Numerical model for the combined simulation of heat transfer and enzyme inactivation kinetics in cylindrical vegetables

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Abstract

In order to elucidate the effect of a heat treatment on the activity of oxidative enzymes, heat transfer in stems of broccoli florets was studied. A conductive heat transfer model with convective boundary conditions was developed and solved using the finite element method. The thermophysical properties of broccoli (Brassica oleracea L. Italica) were estimated by means of fitting the model predictions to the temperature recordings at a specific location in the broccoli stem. The computed parameters were used to generate an overall predictive heat transfer model for a variety of heat treatments where the temperature and time intervals can be changed randomly. A kinetic model of enzyme inactivation was linked to the overall heat transfer model. The temperature–time profiles during a number of heating and cooling processes were evaluated for the effect of the thermal process on the peroxidase activity. As an application the lipoxygenase inactivation in asparagus (Asparagus officinalis L.) was also estimated. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Heat transfer; Finite element model; Enzymatic activity; Peroxidase; Lipoxygenase; Broccoli; Asparagus

1. Introduction

The increased interest of consumers both for healthy food and ready-to-use food products has prompted producers to develop new products like minimally processed vegetables (cut, washed and/or minimally heat-processed). Broccoli florets, for example, could be subjected to a mild heating process in order to obtain a product which approaches the fresh state of the vegetable but which at the same time possesses a substantially prolonged shelf life under refrigerated storage conditions. The latter can be achieved because the heat treatment results in the enzyme inactivation and a decreased microbial activity. In fact, the three processes considered (texture degradation, enzyme inactivation and reduction of the microbial load) are temperature- and time-dependent. To assess their residual levels after the heat treatment, it is important to know how the temperature has evolved in each point of the broccoli stem as a function of time.

In the literature, a lot of studies have been performed to investigate texture changes during and after heat treatment. Paulus and Saguy (1980) studied the effect of a heat treatment on the texture quality of cooked carrots. They experienced a softening of the vegetable that revealed itself by an exponential decay of firmness as a function of cooking time. This thermal softening was also expressed by Huang and Bourne (1983) and Rao and Lund (1986). Harada, Tirtohusodo, and Paulus (1985); Kozempel (1988); Verlinden (1996) and others developed different models to describe the influence of temperature and time on the cooking kinetics.

The inactivation of enzymes by means of a heat treatment is often described by first-order kinetic models, such as

\[
\frac{dA}{dt} = -k_t A, \tag{1}
\]

with \( A \) being the enzyme activity at time \( t \) relative to initial activity (dimensionless) \( A(t = 0) = A_0 = 1 \), \( k_t \) the rate constant (s\(^{-1}\)) and \( t \) is the heating time (s).
A simple integration of this differential equation is not possible because the rate constant is temperature-dependent. This dependency can be described by the Arrhenius equation

$$k_t = k_{\text{ref}}e^{-E_a/RT},$$

with $k_{\text{ref}}$ being the frequency factor or rate constant at infinite temperature ($s^{-1}$), $E_a$ the activation energy (J mol$^{-1}$), $R$ the gas constant (8.31441 J mol$^{-1}$ K$^{-1}$) and $T$ the temperature (K).

Furthermore, the frequency factor $k_{\text{ref}}$ cannot be expressed as a quantitative value. Therefore, the Arrhenius equation can be transformed into a more comprehensible expression (Verlinden, 1996)

$$k_t = k_{\text{ref}}e^{-E_a/R(1/(T^{-1}/T_{\text{ref}}))},$$

with $k_{\text{ref}}$ being the rate constant at a predefined reference temperature ($s^{-1}$) and $T_{\text{ref}}$ is the reference temperature (K).

In fact, the inactivation of enzymes is (theoretically) reversible and reactivation is possible when the heating process has not been sufficient and storage has been carried out at high temperatures. However in practice, this inactivation is an almost irreversible reaction and will not be considered here.

The enzyme peroxidase is said to be the most heat-resistant enzyme in vegetables. However, this enzyme does not have quality-destroying effects and only causes color changes to a lesser extent. Enzymes like peroxidase can therefore be used as indicator enzymes to establish the adequacy of the heating process. Performing a heat treatment until the peroxidase is completely inactivated is sufficient to destroy all the enzymes responsible for quality loss. However, this method of control could lead to overblanching. To obtain a high-quality product it is better that there is still a residual peroxidase activity left after blanching (Günes & Bayindirh, 1993). Less blanching results in improved flavor, color and texture of the processed broccoli. In contrast with peroxidase, lipoxygenase is less heat stable but is mainly responsible for the development of off-flavors. Günes and Bayindirh (1993) studied the inactivation of peroxidase and lipoxygenase in green beans and carrots due to a blanching process. Another study of thermal destruction of peroxidase in green beans (Zoueil & Esselen, 1959) showed a large difference in kinetic data with those of Günes and Bayindirh (1993). This could be related to the fact that one study was performed in vivo and the other in vitro. Ganthavorn, Nagel and Powers (1991) examined the heat inactivation of lipoxygenase and peroxidase in asparagus. Here, the differences between the kinetic data of in vivo and in vitro experiments are also clear. Further differences between the experimental data can easily be explained by the differences in raw material. Therefore, it might be important to determine the model parameters for the product under investigation experimentally (exact variety, maturity, etc.).

This work is part of a larger research project aimed at the optimization and process control of mild heat treatments given the constraints on product quality and safety. The current paper focuses on the design of appropriate heat treatments for experiments with vegetables leading to a desired level of enzyme inactivation. In the field of enzyme kinetics, a lot of literature deals with the experimental determination of enzyme inactivation and the use of models with kinetic parameters. Working with the heat treatment of whole vegetables for such studies implies that the enzyme inactivation is not only affected by the treatment duration but also by the place of the product. The objective of this work was to use models for the simulation of heat transfer and enzyme inactivation kinetics as a guideline for deciding the heat treatments that can be of interest for mild processing. These simulation results are then used to setup experiments for the validation of mild treatments on the basis of experimental determination of the remaining enzyme activity after mild treatment. The calculations were done for peroxidase inactivation in broccoli stems. Afterwards, the developed model was applied to lipoxygenase inactivation in asparagus.

### 2. Heat transfer calculations

In the experiments described further, we are dealing with conductive heat transfer through a vegetable where
a convective boundary condition has to be taken into account. Under the assumption that the thermal conductivity $k$ is not space-dependent throughout the broccoli stem and that the generation of thermal energy in the floret is non-existent, the following equation can be used for the heat diffusion (Incropera & DeWitt, 1990):

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t},$$  \hspace{1cm} (4)

with $\alpha = \frac{k}{\rho c}$ being the thermal diffusivity (m$^2$ s$^{-1}$), $k$ the thermal conductivity (W m$^{-1}$ K$^{-1}$), $\rho$ the density (kg m$^{-3}$), $c$ the specific heat capacity (J kg$^{-1}$ K$^{-1}$) and $T$ is the temperature (K).

In the system under investigation, the boundary conditions are

$$T_{\text{on surface}} = T_{\infty} \hspace{1cm} \text{(during heating phase)}$$

$$k \left[ \frac{\partial T}{\partial n} \right]_{\text{on surface}} = h(T_{\text{on surface}} - T_{\infty}),$$  \hspace{1cm} (5)

with $T_{\infty}$ being the temperature of the heating medium (K), $n$ the unit outward normal vector (m) and $h$ is the heat transfer coefficient (W m$^{-2}$ K$^{-1}$).

The first condition corresponds to a situation in which the surface is maintained at a fixed temperature. The second boundary condition corresponds to the presence of convection heating. When the temperature at the surface of the sample is equal to the temperature of the fluid the heat transfer coefficient $h$ becomes infinitely large.

The initial condition is a uniform temperature at the beginning of the experiment

$$T_{\text{in}} = T_0$$  \hspace{1cm} (6)

with $T_{\text{in}}$ being the temperature at the beginning of the experiment (K).

From the heat treatment experiments, we will try to get estimates of the thermal diffusivity $\alpha$ and the heat transfer coefficient $h$.

3. Heat treatment: experimental setup

In the current research, broccoli florets were subjected to different heat treatments, ranging from 60°C to 90°C. A measurement setup was constructed consisting of a temperature-controlled water bath with a circulating water flow (F10-HC/8, Julabo Laborteknik GmbH, Seelbach, Germany) and a data acquisition/switch unit (HP 34970A, Hewlett-Packard, Colorado, USA), which was connected to a HP BenchLink Data Logger through an RS-232 interface. A copper–constantan type T thermocouple (MTS-55.000 series, Thermo Electric, Waramond, The Netherlands), with a ceramic probe that was mineral insulated, was used to continuously measure the temperature in the broccoli stem. The thermocouple was placed inside the broccoli stem up to a depth of about 20 mm and the part of the thermocouple exposed to air was insulated with a piece of foam. Care was taken to place the thermocouple as exact as possible, in the center of the stem. The temperature evolution was only measured in the stem of the broccoli. The broccoli flowers are much smaller than the stem, which means that a heat treatment leading to sufficient enzyme degradation in the center of the stem will also be sufficient for the flowers.

An average diameter of each broccoli stem was determined with calipers. To determine the exact position of the thermocouple, X-rays were used (Wevers et al., 1993). A special application of X-rays is with computed tomography (CT) (Tollner, Hung, Upchurch, & Prussia, 1992). A sample is subdivided in consecutive planes that are scanned to produce two-dimensional images. The X-ray device was set at a voltage of 50 kV and a current of 0.15 mA. A CT scan was made consisting of 10 consecutive planes. Only the plane that contains the position of the thermocouple when it enters the broccoli stem and the plane that contains the tip of the thermocouple were considered (Fig. 1). In this way, a precise position of the thermocouple could be derived and the deviation from the center could be taken into account when modeling the heat transfer.

For the heat transfer measurements, the broccoli was cut into small pieces (‘florets’) that contained secondary stems with a diameter of 12–17 mm. Three broccoli florets were monitored simultaneously with a sampling frequency of two temperature readings per second. Four temperature/time combinations were investigated: 60°C/10 min, 70°C/7 min, 80°C/5 min and 90°C/2 min. Per combination six florets were measured.

The water bath was filled with 4 l of demineralized water and was heated to the predetermined temperature. When this temperature was reached the broccoli florets were immersed in the heated water and the scan was started. After reaching the predetermined heating time the samples were immediately cooled in an ice bath, where the temperature was measured for another 3 min.

An example of a measurement that was conducted at a temperature of 90°C and a heating time of 2 min is shown in Fig. 2 (left). In this case, the pre-set temperature of 90°C was not reached during the proposed time interval. For a second set of measurements, another thermocouple was added to measure the ambient temperature. In this way, the temperature of the heating medium could be verified against the display of temperature-controlled water and the ice baths. From Fig. 2 (right) (a heat treatment of 5 min at 80°C) it can be seen that the ambient temperature stayed at a constant level except for a small period of decrease immediately after the broccoli was placed in the temperature-controlled
water bath. However, care had been taken that the temperature did not drop by more than 2°C in order to maintain an adequate heat treatment. When the samples were transferred to the ice bath the ambient temperature instantly dropped to 0°C while the temperature of the broccoli samples remained somewhat longer (about 10 s) at the pre-set temperature and never reached 0°C in the observed cooling interval.

4. Estimation of the heat transfer parameters

Since in general, no analytical solutions are available for coupled heat transfer and enzyme inactivation kinetics' problems, the finite element method was used to solve the governing model equations in a numerical way. A research finite element package, CHAMPSPACK (Scheerlinck & Nicolaï, 1999), was used to define and solve the different problems at hand.

The heat transfer in the broccoli stem was assumed to occur only in the radial direction. Therefore, a one-dimensional axi-symmetric geometric model was built consisting of 51 linear elements.

For each heat treatment, the thermophysical properties of the broccoli stem (α) were estimated in such a way that a best fit was obtained between the model predictions and the temperature recordings at specific locations in the broccoli stem. This was accomplished using an automatic, gradient search-based, Least-squares method (Scheerlinck & Nicolaï, 1999). An example of the results obtained using this numerical estimation procedure for the heat transfer model parameters is shown in Fig. 3.

For every heat treatment, an average value of the thermal diffusivity was calculated (Table 1). An analysis of variance was carried out on the data in SAS® (Sas Institute, SAS/Stat® User’s Guide, 1989) and it was concluded that with a confidence level of 95% there were
no significant changes in diffusivity as a function of temperature ($Pr > F = 0.6646$). The diffusivity could thus be considered as temperature independent for the concerned temperature interval. An overall diffusivity could be calculated which equaled $1.48 \times 10^{-7} \pm 0.17 \times 10^{-7}$ m$^2$ s$^{-1}$ and agreed with the thermal diffusivity of broccoli mentioned in the literature ($\alpha = 1.37 \times 10^{-7}$ m$^2$ s$^{-1}$, calculated from the thermophysical properties of broccoli: thermal conductivity $k = 0.46$ W m$^{-1}$ K$^{-1}$, density $\rho = 860$ kg m$^{-3}$ and specific heat capacity $c = 3900$ J kg$^{-1}$ K$^{-1}$, source: Sprenger, 1982) within a confidence interval of 99%. The average thermal diffusivity was used during the cooling phase to estimate an appropriate convective heat transfer coefficient $h$ for this phase ($h = 214$ W m$^{-2}$ K$^{-1}$).

The estimated model parameters could then be used to generate a predictive heat transfer model for a variety of heat treatments, where the temperature and time intervals can be changed randomly, and for broccoli stems with varying diameters. In Fig. 4, the heat transfer is simulated for a broccoli stem of 15 mm when it is subjected to a heat treatment at, respectively, 60°C, 70°C, 80°C and 90°C for a time period of 5 min. The

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>Number of measurements</th>
<th>$\alpha_{\text{average}}$ (m$^2$ s$^{-1}$)</th>
<th>S.D. (m$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>5</td>
<td>$1.57 \times 10^{-7}$</td>
<td>$2.66 \times 10^{-8}$</td>
</tr>
<tr>
<td>70</td>
<td>6</td>
<td>$1.44 \times 10^{-7}$</td>
<td>$2.00 \times 10^{-8}$</td>
</tr>
<tr>
<td>80</td>
<td>5</td>
<td>$1.52 \times 10^{-7}$</td>
<td>$1.30 \times 10^{-8}$</td>
</tr>
<tr>
<td>90</td>
<td>6</td>
<td>$1.42 \times 10^{-7}$</td>
<td>$2.39 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Fig. 4. Prediction of the temperature evolution in a broccoli stem subjected to four heat treatments: 60°C/5 min (upper left), 70°C/5 min (upper right), 80°C/5 min (lower left) and 90°C/5 min (lower right) (— in the center, - - - in the middle between the center and the boundary, - - - at the boundary).
temperature evolution was calculated for the center and the boundary of the stem as well as for the node in the middle between these last two.

5. Modeling the enzyme inactivation

An enzyme kinetics model was linked to the predictive heat transfer model developed in the previous section. This enzyme inactivation model implied a numerical integration of Eq. (1), using Eq. (3) to take the temperature dependency of the rate constant \( k_r \) into account. The integration was performed automatically using a built-in tool available in the finite element software package CHAMPSPACK (Scheerlinck & Nicollai, 1999). The enzyme activity was calculated relative to an activity of 1 at the beginning of the process.

As an example the activity of peroxidase was calculated for a broccoli stem with an average diameter of 15 mm subjected to the four heat treatments mentioned above (Fig. 4) followed by an approximately 3 min cooling in an ice bath. The heat transfer was modeled starting from the optimal value for the diffusivity \( \alpha = 1.48 \times 10^{-7} \text{ m}^2 \text{s}^{-1} \) and the average value for the heat transfer coefficient \( h = 214 \text{ W m}^{-2} \text{K}^{-1} \) during the cooling phase. The kinetic data were taken from literature (Table 2).

Table 2

<table>
<thead>
<tr>
<th>Kinetic data</th>
<th>Peroxidase activity in broccoli</th>
<th>Lipoxygenase activity in asparagus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy, ( E_a ) (J mol(^{-1}))</td>
<td>104 500</td>
<td>140 000</td>
</tr>
<tr>
<td>Reference rate constant, ( k_{r \text{ ref}} ) (s(^{-1}))</td>
<td>0.0622</td>
<td>0.0016</td>
</tr>
<tr>
<td>Reference temperature, ( T_{\text{ref}} ) (°C)</td>
<td>100</td>
<td>60</td>
</tr>
</tbody>
</table>

Fig. 5 shows a simulation of the decrease in peroxidase activity. These figures describe the inactivation at the boundary and in the center of the stem as well as in a node in the middle between these last two. From Fig. 5, it can be concluded that the heating temperature has a major affect on the peroxidase inactivation. At a temperature of 60°C the peroxidase activity remains after 5 min at a level between 70% and 80% of the initial value. For this heat treatment, a heating time larger than 5 min must be applied to obtain adequate inactivation. For a heat treatment of 5 min at 70°C, the activity drops to 40% for the boundary and 60% for the center. Again this is not sufficient. At 80°C (5 min) the

Fig. 5. Simulation of the peroxidase activity level in broccoli when it is subjected to different heat treatments: 60°C/5 min (upper left), 70°C/5 min (upper right), 80°C/5 min (lower left) and 90°C/5 min (lower right) (–– in the center, - - - in the middle between the center and the boundary, - - - at the boundary).
peroxidase activity has decreased to a level between 5% and 20%. This could be sufficient considering that a small residual peroxidase activity can remain. The heat treatment at 90°C for a time interval of 5 min seems to show sufficient peroxidase inactivation. Gines and Bayindirh (1993) mention that a residual peroxidase activity of 10% would be acceptable for preservation by freezing. Based on this assumption the necessary processing times reaching this level can be calculated. For 90°C, a processing time of 5 min is sufficient to reach an adequate peroxidase inactivation as was already concluded from the experiments. At 80°C a heating time of 8 min is necessary to reach sufficient inactivation and processing times at 70°C and 60°C were as much as 15 and 40 min, respectively.

The activity of peroxidase in a processed broccoli shows a decrease in comparison to the activity level in a non-processed broccoli stem. However, monitoring of minimally heat processed vegetables stored for a couple of weeks under refrigerated conditions, indicated that we have to be cautious concluding that all heat treatments will lead to an increased shelf life. The natural resistance of the fresh vegetable to spoilage organisms can be destroyed by the heat treatment. This may even lead to a reduced storage life. Therefore, in the future also, the microbial growth during storage will have to be estimated. Increased convenience of minimally processed vegetables requires better care during the refrigerated storage period.

6. Application: lipoxygenase inactivation in asparagus

The model that was developed for broccoli can easily be used for other vegetables of a cylindrical shape. As in the case of broccoli no lipoxygenase kinetic data were available in literature, a simulation was performed for the inactivation of lipoxygenase in asparagus. Thermal diffusivity data for vegetables are scarce but the thermal diffusivity can easily be estimated by the Riedel’s (1969) correlation

\[ x = 0.088 + \left( z_w - 0.088 \right) \frac{\text{water(mass)}}{100}, \quad (7) \]

with \( z_w \) being the thermal diffusivity of water (mm² s⁻¹).

This equation can only be used to estimate the thermal diffusivity in foods with water content above 40% by mass. The water content for asparagus is 93% (ASHRAE, 1993). Using Eq. (7) the following value for the thermal diffusivity of asparagus was obtained:

\[ x = 1.59 \times 10^{-7} \text{ m}^2 \text{s}^{-1}. \]

The kinetic data for lipoxygenase were taken from literature (Table 2). The heat transfer and the inactivation of lipoxygenase in asparagus were calculated using the simulation program developed for broccoli, with the appropriate values for the thermal diffusivity and the kinetic data. The simulation was performed for an asparagus with a diameter of 10 mm and the heat transfer coefficient \( h \) was assumed to have a value similar to the coefficient used during the cooling phase of broccoli. The temperature evolution was again simulated for a heat treatment at

![Fig. 6. Prediction of the temperature evolution in an asparagus subjected to four heat treatments: 60°C/5 min (upper left), 70°C/5 min (upper right), 80°C/5 min (lower left) and 90°C/5 min (lower right) (— in the center, --- in the middle between the center and the boundary, - - - at the boundary).](image-url)
60°C, 70°C, 80°C and 90°C for a time interval of 5 min (Fig. 6). Fig. 7 shows a simulation of the decrease in lipoxygenase activity for the four considered heat treatments.

The lipoxygenase activity level in asparagus drops in two of the four heat treatments (80°C/5 min and 90°C/5 min) to zero, which means that these processes are sufficient to denature all the lipoxygenase and inhibit the development of off-flavors. At 70°C/5 min the activity drops to 10–20%. An extension of the processing time to 13 min would be adequate to obtain a complete lipoxygenase inactivation. The heating process at 60°C/5 min remains inadequate even for lipoxygenase, which is less heat-resistant than peroxidase.

7. Conclusions

Vegetables can be subjected to a mild heat treatment to obtain a product that resembles the fresh vegetable but at the same time shows a reduced enzymatic and microbial activity and hence a prolonged shelf life. To establish the adequacy of the heat treatments currently used in our research on broccoli florets, the level of enzyme inactivation had to be derived. To what extent the enzymes are being denatured depends on the temperature evolution inside the broccoli during processing.

For this reason, a number of heat transfer measurements were set up. A research finite element package, CHAMPSPACK, was used to solve the heat transfer equations numerically. The thermophysical parameters of broccoli were determined from the best fit (based on a Least-square criterion) between the model and experimental data. The enzyme inactivation equation was solved using a built-in tool, available in CHAMPSPACK, which is automatically linked to the temperature history of the thermal process computations. In this manner, residual enzyme activity levels after a heat treatment could be estimated. The necessary time to obtain the desired inactivation at a certain processing temperature can also be calculated.

This model can now be used to find optimum heat treatments for our future experiments on minimally processed broccoli. Furthermore, the model can easily be adopted for other vegetables of cylindrical shape (green beans, carrots, asparagus, etc.). As reduction of microbial load during heat treatments is often modeled using similar first-order degradation models as for enzyme inactivation, the developed routines could also be applied for estimation of microbial activity levels. However, in the future also the microbial growth and enzyme activity during refrigerated storage will have to be examined.
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