

Study on heat and mass transfer, protein denaturation and physicochemical changes in kuruma prawn *Marsupenaeus japonicus* during thermal processing

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博士学位論文内容要旨
Abstract

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論文題目 Title	Study on heat and mass transfer, protein denaturation and physicochemical changes in kuruma prawn <i>Marsupenaeus japonicus</i> during thermal processing (クルマエビ加熱プロセスにおける、熱・物質移動、タンパク質変性および物理化学的变化に関する研究)		

Thermal treatment is commonly adopted in prawn processing industry in order to obtain good quality. Various factors including heating method, temperature and processing time will impact on the products quality. For kuruma prawn, the presence or absence of shell is also a factor that should be considered. Quality attributes like moisture release, color, shrinkage, texture and protein denaturation are commonly evaluation indicators. Moreover, thermal protein denaturation occurred in kuruma prawn was considered as the main cause of physicochemical changes. However, quantitative analysis and prediction of protein denaturation has always been a difficult issue, and no studies have been analyzed the relationship between protein denaturation and physicochemical changes. Mathematical models involved heat transfer, moisture transfer, shrinkage and protein denaturation are expected to improve our understanding of physics behind the thermal treatment. Therefore, this study aimed to investigate the effect of thermal processing on the quality attributes of kuruma prawn, compare the quality attributes of peeled and unpeeled prawn, and predict the changes of prawn by using mathematical model.

In Chapter 2, in order to analyze the kinetics of protein denaturation and the relationship between the degree of denaturation and chemical changes, changes in Ca^{2+} -ATPase activity, protein solubility, and total sulfhydryl content of whole prawn meat during heating by determining the thermal denaturation kinetics of the proteins were investigated. TPD was described by a first-order reaction. The thermogram obtained by non-isothermal differential scanning calorimetry analysis displayed three endothermic peaks corresponding to myosin, sarcoplasmic-collagen, and actin. Enthalpy values of individual protein were calculated using the area of each endothermic peak divided by the dry matter weight of each DSC samples, which was used to define the total non-denaturation ratio (X_{tot}). Activation energies (E_a) for the denaturation of myosin (183.2 kJ/mol) and actin (178.8 kJ/mol) were obtained. The accuracy verification of the kinetic parameters was conducted, and the calculated peak temperature (T_{max}) of each protein was similar to the value measured by DSC. Using the kinetic parameters, the distribution of protein denaturation was predicted in whole prawns under arbitrary heating conditions. The results revealed an uneven distribution of the protein denaturation in prawns that was dependent on the heating conditions. Ca^{2+} -ATPase activity decreased with increasing heating times at 51 or 85°C and was strongly related to the average degree of total non-denaturation ratio. The results of protein solubility analysis suggested that hydrogen bonds, hydrophobic interactions, and ionic bonds changed with protein denaturation. The number of ionic bonds was reduced, while hydrogen content was enhanced at both temperatures. Hydrophobic interactions increased gradually at 51°C ($p < 0.05$). At 85°C, hydrophobic interactions increased notably at first ($p < 0.05$); however, as heating continued, no significant changes were observed ($p > 0.05$). Our results indicate that the extent of protein solubility is significantly correlated with the average degree of protein denaturation during the heating process.

In Chapter 3, in order to clarify the Multiphysics involved in the shrinkage of prawn during heating, a model that describes changes in moisture content of prawn due to pressure-driven water transport was reported according to Darcy's law. The transport model for the heating process included a stress-strain analysis (a structural mechanics model) coupled to a virtual work principle, which is applicable to a body undergoing shrinkage in two dimensions. Simultaneous calculation of changes in internal pressure and TPD, was used to describe the physics behind shrinkage. Temperature, moisture, pressure, as well as TPD profiles and distributions were calculated, and were validated with measured results. Results indicated that shrinkage was

delayed due to slow rate of water release, which promoted the increment in internal pressure. This phenomenon, in combination with actin denaturation, resulted in dramatic water release and volumetric shrinkage. By the proposed model, the understanding of the shrinkage phenomena of prawn during heating was improved; thus, it can contribute to reduce food quality losses associated with shrinkage and water release. Increased amount of moisture loss might result due to the higher heating temperature and times resulting in the adverse changes in texture and economic losses. The proposed structural mechanics model combined with the pressure driven transport of water allowed calculation of the time evolution of many different variables during heating process of prawn. Similar approach can also be applied for different samples treated using other heating methods, such as drying and broiling. In addition, the employed TPD approach not only have application to simulate the denaturation as a result of the cooking methods employed here, but also, they can be used for the analysis of additional thermal treatments, making possible the evaluation of the changes in other quality attributes besides texture and water retention within the temperature range of protein denaturation.

In Chapter 4, in order to describe effect of presence or absence of prawn shell on the quality of cooked muscle, several factors including heat penetration, moisture content, color distribution, microstructure, and texture changes were tested at several thermal schedules. Thermal protein denaturation was predicted to clarify the quality attribute differences between both samples. Heat penetration was slower in unpeeled than peeled prawns at the initial stage at all evaluated heating temperatures, unpeeled prawns were required one more minute to get equilibrium state compared to peeled prawn. Slower heat penetration was correlated well with the predicted lower denatured rate observed for each protein. The denatured rate of myosin, sarcoplasmic-collagen, and actin in unpeeled prawns at 85 °C decreased by 9.36%, 5.88% and 15.30% compared to peeled prawns. The tissue connection between shell and muscle apparently protects the prawn meat from shrinkage, resulting in a reduction of the water release. L^* values of prawn muscle showed a closed correlation with X_{tot} at 65, 75 and 85 °C. Color values regardless of L^* , a^* , and b^* between unpeeled and peeled prawns in any were not significant different ($p > 0.05$). However, color values of peeled samples showed a slightly higher than unpeeled prawns, which was probably caused by denser structure. Maximum stress of unpeeled prawns at 50, 65 and 75°C were significantly higher than peeled prawns. Moreover, the absence of shell lead to a denser microstructure and slightly higher color profiles in peeled prawns. However, the maximum stress showed no significantly different regardless of the presence or absence of prawn shell underwent 75 or 85 °C for 20min. These results will be helpful in optimizing the thermal treatment conditions of peeled and unpeeled prawns and contributing to provide technical support in the design of high-quality prawn products.

In general, thermal protein denaturation kinetic model was established, which made it possible to predict protein denaturation at an arbitrary temperature. Characteristic indexes which could reflect the degree of the protein denaturation were screened and confirmed. Simply and easily measuring indicators will be used to reflect the complex protein denaturation process. Experimental measuring and mathematical modeling were combined to forecast and control products quality. Effect of heating temperature and time on peeled and unpeeled prawns were investigated. These results will be as the basis theory of the heating for widely application in food industry. It also has great significance to improve the level of the information and automation management of the food industry.