A Kinetic Study of Hardening and Softening Processes in Vegetables during Cooking

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We derived a general expression for the time and temperature dependence of both the hardening and the softening rates of vegetables during cooking on the basis of rate laws. The vegetables studied were such root vegetables as Japanese radish, carrot, burdock and potato. Our kinetic model was based on the following two assumptions: (1) Pectin is transformed into three forms, i.e., the unchanged pectin, the hardening pectin and the softening pectin. (2) Each pectin contributes additively to the hardness of the vegetables. Considering the causes of the hardening and the softening as enzymatic deesterification and $\beta$-elimination, respectively, first-order rate laws were applied to the formation of each pectin and to the inactivation of the enzyme. Rate constants for relevant processes were determined at different temperatures by fitting integrated rate equations to the cooking data by the least-squares method. The hardness calculated from the derived expression was in good agreement with the experimental values for all samples. Using the kinetic parameters determined here, we could reproduce not only the simultaneous occurrence of the hardening and softening processes but also the desired cooking time for optimum hardness. The hardening rate constant showed Arrhenius behavior between 54 and 63°C, but a non-Arrhenius one at higher temperatures. It was suggested that the hardening process was complex in the high temperature region of 70-99.5°C.

In the cooking process of foods, neither an overcooked nor an undercooked state is desired. To optimize the degree of cooking, we need to kinetically control the hardness or softness of food materials through such conditions as cooking temperature and time. Vegetables soften and harden simultaneously during the cooking process; the hardening takes place overwhelmingly at 50-70°C (1), above which the rapid initial hardening is followed by the gradual softening (2-5).

Several approaches have been proposed for the kinetic analysis of the softening process of vegetables during cooking (2-9). One of them is the nth-order rate equation fitting (2,3), and another is the application of the first-order rate equation separately to the first and second half periods of cooking (4,5,6). In the latter case, we separated the cooking process and developed the first-order rate approach to predict the optimum cooking time for vegetables (6,9). In most of the previous studies, however, attention has been paid only to the softening kinetics in the relatively high temperature region above 80°C. Vegetables are sometimes preheated in the low temperature region of 60-70°C to avoid excessive softening during sterilization by heating at higher temperatures (10,11). For general purposes, therefore, we should take into account both the hardening and the softening in a unified manner. Here we examine the kinetic and mechanistic aspects of hardening and softening during the cooking of such root vegetables as Japanese radish, carrot and so on. We have generalized the first-order rate approach by considering the roles of
pectins in controlling both the hardening and the softening.

Causes of the hardening and softening of vegetables are associated with pectins in the cell walls and the middle lamella. BARTOLOME and HOFF reported that the hardening was caused by the demethylation of the cell wall pectin by pectinesterase (PE) activated at temperatures above 50°C and the consecutive formation of a bridge bond between the free carboxyl groups and Ca ions. This mechanism is supported for some vegetables and fruits. The main factor which causes the softening of vegetables during cooking is thought to be the decomposition of pectin by β-elimination.

On the basis of these studies of the mechanisms of hardening and softening, we have applied here the first-order rate to derive a general expression for the time and temperature dependence of the hardness of the vegetables during the cooking process.

Materials and Methods

Sample Preparation

Japanese radish, carrot, burdock, and potato were bought in a retail store on the day of the experiment and used as the samples. The middle parts of the samples were used. In the case of potato, the pith was excluded. The samples were cut into segments of 1 cm × 1 cm × 0.5 cm by means of a mold. The length 0.5 cm was taken in the direction of the axis of the tissue.

Cooking Method

The samples were cooked with distilled water in a waterbath (Yamato Science Co., Ltd.) in the temperature range of 54 to 99.5°C (± 0.5°C) for 0.25 to 120 min, quickly cooled down in flowing water around 15°C for 30 s, and wiped with filter paper. For the heating above 94°C, we used an A-type pipe heater (Hachikou Denki Co., Ltd.) as a supplement.

Measurement of the Hardness

The hardness of the samples was measured by a texturometer (GTX-2, Zenken Co., Ltd.) under the following conditions: The plunger was the V-type, the clearance was 1 mm and the bite speed was 6 times/min. The average hardness (N) was obtained from the values determined for seven to ten samples; the measurements were repeated three times.

Sensory Evaluation

The degree of cooking was tested using a 5-point rating scale (2, overcooked; 1, slightly overcooked; 0, properly cooked; -1, slightly undercooked; -2, undercooked). Twenty panelists who participated in the test were students at the cookery science laboratory of Ochanomizu University.

The hardness of the samples in the point range of -0.5 to 0.5 were regarded as the optimum hardness.

Kinetic Analysis of Hardening and Softening of Vegetables

Changes in Pectins with Cooking Time

Our analysis was based on the first-order rate equations and the following basic assumptions: (1) Pectin is transformed into three forms, the unchanged pectin (denoted by P), the hardening pectin (P_h), and the softening pectin (P_s). (2) Each form contributes additively to the hardness of the vegetables. From these assumptions we developed the following equations:

\[ P_0 = P + P_h + P_s \]  
\[ y = aP + bP_h + cP_s \]

Here, \( P_0 \) is the total concentration of three types of pectins. The terms \( a, b \) and \( c \) denote the hardness coefficients for the pectins, \( P, P_h \) and \( P_s \), respectively, in the contribution to the hardness, and \( y \) is the hardness.

Rate Equations for the Pectins

Because it was unclear whether the Michaelis-Menten mechanism was applicable to the enzymic reaction in the polymeric system of our interest, we simply assumed that the formation of the hardening pectin \( P_h \) was proportional to the concentrations of both the enzyme E and the unchanged pectin P as follows:

\[ \frac{dP_h}{dt} = k_h EP \]

where \( k_h \) is the hardening rate constant and \( t \) is the time. Because the enzymes in the vegeta-
bles in our study are inactivated by cooking at high temperature\(^{14}\), this process may be treated by the first-order rate law and expressed as:

\[
\frac{dE}{dt} = -k_E E \tag{4}
\]

\[
E = E_0 \exp (-k_E t) \tag{5}
\]

where \(k_E\) is the rate constant for the apparent enzyme inactivation. We regarded \(k_E\) as the apparent rate constant because we did not treat the rate of the inactivation itself. \(E_0\) is the initial concentration of the enzyme at \(t = 0\). By inserting Eq. (5) into Eq. (3), we obtain

\[
\frac{dP_h}{dt} = k_E E_0 \exp (-k_E t) P \tag{6}
\]

For the non-enzymic formation of the softening pectin \(P_s\) in Eq. (1), we assume the first-order rate law. It follows that

\[
\frac{dP_s}{dt} = k_s P \tag{7}
\]

where \(k_s\) is the softening rate constant.

**Time dependence of the three forms of pectins**

We derived an expression for the time dependence of the concentration of the unchanged form of the pectin in Eq. (1). By differentiating Eq. (1) with respect to time, we obtain

\[
\frac{dP}{dt} = \frac{dP_h}{dt} + \frac{dP_s}{dt} \tag{8}
\]

The substitution of Eqs. (6) and (7) into the right side of Eq. (8) leads to the equation

\[
-\frac{dP}{dt} = k_E E_0 \exp (-k_E t) P + k_s P \tag{9}
\]

Using the initial value of \(P\) in Eq. (1), we integrated this equation with respect to time and obtained

\[
\ln \frac{P}{P_0} = k_E E_0 \frac{\exp (-k_E t) - 1}{k_E} - k_s t \tag{10}
\]

\[
\frac{P}{P_0} = \exp \left( K_s [\exp (-k_s t) - 1] - k_s t \right) \tag{11}
\]

where

\[
K_s = \frac{k_E E_0}{k_s} \tag{12}
\]

As for the other forms of pectins, \(P_h\) and \(P_s\), we obtained expressions corresponding to Eq. (11). By dividing Eq. (6) by \(P_0\) and by integrating it with respect to time, we obtained

\[
\frac{R}{R_0} = \int k_E E_0 \exp (-k_E t) \frac{P}{R_0} dt \tag{13}
\]

From Eq. (7), in the same way we obtained

\[
\frac{P}{P_0} = \int k_s \frac{P}{R_0} dt \tag{14}
\]

The term \(P/P_0\) involved in Eqs. (13) and (14) is given as a function of time in Eq. (11), and its logarithmic average value for a short time interval can be obtained so that it may be used for the integrands of Eqs. (13) and (14). If we take a sufficiently short time interval, the relative concentrations of the pectins can be calculated to a good approximation.

**Expression for the hardness variations**

To derive the expression for the hardness from the relative concentrations of pectins thus obtained, we divide Eq. (2) by \(P_0\) and rewrite it as

\[
Y = a \left( \frac{P}{P_0} \right) + b \left( \frac{P_h}{P_0} \right) + c \left( \frac{P_s}{P_0} \right) \tag{15}
\]

where \(Y\) is the hardness defined by \(y/P_0\), and \(a\), \(b\) and \(c\) are the hardness coefficients of \(P/P_0\), \(P_h/P_0\) and \(P_s/P_0\), respectively. Each pectin term on the right side is given as a function of time in Eqs. (11)-(14). Thus we can obtain the calculated values of the hardness from Eq. (15).

**Determination of the hardness coefficients, \(a\), \(b\) and \(c\)**

We have determined the values of \(a\), \(b\) and \(c\) in Eq. (15) in the following way: \(a\) is easily determined as the initial hardness from the initial conditions that at \(t = 0\), \(P_h = P_s = 0\) and \(P = P_0\). The term \(b\) is an equilibrium value of the hardness in the low temperature region, because \(P = P_s = 0\) and \(P_h = P_0\) in the limit of infinite time in the low temperature region where the hardening is dominant. In contrast, the softening is dominant after the initial slight hardening in the high temperature region. In this case, \(P = P_h = 0\) and \(P_s = P_0\) in the limit of infinite time, and \(c\) is regarded as an equilibrium value of the hardness in the high temperature region.

**Determination of the rate constants**

In the low temperature range of 54–63°C, the hardening process was dominant, and both \(P_h\),
and $k_s$ can be set equal to zero. In this case, Eqs. (11) and (15) are, respectively, simplified as

$$P = \exp \{K_h(\exp (-k_{st}) - 1)\} \quad (19)$$

$$\frac{Y - b}{a - b} = \frac{P}{P_0} \quad (17)$$

These equations are combined as

$$\frac{Y - b}{a - b} = \exp \{K_h(\exp (-k_{st}) - 1)\} \quad (19)$$

In the limit of infinite time, this gives the relation

$$-\ln \{(Y - b)/(a - b)\}_\infty = K_h \quad (13)$$

Using this, $K_h$ is determined. We rewrite Eq. (18) as

$$\ln \{(1/K_h) \ln \{(Y - b)/(a - b)\} + 1\} = -k_{st} \quad (20)$$

By plotting the left-hand side of this equation against time, we can determine the rate constant $k_{st}$ from the (negative) slope.

In the high temperature region of 94-99.5°C, on the other hand, the softening process is dominant, and both $P_h$ and $k_{hs}$ can be made equal to zero. In this case, Eqs. (11) and (15) are, respectively, simplified as

$$\frac{P}{P_0} = \exp (-k_{st}) \quad (21)$$

$$\frac{Y - c}{a - c} = \frac{P}{P_0} \quad (22)$$

These equations are connected as

$$\frac{Y - c}{a - c} = \exp (-k_{st}) \quad (23)$$

Thus we can obtain the value of the rate constant $k_{st}$ from the plot of the logarithm of the left side of Eq. (23) against time.

Following the procedure described above, we determined the rate constants $k_h$ and $k_{hs}$ as a function of temperature. It was somewhat complicated to determine the temperature dependence of the hardening rate constants $k_h$ involved in the quantity $K_h$; see Eq. (12). We determined the value of $K_h$ using Eq. (19) in the range of 54-63°C from the measured hardness. In the range of 70-99.5°C, however, we obtained it by a curve fitting method so that the differences between the calculated values from Eqs. (11)-(15) and experimental ones may be minimized. Using the $K_h$ and $k_{st}$ values in Eq. (12), we obtained the values of $k_h$.

## Results and Discussion

### Hardness coefficients, $a$, $b$ and $c$

Hardness coefficients, $a$, $b$ and $c$, for the pectins in Eq. (15) are summarized in Table 1. Also included are the ratios of the hardness variations expressed as $(b-c)/(a-c)$. The ratios of the hardness variations were similar except for Japanese radish. The result that the degree of the hardening of Japanese radish was more marked than that of the other vegetables agreed with that in the previous papers. This might be attributed to the high PE activity of Japanese radish.

The values of $a$, $b$ and $c$ mean the magnitude of the contribution to the hardness of each pectin per unit concentration of pectin. The value of $b$ is the largest among the three for all samples. As seen later, the rate of the hardening depended strongly on temperature, so we need to control both time and temperature to optimize the hardness of cooked vegetables.

### Time dependence of pectin forms and their effect on hardness

It is important to understand how the hardness of cooked vegetables depends on the pectin forms. Fig. 1 illustrates how the relative concentration of pectins, such as $P/P_0$, $P_h/P_0$ and $P_s/P_0$ depended on time for carrot at 90°C, and Fig. 2 depicts the time dependence of the calculated hardness values $Y$ together with $a (P/P_0)$, $b (P_h/P_0)$ and $c (P_s/P_0)$ in Eq. (15). The comparison of Figs. 1 and 2 shows the contribu-

## Table 1 Hardness coefficients $a$, $b$ and $c$ in Eq. (15)

<table>
<thead>
<tr>
<th>Samples</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$(b-c)/(a-c)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Japanese radish</td>
<td>22</td>
<td>40</td>
<td>1</td>
<td>1.8</td>
</tr>
<tr>
<td>Carrot</td>
<td>48</td>
<td>69</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>Burdock</td>
<td>50</td>
<td>68</td>
<td>8</td>
<td>1.4</td>
</tr>
<tr>
<td>Potato</td>
<td>27</td>
<td>39</td>
<td>1</td>
<td>1.4</td>
</tr>
</tbody>
</table>

$a$, initial hardness for the samples (N); $b$, equilibrium value of hardness of the hardening (N); $c$, equilibrium value of hardness of the softening (N); $(b-c)/(a-c)$, hardening ratio (-).
tion of each pectin form to the hardness. The calculated hardness values decrease even with a slight increase in the softening pectin. Most of the natural pectin was transformed into the softening pectin during the cooking process as seen in Fig. 1, and accordingly, the hardness was reduced markedly as seen in Fig. 2. On the other hand, the increase in a relatively small concentration of the hardening pectin at an early time caused the initial hardening and contributed substantially to the hardness in subsequent cooking. These differences in the contribution to the hardness between the softening pectin and the hardening pectin are ascribed to the values of \(b\) and \(c\) as mentioned above. Because the effect of the hardening pectin on the hardness at the initial stage is so large, controlling the initial hardening is of great importance for maintaining the structural strength to avoid the destruction of the vegetable tissue. These features were common to all vegetables investigated here.

**Comparison of calculated and experimental hardness values**

As seen in Figs. 3 a–d, the calculated and experimental results for the hardness were in good agreement for all samples investigated in the high and low temperature regions. This indicates the success of the present kinetic study where the hardening and the softening during cooking are quantitatively taken into account simultaneously in contrast to the previous separate approach. The kinetic treatment of the low and high temperature processes, where the hardening and softening are predominant, respectively, enables us to predict the time and temperature dependence of the hardness of vegetables. By applying the kinetic approach developed here, we can control and optimize the cooking conditions so that they may guarantee a desired hardness value in the low and high temperature regions.

In the intermediate temperature region of 80–90°C, however, the agreement becomes less satisfactory at longer times. This would be ascribed to some interaction of the hardening and the softening. Although their coupling is neglected in Eqs. (1) and (2), it may not be the case when the degree of esterification of the pectin becomes low. The lower the degree of esterification, the lower becomes the extent of the \(\beta\)-elimination. Unless either the hardening or the softening process predominates, the competing terms in Eq. (15) are not strictly independent in the temperature region.
Fig. 3 Calculated and experimental values for the hardness

The symbols represent the experimental values: ■, 60°C; □, 70°C; △, 80°C; ▲, 90°C; ●, 99.5°C.
The solid curves represent the calculated values from Eqs. (11)-(15).
Horizontal lines represent the optimum hardness determined by sensory evaluation in the point range of −0.5 to 0.5.

under consideration.

Despite the limitations, the present quantitative kinetic approach is generally useful for determining optimum conditions for cooking because of the absence of any adjustable parameters.

Temperature dependence of rate constants

The activation energy and frequency factor are defined by the Arrhenius equation.

\[ k = A \exp \left( -\frac{E_a}{RT} \right) \]

where \( k \) is the rate constant \((k_E, k_s, \text{and } k_h)\) given in \( \text{min}^{-1} \), \( A \) is the frequency factor given in \( \text{min}^{-1} \), \( E_a \) is the activation energy (kJ/mol), \( R \) is the gas constant (8.314 J/K mol), and \( T \) is the absolute temperature (K). The relationships between \( \ln k \) and \( 1/T \) are linear for both \( k_E \) and
Table 2: Apparent activation energy and frequency factor of rate constants

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k_E$ (min(^{-1}))</th>
<th>$E_a$ (kJ/mol)</th>
<th>$k_s$ (min(^{-1}))</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Japanese radish</td>
<td>$1.2 \times 10^{10}$</td>
<td>120</td>
<td>$1.4 \times 10^{16}$</td>
<td>120</td>
</tr>
<tr>
<td>Carrot</td>
<td>$1.5 \times 10^8$</td>
<td>51</td>
<td>$4.5 \times 10^{11}$</td>
<td>88</td>
</tr>
<tr>
<td>Burdock</td>
<td>$3.8 \times 10^{10}$</td>
<td>99</td>
<td>$2.5 \times 10^{18}$</td>
<td>130</td>
</tr>
<tr>
<td>Potato</td>
<td>$5.1 \times 10^{10}$</td>
<td>99</td>
<td>$2.8 \times 10^{18}$</td>
<td>140</td>
</tr>
</tbody>
</table>

$k_E$: apparent rate constant of the enzyme inactivation (min\(^{-1}\));
$k_s$: rate constant of the softening (min\(^{-1}\));
$A$: frequency factor (min\(^{-1}\));
$E_a$: apparent activation energy (kJ/mol).

$k$, with a correlation coefficient larger than 0.96 for all samples. The obtained values for $E_a$ and $A$ are summarized in Table 2. The apparent activation energies of $k_E$ and $k_s$ were in the ranges of 51-120 kJ/mol and 88-140 kJ/mol, respectively. The non-enzyme reaction has a larger activation energy than the enzyme reaction, with a difference of about 30 kJ/mol. In the case of Japanese radish, however, the activation energy difference between $k_E$ and $k_s$ was negligibly small. The anomaly might correspond to the exceptional behavior of the hardness coefficient $b$ mentioned before. As a result of the large activation energy for $k_s$, the softening step becomes dominant at higher temperatures as shown in Fig. 3.

We wished to obtain the $k_h$ value to determine its temperature dependence. By inserting the determined values of $k_E$ and $k_s$ into Eq. (12), we have obtained the value of $k_h$ multiplied by $E_0$. The Arrhenius plots of $k_hE_0$ for Japanese radish and carrot are shown in Fig. 4. Because $E_0$ is temperature independent, the slope is equal to the activation energy for the hardening process. The plots were linear below 63°C, indicating the Arrhenius behavior of $k_h$ in this temperature region. The activation energies for the hardening were in the range of 117-221 kJ/mol, which are much larger than those for $k_E$. This trend is common to all vegetables studied. The large activation energy for the hardening process accounts for why the hardness of cooked vegetables is so sensitive to cooking temperature.

In a homogeneous solution of pectin, a much smaller activation energy (30 kJ/mol) has been reported for the pseudo first-order enzyme demethylation reaction\(^{21}\). Above 70°C, however, the Arrhenius plots in Fig. 4 were not linear, showing weaker temperature dependence. This means that the hardening and the softening processes were not independent of each other above 70°C. Several reasons for the nonlinearity may be conceivable: (1) Some reaction other than the formation of the hardening pectin may be involved above 70°C. (2) Some structural changes such as conformation changes and drastic collapse of cell walls may begin to take place around
70°C. (3) Some components in the tissue may change within a short period at higher temperatures than 70°C, as in the case of protein denaturation and starch gelatinization\(^{22}\). Because the cooking processes considered here are not simple, the elucidation of the mechanism of the hardening process over the whole temperature range requires more information. At any rate, the present kinetic study is in favor of the previous conclusion that a border exists around 70°C in the temperature effect on the hardening processes\(^{17}\).

In contrast, we have seen the simple Arrhenius behavior for \(k_E\) and \(k_s\). The activation energy 90–140 kJ/mol obtained here for the softening process is comparable with the reported value\(^{2–6,9}\). The activation energy for the hardening process has been obtained for the first time in the present study. No comparison is therefore possible.

To avoid overcooking of vegetables, it is important to control the hardening process. In this respect, a further study of the non-Arrhenius behavior of the hardening process found here at high temperature is necessary for developing a more efficient food process. In this study we have proposed a unified manner of treating both the hardening and the softening of vegetables on the basis of kinetic models.

**Nomenclature**

\[P_0=\text{initial value of total pectin concentration} \quad [\text{kg/kg}]\]

\[P_h=\text{hardening pectin} \quad [\text{kg/kg}]\]

\[P_s=\text{softening pectin} \quad [\text{kg/kg}]\]

\[P=\text{unchanged pectin} \quad [\text{kg/kg}]\]

\([a, b\text{ and }c=\text{hardness coefficients of the pectins}, P, P_h\text{ and }P_s\text{, respectively, in the contribution to the hardness} \quad [N/(kg/kg)]\]

\[y =\text{hardness} \quad [N]\]

\[t =\text{time} \quad [\text{min}]\]

\[E =\text{enzyme concentration} \quad [\text{kg/kg}]\]

\[E_0 =\text{initial concentration of the enzyme} \quad [\text{kg/kg}]\]

\[k_e =\text{apparent inactivation rate constant of the enzyme} \quad [\text{min}^{-1}]\]

\[k_s =\text{hardening rate constant} \quad [(\text{kg/kg})^{-1}]\]

\(K_s =\text{relative ratio of the hardening (dimensionless)}\)

\[k_E =\text{softening rate constant} \quad [\text{min}^{-1}]\]

\(Y =\text{hardness defined by } y/P_0 \quad [N/(kg/kg)]\)

\(A=\text{frequency factor} \quad [\text{min}^{-1}]\)

\(E_a =\text{activation energy} \quad [\text{kJ/mol}]\)

\(R =\text{gas constant} \quad [8.314\text{J/K mol}]\)

\(T =\text{absolute temperature} \quad [\text{K}]\)

**Subscripts**

\(h =\text{hardening}\)

\(s =\text{softening}\)

\(0 =\text{initial value}\)

**References**

加熱における野菜の硬化・軟化過程の速度論的解析

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野菜の加熱による硬化・軟化過程を速度式に基づいて数式化し、時間および温度依存性を明らかにした。試料はダイコン、ニンジン、ゴボウおよびジャガイモとした。次の2つを仮定して速度論的モデルをたてた。(1) ベクチンは加熱と共に3つの形（未変化ベクチン、硬化ベクチンおよび軟化ベクチン）に変化する。(2) 3種のベクチンの各々が硬さに影響し、硬さはそれらの和で表せる。硬化的原因を酵素によるベクチンの脱メチル化、軟化の原因をベクチンのβ脱離として硬化、軟化および酵素失活に対して、各々一次の反応速度式を適用した。各速度定数を対応する温度範囲における実験値を用いて最小自乗法により求めた、計算による硬さの値は実験値とよく一致した。本式により硬化・軟化過程が同時に表現され、速度パラメーターによって適度な硬さに達するまでの最適加熱時間が算出された。硬化の速度定数は低温域（54-63℃）ではアレニウス型を、高温域（70-99.5℃）では非アレニウス型を示した。高温域では硬度の変化の機構が複雑であることから示唆された。