1998). The major advantage of TTI is the ability to quantify the impact of time-temperature exposure on the target attribute without having the information on the actual time-temperature history of the product (VanLoey *et al.*, 1996a).

During the last decade, the development of TTIs has received considerable attentions. The application of TTI in thermal process validation has been investigated intensively by Katholike Universiteit Leuvan, Belgium (Hendrickx *et al.*, 1993, VanLoey *et al.*, 1996a, VanLoey *et al.*, 1997, Haentjens *et al.*, 1998, VanLoey *et al.*, 1998, VanLoey *et al.*, 1999, Guiavarc'h *et al.*, 2003) and Campden & Chorleywood Food Research Association Group (CCFRA) (Tucker *et al.*, 2002, Tucker *et al.*, 2006a, Tucker *et al.*, 2006b). All the mentioned projects involve the use of enzyme, particularly α-amylase, in the developing of TTIs for thermal process evaluation. However, it requires lots of effort in the enzyme extraction and TTI fabrication in order to match with the processing conditions as well as the kinetic behaviours of the target attributes. Moreover, the heat sensitivity of enzyme is rather low, which makes the development of enzymatic TTI a much complicated work.

In this study, Maillard reaction was proposed as the basis of developing a new TTI for thermal process evaluation. This was based on the notion by the US Army Natick Soldier Center, where Maillard reaction products have been developed as intrinsic chemical markers in food during thermal process (Lau *et al.*, 2003, Wong *et al.*, 2004). In general, three chemical markers were recognized. The first marker is 2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one (**M-1**), which is formed at sterilization temperatures from D-glucose and amines through 2,3-enolization under weak acidic or neutral conditions. The second marker is 4-hydroxy-5-methyl-3(2H)-furanone (**M-2**) that is similarly formed from D-ribose or D-ribose-5-phosphate. Another thermally produced compound is 5-hydroxymethylfurfural (**M-3**). The formation of these markers is directly proportional to the heating time at a given temperature; hence they are suitable as TTI in estimating the extent of thermal process. However, the application of this approach is limited to high temperature treatments (110 – 130°C) because the chemical markers form rather slowly under 100°C (Wnorowski and Yaylayan, 2002, Eliot-Godereaux *et al.*, 2003, Lau *et al.*, 2003, Wong *et al.*, 2004).

Despite of the chemical marker formation, there are several physical changes that occur along with the Maillard reaction; for instance, brown colour formation, pH decrease and changes in rheological properties (Easa *et al.*, 1996b, Manzocco and Maltini, 1999, Gerrard *et al.*, 2002, Delgado-Andrare *et al.*, 2004). Regardless of the mentioned situation for chemical marker formation, in this study, Maillard reaction-induced pH decrease was used to monitor food quality changes during thermal process at temperature ranging from 80 to 100°C. This was to reveal another site of TTI application since most of the TTI responses were often related to microbiological quality (VanLoey *et al.*, 1997, VanLoey *et al.*, 1999, Tucker *et al.*, 2002). With quality loss being a function of time–temperature history and with TTI giving the measure of that history, TTI response could presumably be correlated to quality level of the food model systems. Moreover, the analytical approach used for chemical markers formation was complicated and required specific equipments (i.e. HPLC), whereas only pH meter was needed in this study.

1.2 Rationales of this study

Thermal processing is one of the utmost important processes in producing safe and high quality food products. However, without the application of an appropriate evaluation method, the meaning of safe and high quality food product is totally obscure.

The purpose of this study was to evaluate the possibility of Maillard reaction-induced pH decrease as a potential TTI response. One further aim was the estimation of kinetic parameters for TTI response as well as the target attributes. Finally, the potential of Maillard-based TTI as thermal process evaluation tool was determined.

By introducing a Maillard-based TTI in food thermal processing, the problem of lacking suitable validation method will be solved and this is important to control the quality management of thermal processing especially for Small-Medium Industries (SMIs) in food processing, which lack of financial support and technical knowledge.

Furthermore, the scientific knowledge generated through this study will contribute to the development of a new thermal process validation tool for the food industry. With the development of new and better controlled validation tools, it will permit production of safe products with higher quality.

1.3 Hypotheses and research questions

Some Maillard systems have been used as TTIs for the assessment of efficacy of food thermal processing. However, there is no study that reveals the application of Maillard reaction-induced pH decrease as the response status of a TTI. Most of the studied Maillard-based TTIs relied on the formation of by-products as chemical markers to indicate the extent of a thermal process. On the other hand, Maillard reaction-induced pH decrease has been well established, thus it was hypothesized that Maillard reaction-induced pH decrease could be applied to the development of a rapid and inexpensive tool for monitoring thermal impact on food quality changes during thermal processing. In conducting this study, another specific hypothesis was tested, that was the kinetic parameters for a response function of TTI could be manipulated in order to suit the kinetic behaviour of the selected target attribute from food model system.

This study addressed a number of issues in relation to the implementation of the Maillard-based TTI in food thermal processing. Specific questions addressed in this study include:

1. Whether the Maillard reaction fits the basic criteria as a TTI for thermal process validation?

2. Whether the kinetic parameters of the Maillard-TTIs match with those of target attributes?

3. How accurate/reliable is this Maillard-based TTI in estimating the thermal impact on food quality?

4. What are the potential applications of Maillard-based TTI in thermal processing?

Lastly, the advantages and disadvantages of the Maillard-based TTI were highlighted.

1.4 Objectives

The main objective of this study was to develop a Maillard-based time-temperature integrator (TTI) for the assessment of thermal impact on quality changes of thermally processed foods. This TTI was further validated to predict the changes on quality characteristics of foods, i.e. nutritional properties and textural attributes.

The measurable objectives of this study were:

- to study the feasibility of Maillard reaction-induced pH decrease as the basis of TTI development in terms of theoretical considerations and kinetic behaviours

- to estimate the thermal kinetic parameters under isothermal conditions for TTI response as well as the selected target attributes in food model systems

- to construct prediction graphs or equations that correlate thermal inactivation of the TTI with the thermal inactivation of target attributes

- to evaluate the performance and the reliability of TTI in predicting the changes on target attributes of food model systems

1.5 Dissertation outline

The evaluation of the Maillard reaction as time-temperature integrators (TTI) for the assessment on food quality changes is presented in this dissertation. The main body of this dissertation consists of a general introduction and background, literature reviews, material and methods, results and discussions, general conclusions as well as recommendations for future studies.

Chapter *One* is a general introduction on the background of this study in which the current situations and the challenges faced by the food industry regarding thermal process validation techniques are discussed. It also presents the proposed method (by using Maillard-based TTI) to overcome the limitations with detailed background that supports the application of TTI in thermal processing. Besides, the purpose and the rationales of this study are discussed briefly. Finally, the hypotheses and objectives of the study are stated together with a series of research questions.

The first stage of this study deals with the identification of the basic requirements and theoretical considerations in developing a TTI for thermal process validation and the kinetic modelling of food quality during thermal processing. The general literature review of each topic is illustrated in Chapter *Two*.

Chapter *Three* lists down all the used materials as well as the methodology for every single assay conducted throughout the whole study.

In Chapter *Four*, the experimental results with discussions are presented. Before the experimental results are analyzed, the theoretical considerations on characteristics of Maillard reaction-induced pH decrease which fulfill the basic criteria of a TTI are interpreted. Basically, the experimental results are divided into three sub-sections: (1) preliminary studies on the Maillard reaction, (2) the development of

Maillard-based TTI; and (3) the applications of TTIs in monitoring the quality attributes. Each subsection describes and summarizes the results and statistical analyses used to evaluate the proposed research questions and hypotheses established in Chapter One. At the end of this chapter, the advantages and limitations of this Maillard-based TTI will be reviewed. In addition, the potential use of this Maillard-based TTI at elevated temperatures (> 100°C) will be identified.

The last chapter (Chapter *Five*) consists of general conclusions on the whole study, limitations of this study and recommendations for future studies of the Maillard-based TTI in the aspect of food safety and other processing conditions.

CHAPTER 2
LITERATURE REVIEW

2.1 Food thermal processing

2.1.1 Introduction

Since around 70 000 years ago, heat has been used to prepare foods. Down the millennia, food revolution occurred through the development of cooking methods with increasing scientific knowledge, whereby nowadays thermal treatment has become the most widely used method in food processing and preservation. Although numerous novel technologies (e.g. irradiation, ultra high pressure, and pulsed electric fields) loom on the horizon for the broader food industry, the application of heat certainly continue to be the dominant means to impart desirable characteristics, add economic value and ensure product safety. Additionally, major shifts in consumer demand and regulatory burden certainly increase the importance of thermal treatment in the field of food processing (Hardy *et al.*, 1999, Marks, 2001, Stoforos, 2005).

The methods and the extent of heat treatment vary upon the specific objectives as well as the nature of the food products. One of the main purposes of thermal processing is to improve the attractiveness, digestibility as well as eating properties of food products. Thermal treatments which have been applied for this purpose are like cooking, baking, roasting, boiling, frying and stewing. Whereas, blanching, pasteurization and sterilization are meant for preserving purposes in order to ensure the product safety and prolong the storage-life. In this case, heat treatment can either be used as the single preserving technique such as commercial sterilization or it can be used in conjunction with other preserving factors or processes. For instance, blanching and pasteurization are normally applied prior the further processing or refrigerated storage (Stoforos, 2005).

2.1.2 Effects of heat on food quality

Heat imposes both desirable and undesirable changes in foods. Although heat is essential to stabilize foods, the heating conditions applied are beyond the level of retaining the desired food quality. Moreover, under certain circumstances, the formation of mutagenic and carcinogenic compounds may even occur and consequently poses public health issues (Hardy *et al.*, 1999, Stoforos, 2005).

The major drawback of thermal processing is the significant destruction on nutritional quality such as the loss of vitamins; and organoleptic quality such as the changes of taste, colour and texture of food products. This is because thermal treatment induces or even accelerates several biological, chemical and physical modifications that eventually lead to these destructions. Therefore, the processing conditions that give the maximization of the final nutritional and organoleptic quality are needed (Silva, 1996, Teixeira and Tucker, 1997, Hardy *et al.*, 1999, Eliot-Godereaux *et al.*, 2003).

In most situations, thermal processing results in changes that lead to food quality losses. These changes are mainly due to biological, chemical and physical reactions, which proceed at certain rates and with certain kinetics. In order to evaluate and monitor the thermal impact on food quality, it is required to reveal the kinetics of these changes. Obviously, kinetic modelling is a powerful tool in relation to food processing and quality control. It can describe the changes and their rates quantitatively, which is vital for quality modelling and control. Thus, kinetic modelling is gaining increasing interest and scientists attempt to derive basic kinetic information for a system in order to predict changes in a particular food during processing and storage (VanBoekel, 1996, Martins *et al.*, 2001, VanBoekel and Tijskens, 2001).

2.1.3 Food quality attributes

To predict food quality deterioration, the knowledge on kinetics for the quality degradation is required. The kinetic of quality degradation has been studied extensively in model systems (Appendix D). Nevertheless, data available for the quality losses (ascorbic acid destruction, texture softening, etc.) in actual food systems are insufficient to calculate the kinetic parameters during heat treatment. Hence, it is necessary to study the effect of different processing temperatures on the retention of quality in the product and then the kinetic modelling is applied to predict the losses during processing (Vikram *et al.*, 2005).

2.1.3.1 Overall quality loss

During a thermal process, some quality degradations occur along with the achievement of process sterilization values (F_0 -value). This relative thermal impact on food quality can be quantified by using the concept of "cook value" (C-value). Specifically, cook value is related to the quality loss during a high temperature thermal process to an equivalent cooking process at 100°C (stove temperature) and assigned as C_0 (Lund, 1986). This is a standard nomenclature that originated by Manfield (1962) and it has been used as an overall index of quality degradation. The calculation of C-value is similar with the calculation of F-value and the equation as expressed in Eq. 2.1:

$$C_0 = \int_0^t 10^{T-100/z_c}\, dt \qquad \text{Eq. 2.1}$$

where z_c is the thermal destruction rate analogous to the z-value for microbial inactivation.

This value characterizes the product cooking degree and enables the comparison of the quality changes caused by the thermal degradation for a given product at certain levels of heat treatment. The method comes from the presupposition that the considered quality changes occur according to the first order reaction kinetics (Mraz, 2001). It appears that the dependence of quality degradation rate on temperature can be expressed in the same way as for microorganisms and enzymes – by using the Arrhenius model or Bigelow model.

The cook value parameters z_c and T_{ref} vary according to the target attribute of interest. According to Holdsworth (1997), the value of *z* for quality degradation varies between 17 to 45°C, corresponds to sensory attributes, texture softening and colour changes in food (Holdsworth, 1997). Generally, z_c-value equals 33˚C (or *Ea* of 76.17 kJ/mol for temperature range from 80 – 100°C) is mostly used as an overall quality loss from the approximation for chemical changes based on the deterioration of chemical components such as thiamine, vitamin C and chlorophyll (Mraz, 2001, Lau and Tang, 2002). The higher the z_c (lower the *Ea*-value), the more resistant is the given food component against the influence of thermal energy. In fact, very few experimental measurements of *C*- and z_c- values for different foods have been reported in the literature. Minimum *C*-value is determined on the basis of *z*-value for the selected components (Mraz, 2001). A maximum range in the region of 100 – 200 min is commonly considered as the range beyond which quality is said to be impaired (Awuah *et al.*, 2006).

On the other hand, optimization of a thermal process is based on the fact that the rate of destruction of nutrients is less dependent on the temperature than the rate of destruction of microbial spores. It is often desirable to assume an acceptable sterility (F_0-value) and a maximum cook value, both of which give the desired product. A safe product will then require that the actual lethality will exceed sterility while the cook value will be less than C_{max} (Awuah *et al.*, 2006).

2.1.3.2 Ascorbic acid degradation

Ascorbic acid (vitamin C) is a water-soluble vitamin that plays such a vital role in our health and well being. Despite its nutritional value, ascorbic acid has been widely used in food industry for its many functional contributions to product quality. Based upon its oxidation-reduction properties, ascorbic acid is used as nutritional food additives, antioxidant, browning inhibitor, reducing agent, flavour and colour stabilizer, dough modifier as well as food enhancer (Etenmiller and Landen, 1999).

During processing of foods, the loss of nutritional quality has become a big concern. Since ascorbic acid is known to be thermo-liable, its retention is often regarded as a significant index of nutritional quality of a product. Particularly in fruit and vegetable canning industry, products have been fortified with ascorbic acid as to restore the nutritional loss during thermal process. Simultaneously, the loss of ascorbic acid can also be used as an indicator of the loss of other nutrients and organoleptic properties after thermal processes (Abdelmageed *et al.*, 1995, Esteve *et al.*, 1998, Karhan *et al.*, 2004, Erenturk *et al.*, 2005).

However the available analytical methods often show certain limitations that affect the accuracy of determination such as being time-consuming, easily interfered by colouring substances and lack of specificity or good sensitivity. On the other hand, lack of information about the mechanism and degradation kinetics of ascorbic acid causes the determination even more complicated (Vikram *et al.*, 2005). Therefore, there has been considerable interest in alternative methods for determining ascorbic acid content in food products (Abdelmageed *et al.*, 1995, Zeng *et al.*, 2005).

In this study, the direct colorimetric method was used instead of the classic titration method and HPLC methods for the titration method is time-consuming and the endpoint determination is very subjective (Abdelmageed *et al.*, 1995, Zeng *et al.*, 2005).

On the other hand, the implementation of HPLC methods requires specialized equipment and the procedures may be rather lengthy although they have good sensitivity and specificity (Zeng *et al.*, 2005).

2.1.3.3 Texture of potato

Texture is one of the most important quality parameters, which is crucial to ensure the product acceptability. According to Nisha *et al.* (2005), texture can be defined as “the way which the structural components of a food are arranged in a micro- and macro-structure and the external manifestations of this structure” (Nisha *et al.*, 2005).

In raw produce, the present of physiological processes maintains cell turgor pressure, which imparts textural characteristics to fruits and vegetables. As a consequence of thermal processing, the hydrostatic pressure responsible for maintaining turgor is absent in processed plant tissues and usually they are softer than the original raw produce. After the loss of turgor brought by heating, the remaining mechanical properties of the tissues depend on the structure, arrangement and chemical composition of the cell wall (Corzo and Ramirez, 2005).

On the other hand, during thermal process a variety of enzymatic and chemical reactions occur and hence alter the texture in processed fruits and vegetables. The chemical changes such as solubilization and depolymerization of pectic polysaccharides, affect the constituents of the cell wall and middle lamella, and hence bring a major change in the firmness of fruits and vegetables (Nisha *et al.*, 2005, Smout *et al.*, 2005).

In this study, potato had been chosen as a model system which represents the changes in texture due to thermal processing. In consumer’s perception, textural property is the main consideration in determining the quality and acceptability of cooked potatoes (Thybo *et al.*, 2000, Corzo and Ramirez, 2005). The preference of cooked potatoes varies with age, with and between countries and is highly dependent on processing; therefore there is a need for sensory texture characterization of cooked potatoes (Thybo *et al.*, 2000).

Not only consumers are concerned about the texture of potatoes, but also the potato processing industry which produces various products which are highly dependent on the rheological properties of the cooked product. Measurement of quality characteristics by sensory method is in general time-consuming and not well suited for industrial routine control. For this reason, the industry is demanding on-line instrumental methods which are able to predict sensory texture quality of the processed product or, even better, to predict sensory texture quality of the product directly from the raw material (Thybo *et al.*, 2000).

2.1.4 Food quality modelling

Food is a very complex physicochemical system involving many biological, chemical and physical variables. In today highly competitive market, high quality of product is the key factor in determining the success of a modern food industry. Food quality is more difficult to specify than safety, but it basically means the control of chemical and physical changes during processing and storage (VanBoekel, 1996).

Generally, food quality change may be expressed as a function of composition and environmental factors:

$$\frac{dA}{dt} = F(C_i, E_j) \qquad \text{Eq. 2.2}$$

where A is the quality attribute; t is the time; and C_i are the composition factors, such as concentration of reactive compounds, inorganic catalysts, enzymes, reaction inhibitors, pH, water activity, and microbial populations. Whereas, E_j are environmental factors such as temperature, relative humidity, total pressure and partial pressure of different gases, light and mechanical stresses (Taoukis, 2001).

Although it is possible to express food quality change explicitly in terms of measurable parameters, but no analytical solution is available to consider all the parameters in a single function and the possible numerical solutions attainable are too elaborate for any practical purpose. Therefore, the first requirement for this type of study is the identification of the reactions that have the most critical impact on the quality degradation. Moreover, before a model of quality changes due to processing can be developed, kinetics of the relevant reactions must be ascertained (Taoukis *et al.*, 1997, Taoukis, 2001).

Due to the complexity of food systems, the quality degradation is practically represented by the loss of desirable quality factors (e.g. nutritional and organoleptic properties) or the formation of undesirable factor (e.g. off flavour and discoloration). The general equation for studying the kinetic of these reactions is expressed as:

$$\frac{d[A]}{dt} = k\,[A]^n \qquad \text{Eq. 2.3}$$

The quality attributes [*A*] are usually quantifiable chemical, physical, microbiological or sensory parameters characteristics of the particular food system, *n* is the apparent reaction order and *k* is the reaction rate constant (positive values represent formation of [*A*] while negative values represent degradation of [*A*]).

2.1.4.1 Reaction order determination

The order of reaction is a parameter, which describes mathematically that a reaction is either time- or concentration- dependence. It does not necessarily give information on the reaction mechanism but it is suitable for modelling changes in food during processing (Martins *et al.*, 2001). When studying the kinetics of thermal treatment, firstly, it is necessary to determine the apparent reaction order, so that an appropriate kinetic equation can be obtained for subsequent use. The apparent reaction order (*n*) and rate constants (*k*) are determined by fitting the change with time of the experimentally measured values of [A] to Eq. 2.3. This can be done by using either differential methods or integral methods (Taoukis *et al.*, 1997, Taoukis, 2001).

For the integral method, variables are separated and integration is carried out for Eq. 2.3. Hence, the following equation is obtained:

$$\int_{A_0}^{A} \frac{d[A]}{[A]^n} = kt \qquad \text{Eq. 2.4}$$

Regardless to the apparent reaction order (*n*), Eq. 2.4 can be expressed in the form of quality function *f* (*A*) of the food system as:

$$f(A) = k\,t \qquad \text{Eq. 2.5}$$

The form of quality function of food for different apparent reaction orders (usually 0 ≤ *n* ≤ 2) can be derived from Eq. 2.5 by substituting with different value of *n* and the change of quality factors [A] and are shown in Table 2.1.

Table 2.1: Quality function for the change of quality factor [A].

Apparent reaction order (n)	Quality function $f(A)_t$
0	$A - A_0$
0.5	$2\left(A^{0.5} - A_0^{0.5}\right)$
1	$ln\left(\frac{A}{A_0}\right)$
1.5	$-2\left(A^{-0.5} - A_0^{-0.5}\right)$
2	$\frac{1}{A_0} - \frac{1}{A}$
n (n ≠ 1)	$\left(\frac{1}{1-n}\right)\left(A^{1-n} - A_0^{1-n}\right)$

To determine the correct apparent reaction order, experimental data can be fitted tentatively to Eq. 2.5 according to the quality function for different apparent reaction orders in Table 2.1. A linear regression analysis can be carried out to determine the best-fitted lines by comparing the coefficient of determination (R^2). The correct apparent order is that for which the R^2 is closer to unity (Taoukis *et al.*, 1997).

2.1.4.2 Temperature dependence models

In order to quantify the influence of temperature on the reaction rate constants, two temperature dependence models are usually applied: the Arrhenius model and the Bigelow model as illustrated in Figure 2.1.

The Arrhenius model, expressed in rate constants (k) and activation energy (Ea), has been extensively used to modelling the effect of temperature on chemical reaction kinetics and can be used for thermal death. In this model, the logarithm of the reaction rate constants is related to the reciprocal of the absolute temperature with the activation energy (Ea) representing the slope index if the semi-logarithm curve (Holdsworth, 1997, Tantchev *et al.*, 1997) and it can be expressed as: (Hendirckx *et al.*, 1992)

$$k = k_{ref}\, exp\left[-\frac{Ea}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right] \qquad \text{Eq. 2.6}$$

where Ea is the activation energy (J/mol), k_{ref} is the rate constant at a reference temperature (T_{ref}) and R is the universal gas constant (8.314 $Jmol^{-1}K^{-1}$).

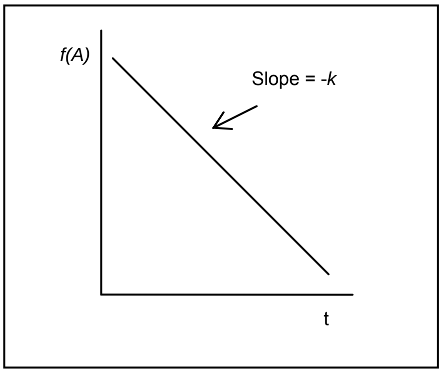
The Bigelow model, which is also known as thermal death time (TDT) model, is expressed in decimal reduction time (*D*) and *z*-value, usually is used in microbiology and specifically for the case of first-order kinetics. In this model, decimal reduction times are described as a direct exponential function of temperature with the *z*-value as the negative reciprocal slope of the semi-logarithmic curve (Holdsworth, 1997, Tantchev *et al.*, 1997). According to this model the rate constants can be expressed as: (Hendirckx *et al.*, 1992)

$$k = \frac{2.303}{D} = \frac{2.303}{D_{ref}} 10^{(T - T_{ref})/z} \qquad \text{Eq. 2.7}$$

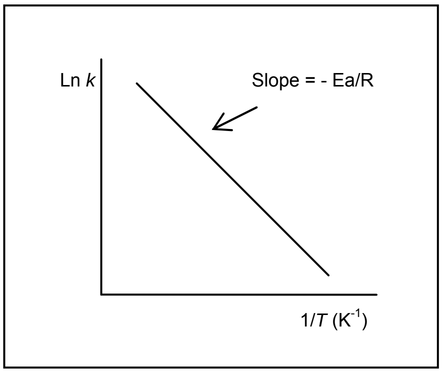
where z is the z-value and D_{ref} is the D-value at reference temperature.

Arrhenius Model

1. Estimating rate constants

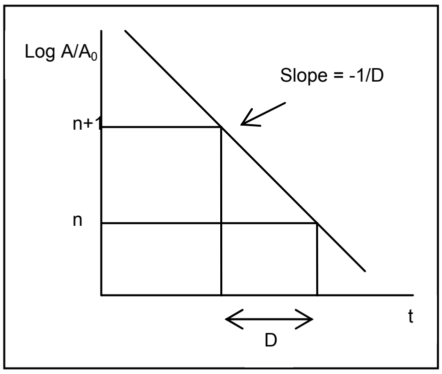


2. Estimating *Ea*-value



Bigelow Model

1. Estimating *D*-values



2. Estimating *z*-value

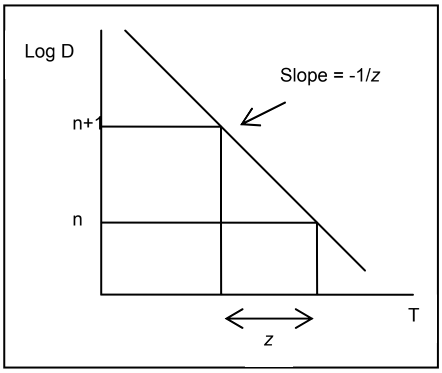


Figure 2.1: Graphical representation for estimating kinetic parameters for Arrhenius (*k*- and *Ea*-value) and Bigelow models (*D*- and *z*-value).

2.1.5 Concept to express thermal impact (Thermal process calculation)

It is of utmost importance to determine thermal impact quantitatively in terms of food safety and quality in order to evaluate, control, and optimize a thermal process. The impact of a thermal treatment on a product safety or quality attribute relies on the rates of the heat-induced reactions that affect this attribute and on the time interval during which these reaction rates occur (VanLoey *et al.*, 1996a).

In thermal processing, the impact of time and variable temperatures on a specific food quality attribute (microbial load, vitamin content, colour, etc.) is usually expressed as the equivalent time at a chosen constant reference temperature which causes the same change in the quality attribute (Maesmans *et al.*, 1995).

In this study, the definition of F-value is only referring to the thermal impact on a selected target attribute. It must be stated that in most of the published journals, F-values are mostly related to food safety and used to represent the necessary processing time at a constant temperature for a certain level of microorganisms inactivation, which normally referred as sterility or lethality. However, in this study, F-value is just a simple cumulative thermal effect (cumulative time-temperature effect of a thermal process) that represents the effectiveness of a thermal process based on the changes of certain quality factors.

The impact of heat treatment can be assigned as processing value (F-value). The processing values can be written mathematically in terms of time-temperature history of the product($F_{t\text{-}T}$); or in terms of a change in response status before and after thermal processing ($F_{response}$) (VanLoey *et al.*, 1996b).

The processing value ($F_{response}$) in terms of a change in response status is based on the actual measurement of the initial and final loads of heat-liable substance and is defined as the integral of the rate constants over time at each encountered temperature relative to the rate constant at a chosen reference temperature (T_{ref}) that is denoted as subscript in Eq. 2.8:

$$\left({}^{Ea}F_{T_{ref}}\right)_{response} = \int_0^t \frac{k}{k_{ref}} dt \qquad \text{Eq. 2.8}$$

where F is the processing value, k the rate constant at T and k_{ref} the rate constant at reference temperature T_{ref}.

The processing value $F_{response}$ in the case of first-order reaction (n = 1) can be written as Eq. 2.9; and in the case of n^{th}-reaction order ($n \neq 1$) $F_{response}$ is expressed as Eq. 2.10:

n = 1

$$\left({}^{Ea}F_{T_{ref}}\right)_{response} = \frac{1}{k_{ref}} ln\left(\frac{A_0}{A}\right) \qquad \text{Eq. 2.9}$$

$n \neq 1$

$$\left({}^{Ea}F_{T_{ref}}\right)_{response} = \frac{1}{k_{ref}}\left(\frac{A^{1-n} - A_0^{1-n}}{n-1}\right) \qquad \text{Eq. 2.10}$$