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### Technical paper

## The Kinetic Analysis and Simulation of Hardening in Bread Made by the Yudane Dough Method

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Pullman type white breads with or without Yudane dough at 10 and 20% (w/w, flour base) were made by the no first fermentation method. Yudane dough was prepared by mixing boiling water and flour at a 1:1 ratio. The breads were stored at various temperature conditions and then subjected to analyses of bread hardening (temporal changes in hardness), hardening rate constant of bread (HRC), and simulation of hardening behavior using a hardening model. The results were as follows: The hardening of all breads slowed with the increase in storage temperature. The hardening of breads made with Yudane dough (Yudane breads) was slower than that without Yudane dough (Control) at any storage temperature. The HRC of all breads sharply decreased with the increase in storage temperature. By using the hardening model, the hardening behavior of all breads stored at various temperature conditions was simulated with considerable accuracy.

Keywords: bread, temperature, hardening, kinetic model, simulation

#### Introduction

White bread made with Yudane (in Japanese) dough (Yudane bread) has recently become popular in Japan. Yudane bread is characteristically moist, very soft, and sticky with a texture like cooked rice. It also has a desirable flavor, slightly sweet taste, good crust color, and slow staling as evaluated mainly by hardening (hardening) compared to conventional bread (control) (Shibata and Kato, 2001; Fukazawa and Kainuma, 2004; Yamada *et al.*, 2004, Yamauchi *et al.*, 2014). Thus, new items produced using the Yudane dough bread making method (Yudane method) are continuously being developed, and these breads have a market worth of more than a hundred billion yen in Japan. Moreover, the Yudane method has recently become the main bread making

process, especially in large-scale Japanese bakeries.

Previous studies of the storage of loaf type Yudane bread at room temperature revealed slower hardening compared to the control. On the other hand, kinetic analysis of Yudane bread showed that its hardening rate constant (HRC) and retrogradation rate constant of starch gel in the bread were lower than those of the control. The main factors responsible for these phenomena in Yudane bread are the high moisture and sugar contents (Yamada *et al.*, 2004; Yamauchi *et al.*, 2014).

Study of the hardening behavior of Yudane bread during storage has been conducted at room temperature (20°C), whereas hardening analysis at various storage temperatures has not yet been explored (Yamada *et al.*, 2004; Yamauchi *et al.*, 2014). Moreover,

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Materials	Yudane 0% (Control) (g)	Yudane10% <sup>2)</sup> (g)	Yudane 20% <sup>2)</sup> (g)
Wheat flour			
Dough except of Yudane dough	100	90	80
Yudane dough	-	10	20
Wet yeast	2	2	2
Sugar	5	5	5
Salt	2	2	2
Shortening	5	5	5
L-Ascorbic acid	0.01	0.01	0.01
Water			
In dough except of Yudane dough	68.0	59.5	51
In Yudane dough	-	10	20

**Table 1.** Formulation of bread making<sup>1)</sup>

<sup>1)</sup>Formulation of Yudane dough was expressed on flour basis and formulation of all materials was described in baker's percent.

<sup>2)</sup>The Yudane dough was added to total bread dough based on w/w flour.

it is very important to predict the hardening behavior of actual bread products during distribution from the point of manufacture to the store shelf, a condition characterized by random temperature changes in a non-steady-state.

Thus, in this study, we applied the rate equation of bread hardening as a function of storage temperature and time to the analysis of Yudane bread, which is based on the first order reaction of starch gel in bread as reported by Cornford *et al.* (1964) and Yamauchi *et al.* (1993).

In this study, we analyzed the hardening (temporal changes in hardness) and HRC of Yudane bread at various storage temperatures, derived the hardening equation of Yudane bread as a function of storage temperature and time, and evaluated whether the hardening behavior of Yudane bread stored at various storage temperatures could be accurately simulated using this equation.

#### **Materials and Methods**

*Flour sample* Commercial strong wheat flour, Camellia, purchased from the Nisshin Flour Milling Co., Ltd. (Tokyo, Japan) was used in this study. The protein and ash contents were 12.2% and 0.39% (w/w, 13.5% moisture base), respectively. The protein content was measured using a near-infrared reflectance instrument (Infratec<sup>TM</sup> 1241 Analyzer; Foss Japan Ltd., Tokyo, Japan). The ash content was measured according to the method of the American Association of Cereal Chemists (AACC) (1991a).

*Bread making* The formulations and procedures for the bread making in this study are summarized respectively in Tables 1 and 2. The bread making tests were performed using the no first fermentation method following the standard white bread formulation: 2100 g of flour, 105 g of sugar (Nippon Beet Sugar Mfg. Co., Ltd., Tokyo, Japan), 105 g of shortening (Snowlight; Kaneka Corp., Osaka, Japan), 42 g of salt (The Salt Industry Center of Japan, Tokyo, Japan), 42 g of wet yeast (Regular yeast; Nippon

Beet Sugar Mfg. Co., Ltd.), 0.21 g of L-ascorbic acid (special grade) (Wako Pure Chemical Industries, Ltd., Osaka, Japan), and a suitable quantity of water (Yamauchi et al., 1992; Yamauchi et al., 2001). Yudane dough was prepared by mixing boiling water and flour at a ratio of 1:1 in a dough mixer (Mighty-25 mixer; Aicohsha Manufacturing Co., Ltd., Saitama, Japan) at a low speed for 4 min. After mixing, the partially gelatinized dough was immediately stored in a polyethylene bag, cooled at ambient temperature for a few hours, and then stored in the refrigerator at 5°C for about 1 day before use. All other materials (except for the shortening and wet yeast, which were stored at 5°C in a refrigerator) were stored at 20°C and 70% relative humidity for about 1 day before use. Yeast was pre-hydrated with the water, and all materials were put into the mixer bowl and mixed. To prepare the 10% and 20% Yudane breads, 10% and 20% of flour and water were partially replaced with Yudane dough, respectively, which was added at 10% and 20% (w/w, flour base) of the total bread dough. The optimal water absorption of the dough was determined using a Farinograph at 500BU, according to the AACC method (1991b). The optimal mixing conditions for individual doughs were set as the dough mixing time at which the dough showed maximum gas retention, which was measured using the method of Yamauchi et al. (2000). The bread making tests (2100 g scale on a flour basis) were then conducted. The dough was mixed for the optimal time and then divided into 230 g pieces, rounded by hand, and allowed to rest for 20 min (bench time) in a fermentation cabinet (QBX-232DCST2; Fukushima Industries Corp., Osaka, Japan) at 30°C and 75% relative humidity. Eight pieces of dough were panned, with 4 pieces of dough used to form a U-shape in each of the two loaf cases for the Pullman-type white bread, after shaping using a molding machine (MMR230-2; Aicohsha Manufacturing Co., Ltd.). The panned doughs were proofed for 60 or 65 min at 38°C and 85% relative humidity and then baked in an oven (MOC-GGH-

Table 2.	Procedure	of bread	making
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	Conditions			
process	Yudane 0% (Control)	Yudane10% and 20% <sup>2)</sup>		
Mixing of Yudane dough	-	Low speed, 4min Temperature of mixing end point, $55^{\circ}C \pm 1^{\circ}C$		
Mixing of bread dough	Low speed, 5min, Medium speed 5min, High speed 3min Temperature of mixing end point, 30°C±1°C)	Low speed, 5min, Medium speed 5min, High speed 3.5min Temperature of mixing end point, $30^{\circ}C \pm 1^{\circ}C$ )		
Dividing and rounding	230 g, 16 pieces, hand rounding	230 g, 16 pieces, hand rounding		
Bench time	30°C, relative humidity 75%, 20min,	30°C, relative humidity 75%, 20min,		
Molding	1st sheeting clearance: 7.9 mm 2nd sheeting clearance: 4.7 mm Rolling plate clearance, 2 cm	1st sheeting clearance: 7.9 mm 2nd sheeting clearance: 4.7 mm Rolling plate clearance, 2 cm		
Final proof	38°C, relative humidity 85%, 60min,	38°C, relative humidity 85%, 65min,		
Baking	Top: 190°C, bottom; 210°C, 35min	Top: 190°C, bottom; 210°C, 35min		

<sup>1)</sup>Bread making was done using no first fermantation method.

<sup>2)</sup>The Yudane dough was added to total bread dough based on w/w flour.

11S; Sankokikai Co., Ltd., Tokyo, Japan) at 190°C (top) and 210°C (bottom) for 35 min.

Hardening characteristics of breads and simulation method The hardening characteristics of breads were evaluated by measuring crumb hardness using the method of Yamauchi at al. (2001). After baking, the loaves were immediately cooled for 3 h at 20°C and 70% relative humidity in the fermentation cabinet and then packed into double polyethylene bags to prevent water evaporation until used. Samples were stored at  $5^{\circ}$ C in a refrigerator and at 10, 15, 20, 25, and 30°C in a fermentation cabinet. After storage for 12, 24, 36, 60 and 84 h, the hardness of the samples was measured. The stored breads were kept at 20°C for 2 h under conditions preventing water evaporation before cutting of bread crumbs for hardness analysis. Samples were sliced to 20 mm thickness, and a square  $(30 \text{ mm} \times 30 \text{ mm})$  of crumb was cut from the center of the slices using an ultrasonic cutter (model USC-3305; Yamaden Co., Ltd., Tokyo, Japan). The hardness of five bread crumbs was measured by compressing them twice from 20 mm to 10 mm thickness at a 1 mm/s compression rate, using a creep meter (RE2-33005C; Yamaden Co., Ltd.) with a square plunger (W:60 mm × D:60 mm × H:20 mm). Initial hardness measurement (the value at 0 h) was performed in 3 h after baking. The limiting value of crumb hardness (the highest possible value) was determined from the hardness of breads stored at  $5^{\circ}$ C in the refrigerator for 10 days, as reported by Axford et al. (1968). A HRC was obtained using the method developed by Yamauchi et al. (2001) and determined using the following equation 1. The boundary conditions in equation 1 are  $H_t = H_0$  when t is zero and the left-hand side equation 1 is zero. Therefore, the slope of the straight line in Fig. 2a was determined using the least squares method through the origin.

$$\ln\{(H_{L} - H_{0})/(H_{L} - H_{t})\} = kt$$
 .....Eq. 1

Where  $H_L$  (Pa),  $H_0$  (Pa), and  $H_t$  (Pa) are the limiting value of hardness and the hardness at storage time 0 and t, respectively. The k (h<sup>-1</sup>) and t (h) are also HRC and storage time, respectively.

Assuming that the hardening of bread during storage is substantially determined by the hardening (recrystallization) of starch gel in bread, the recrystallization rate of starch gel in bread generally appear to be expressed as a function of the degree of super cooling from the stopping temperature of bread hardening close to the gelatinization temperature of the bread starch (the difference between stopping temperature of bread hardening and storage temperature of bread) and this could be applied for HRC analysis of breads (Baik *et al.*, 1997; Okada, 1984; Xie *et al.*, 2004; Yamauchi *et al.*, 1993). As a result, it was found that HRC was in proportion to the cube of the degree of super cooling on starch gel in bread, which was expressed using the following equation 2 (Yamauchi *et al.*, 1993).

$$k = A (\theta_m - \theta)^3 \qquad \cdots Eq. 2$$

Where k (h<sup>-1</sup>), A (h<sup>-1</sup>  $\cdot$ °C<sup>-3</sup>),  $\theta_m$  (°C), and  $\theta$  (°C) are HRC, the constant, the stopping temperature of bread hardening (the stopping temperature of starch gel retrogradation in bread), and the storage temperature of bread (the bread temperature), respectively. The values of A and  $\theta_m$  of each bread (Yudane 0% (Control), Yudane 10% and Yudane 20%) were determined with the non-linear least squares method of the software package JMP version 11 (SAS Institute Co., Ltd., NC), using the HRC values at a variable storage temperature.

The following equation 3 expresses the hardness of bread stored for t hours at a variable storage temperature. This equation

**Table 3.** HRC,  $H_0$ ,  $H_L$ , and  $H_L - H_0$  of breads stored at 20°C<sup>1)</sup>

Staling data	Yudane 0% (Control)	Yudane10% <sup>2)</sup>	Yudane20% <sup>2)</sup>
$HRC^{3}(k, h^{-1} \times 10^{-2})$	0.89	0.87	0.65
$H_0^{(4)}$ (Pa×10 <sup>3</sup> )	$1.13\pm0.12^a$	$0.87\pm0.09^a$	$1.00\pm0.27^a$
H <sub>L</sub> <sup>5)</sup> (Pa×10 <sup>3</sup> )	$7.67\pm1.13^a$	$6.29 \pm 1.33^{\text{b}}$	$5.65\pm1.37^{\text{c}}$
$H_{L} - H_{0} (Pa \times 10^{3})$	$6.54\pm0.12^a$	$5.42\pm0.09^{b}$	$4.65\pm0.27^{c}$

<sup>1)</sup>Each value except for HRC is the mean  $\pm$  SD. Values followed by the same letter in a column are not significantly different (p < 0.05). The analysis of variance between the data was evaluated by Tukey's multiple range test of Excel statistical software 2012.

 $^{2)}\mbox{The}$  Yudane dough was added to total bread dough based on w/w % flour. k was determined from data of hardness of breads shown in Fig. 1.

<sup>3)</sup>HRC: Hardening rate constant. The HRC (k) was determined from data of bread's hardness shown in Fig. 1.

 $^{5)}\mathrm{H}_{\mathrm{L}}$ : Limiting value of hardness.

is given by integration and transformation after substituting equation 2 into equation 1.  $H_t$  of equation 3 is also a function of the storage temperature and time.

$$H_t = -(H_L - H_0) \exp \{-A (\theta_m - \theta)^3 t\} + H_L$$
 .....Eq. 3

When it is assumed that the next hardening of bread proceeds without delay by the new HRC (k) at various changes in the storage temperature of bread (the temperature of bread), it is possible to easily simulate the bread hardness during the storage time at various storage temperature conditions, including non-stationary conditions by using equation 3. Furthermore, in this study, since the hardening speed of bread was a fairly slow reaction and the internal temperature of the bread does not immediately follow the rapid change in storage temperature, the hardening (temporal changes in hardness) of bread under non-stationary changing storage conditions, i.e., cyclical storage temperature conditions changing over a short time, was simulated by using the average data of the hourly measured bread temperature. The bread storage condition in a room with no temperature control during summer was simulated by cyclically controlling the storage temperature at 30°C for 12 h and at 20°C for another 12 h. Meanwhile, the winter storage condition was simulated by cyclically controlling the storage temperature at  $15^{\circ}$ C for 12 h and then at 5  $^{\circ}$ C for another 12 h. These conditions were repeated in 24 h cycles until 84 h of storage time was reached.

Statistical analysis Measurement of protein and ash contents were performed in duplicate. Crumb hardness was measured in quintuplicate. All data in Table 3, except for HRC, are shown as the mean  $\pm$  standard deviation (SD). The measurement of H<sub>L</sub> (the limiting value of crumb hardness) was performed 60 times. Significant differences in the data presented in Fig. 1 were evaluated using an analysis of variance with Tukey's multiple range test, using Excel statistical software 2012, to compare means at a 5% significance level.

#### **Results and Discussion**

Characteristics of the hardening of breads Figure 1 shows the temporal changes in hardness of all breads during storage at constant temperature (5, 10, 15, 20, 25, and 30°C). From these results, all breads showed lower hardening with the increase in storage temperature. When the bread was stored at the same temperature, the hardening of Yudane breads, especially that of the 20% Yudane bread (Yudane 20%), tended to be retarded compared to the control at all storage temperatures. From these results, it appeared that the hardening of Yudane breads, even as Pullman type bread, was lower than that of the control. The lower hardening of breads with an increase in storage temperature was similar to previous reports by Cornford et al. (1964), Kim and D'Appolonia (1977), Yamauchi et al. (1993), Gray and Bemiller (2003), Bosmans et al. (2013), and Njafabadi et al. (2014). The lower hardening results of Yudane breads in Fig. 1 also corresponded to previous reports by Yamada et al. (2004) and Yamauchi et al. (2014).

Hardening characteristics of breads Figure 2a shows the relationship between  $\ln \{(H_{L} - H_{0})/(H_{L} - H_{t})\}$  (-) and storage time (h), which was based on the results of hardening in the control bread stored at various temperatures in Fig. 1. Numerical values in Fig. 2a are the HRC  $(k, h^{-1})$  of the control bread stored at each temperature, which was determined from the slope of the regression line passing through the origin using the data of the bread stored at each temperature. The HRC of Yudane 10% and 20% breads stored at various temperatures was also determined in the same manner (data not shown). The relationship between storage temperature and HRC in all breads is shown in Fig. 2b. Although the HRC among breads stored under various storage temperatures conditions did not significantly differ, the HRC of all breads sharply decreased with the increase in storage temperature. The HRC of Yudane breads was slightly higher compared with the control at low temperature storage, whereas slightly lower values tended to be observed at higher temperature storage. In addition,

<sup>&</sup>lt;sup>4)</sup>H<sub>0</sub>: Hardness at storage time 0.



**Fig. 1.** Temporal changes in hardness of breads made using Yudane dough method<sup>1)</sup> <sup>1)</sup> Vertical bars indicate the standard deviation of each value.

Yudane dough was added to total bread dough based on w/w% flour; •:Yudane 0% (Control), •:Yudane 10%, I:Yudane 20%. The bread of each graph was stored at 5 (a), 10 (b), 15 (c), 20 (d), 25 (e), and 30°C (f), respectively. The data points followed by the same letter are not significantly different (p < 0.05).



Fig. 2. Relationship between  $\ln \{(H_L - H_0)/(H_L - H_i)\}$  and storage time on bread (control) (a) and relationship between hardening rate constant and storage temperature (b).<sup>1</sup>

<sup>1)</sup> Values in Fig. 2 a indicate the hardening rate constant of the control bread stored at 5, 10, 15, 20, 25, and  $30^{\circ}$ C, respectively and the values was determined from the slope of a straight line calculated by using least squares method. Each symbol,  $\bullet$ ,  $\blacktriangle$ ,  $\blacksquare$ ,  $\bigcirc$ ,  $\triangle$ , and  $\Box$ , in Fig.2 a shows the data at 5, 10, 15, 20, 25, and  $30^{\circ}$ C, respectively. Yudane dough was added to total bread dough based on w/w% flour and each symbol,  $\bullet$ ,  $\blacktriangle$ , and  $\blacksquare$  in Fig. 2 b shows Yudane 0% (Control), Yudane 10%, Yudane 20%, respectively.

Each curve in Fig. 2 b was calculated by using Equation 2 and each curve, —, -----, and - - -, in Fig. 2 b shows Yudane 0% (Control), Yudane 10%, Yudane 20%, respectively.

the regression curves in Fig. 2b, showing the relationship between bread storage temperature and HRC, were determined using equation 2 for each of the breads. The values of the parameters for each bread, as determined by regression analysis with equation 2 (Fig. 2b), are as follows: the stopping temperature of hardening ( $\theta_m$ ) of the control, Yudane 10%, and Yudane 20% was 67.6, 61.3, and 58.8°C, respectively. The A values of the control, Yudane 10%, and Yudane 20% were  $7.20 \times 10^{-8}$ ,  $1.10 \times 10^{-7}$ , and  $1.22 \times 10^{-7}$  (h<sup>-1</sup>·°C<sup>-3</sup>), respectively. Although the  $\theta_m$  value differed among the three breads, all values were close to the gelatinization peak temperature of wheat starch. The  $\theta_m$  of the control bread was also higher compared to the Yudane breads. These results suggest that complete cessation of hardening in the control bread occurs at a higher temperature compared to that of the Yudane bread, and the



Fig. 3. Comparison of simulation curves and experimental data on hardness of breads stored for 84 h in the step-up and step-down change conditions of bread storage temperature.<sup>1)</sup>

<sup>1)</sup> Fig. 3 a: in the step-up change condition of bread storage temperature from  $10^{\circ}$ C to  $25^{\circ}$ C at 42 h.

Fig. 3 b: in the step-down change condition of bread storage temperature from 25°C to 10°C at 42 h.

Vertical bars indicate the standard deviation of each value.

Experimental data in Fig. 3 were measured at 0, 12, 24, 36, 60, 84 h on storage, respectively.

Yudane dough was added to total bread dough based on w/w flour and each symbol,  $\bullet$ ,  $\blacktriangle$ , and  $\blacksquare$  in Fig. 3 shows Yudane 0% (Control), Yudane 10 %, Yudane 20 %, respectively.

Each curve in Fig. 3 was calculated by using Equation 3 and each curve, —, ----, and – –, in Fig. 3 shows Yudane 0% (Control), Yudane 10%, Yudane 20%, respectively.

complete stopping temperature of bread is reduced by the addition of Yudane dough. In addition, the A value of the control bread was small compared to the Yudane breads, which shows a reverse tendency to that of  $\theta_m$ . This indicates that the HRC of the control bread does not rapidly increase with a decrease in storage temperature compared to that of Yudane breads. It appeared that the HRC of Yudane bread showed a slightly larger value compared with the control at low temperature storage, and the tendency to show a slightly lower value at high temperature storage can be explained from the above values of the two parameters from equation 2 for all breads.

The HRC,  $H_0$ ,  $H_L$ , and  $H_L$ - $H_0$  of all breads stored at 20°C are shown in Table 3. Table 3 shows that the HRC of Yudane breads, especially the Yudane 20% bread, was slightly lower than that of the control. Similarly, the  $H_L$  and  $H_L - H_0$  values of Yudane breads were significantly lower than the control. The  $H_{L}$  and  $H_{L} - H_{0}$ values significantly decreased with increasing additions of Yudane dough. The above results indicated that the slow hardening of Yudane bread, especially Yudane 20%, is partially influenced by the low HRC. However, the main factor in the slow hardening is attributed to the lower  $H_L - H_0$  value with decreasing  $H_L$ . These results basically corresponded to the report of Yamauchi et al. (2014) regarding hardening of Yudane bread. However, in a comparison of the individual values of HRC, H<sub>0</sub>, H<sub>1</sub>, and H<sub>1</sub>-H<sub>0</sub> in control and Yudane 20% breads made using the same bread formulations as in this study, the values reported by Yamauchi et al., (2014) were higher than those reported here. These differences appear to mainly relate to the small one-loaf type breads of the previous paper, which differed from the Pullman type breads in this paper. As the Pullman type bread is baked with a lid covering the



Fig. 4. Measured data of central temperature on bread (control) stored for 84 h in the cyclic change conditions of storage temperature<sup>1)</sup>

<sup>1)</sup> Central temperature data of bread in Fig. 4 were continuously measured during storage.

Each curve in Fig. 4, — and -----, shows the central temperature of bread in respective storage conditions for 84 h in the step-down from  $30^{\circ}$ C to  $20^{\circ}$ C at 12 h and then step-up from  $20^{\circ}$ C to  $30^{\circ}$ C at an interval of 24 h or in the stepdown from  $15^{\circ}$ C to  $5^{\circ}$ C at 12 h and then step-up from  $5^{\circ}$ C to  $15^{\circ}$ C at an interval of 24 h.

Each storage condition assumes the typical summer and winter, respectively.

bread pan, the moisture loss during baking is small and bread with a high moisture content is obtained. Therefore, bread hardening showed a general tendency to be retarded. From that discussed above, it appears that the individual data of Table 3 in this paper shows somewhat lower values compared to those of the previous paper.

Furthermore, the  $H_L$ ,  $H_0$  and  $H_L - H_0$  of breads stored at other storage temperatures were similar to the breads stored at 20°C (data



Fig. 5. Comparison of simulation curves and experimental data on hardness of breads stored for 84 h in the cyclic change conditions of storage temperature.<sup>1)</sup>

 $^{1)}$  Fig. 5 a: bread storage condition in the step-down from 30°C to 20°C at 12 h and then step-up from 20°C to 30°C at an interval of 24 h.

Fig. 5 b: bread storage condition in the step-down from  $15^{\circ}$ C to  $5^{\circ}$ C at 12 h and then step-up from  $5^{\circ}$ C to  $15^{\circ}$ C at an interval of 24 h.

Vertical bars indicate the standard deviation of each value.

Experimental data in Fig. 5 were measured at 0, 12, 24, 36, 60, and 84 h on storage, respectively .

Yudane dough was added to total bread dough based on w/w flour and each symbol,  $\bullet$ ,  $\blacktriangle$ , and  $\blacksquare$  in Fig.5 shows Yudane 0% (Control), Yudane 10%, Yudane 20%, respectively.

Each curve in Fig. 5 was calculated by using Equation 3 and each curve, —, ----, and – –, in Fig. 5 shows Yudane 0% (Control), Yudane 10%, Yudane 20%, respectively.

not shown). However, as mentioned above, the HRC values of Yudane breads were slightly higher than the control at low temperature storage of less than 20°C, and these tended to decrease at temperature storage of 20°C and higher compared to the control. This showed that the slow hardening of Yudane bread at a low storage temperature of less than 20°C is minimally affected by the HRC and can mainly be attributed to the lower  $H_L - H_0$ . On the other hand, the slow hardening of Yudane bread at a high temperature storage of 20°C or greater is influenced to some extent by the low HRC of the bread.

Comparison of simulation curves and experimental data Figure 3 shows the simulation curves and the experimental data on the hardness of all breads stored for 84 h in the step-up ( $10^{\circ}C$  to  $25^{\circ}C$ ) and step-down ( $25^{\circ}C$  to  $10^{\circ}C$ ) changing conditions of bread storage temperature after 42 h, respectively. Figure 3 shows that the simulation results and the experimental values were in agreement, allowing us to estimate the hardening behavior of bread under conditions of rapidly changing storage temperature with considerable accuracy using equation 3. The above simulation results basically corresponded to the report of Yamauchi *et al.* (1993) in breads without or with monoglycerides.

Figure 4 shows the changes in the measured internal temperature of bread stored under cyclically changing storage temperatures every 12 h. The changes of the internal measured temperature of bread showed wavy changes without following changes in the storage temperature. Therefore, as described above, the simulation of hardening at this storage conditions was conducted by using the average data of the internal bread temperature measured hourly.

Figure 5 shows the simulation curves and the experimental data on the hardness of breads stored under a cyclically changing storage temperature, which was controlled for 12 h at  $30^{\circ}$ C, then for 12 h at  $20^{\circ}$ C as the summer condition, and for 12 h at  $15^{\circ}$ C, then for 12 h at  $5^{\circ}$ C as the winter condition at an interval of 24 h. The simulated and experimental values showed fairly good agreement, indicating that we were able to estimate the hardening behavior of breads under conditions in which the internal temperature of the bread changed in a non-steady state, with considerable accuracy using equation 3. From the above results, we were able to estimate the hardening of breads showing steady state or non-steady state changes in internal temperature with considerable accuracy, using the simulation method with equation 3.

For actual bread products, a simple method to estimate the hardening behavior of bread during distribution, i.e., under conditions of random temperature change in a non-steady-state, has been anticipated. For this purpose, the simulation model of equation 3 derived in this study could be effectively used to determine the hardening behavior of bread stored under nonsteady-state temperature conditions when the temperature change data of the bread during storage is known. Simulation of hardening (temporal changes in hardness) using this simple model shows that the hardening of Yudane bread at various storage temperature conditions was obviously retarded compared to the control. These results revealed that this model can easily predict bread hardening in the absence of actual experimentation.

#### Conclusion

Using kinetic analysis to predict bread hardening, the following conclusions were obtained about the hardening characteristics of Pullman-type white bread made by the Yudane dough method, which is a very popular bread product with a large market share in Japan. 1) The hardening of all breads slowed as the storage temperature increased. However, when comparing the hardening of these breads under the same temperature conditions, the hardening of the Yudane bread was slower than that of the control at any storage temperature. 2) Although the HRC of all breads stored at various storage temperatures conditions were not significantly different, the HRC of all breads sharply decreased with the increase in storage temperature. Moreover, the HRC values of the Yudane breads were slightly higher at low temperature storage and slightly lower at high temperature storage compared to the control. 3) From the analysis of the hardening behavior of all breads, the main factor affecting the lower hardening of the Yudane bread was due to the decrease in its limiting value of hardness. 4) By using a simple model of hardening as a function of storage temperature and time, we could simulate the hardening behavior of bread stored at various temperature conditions with considerable accuracy. Simulated hardening (temporal changes in hardness) using this simple model could easily predict (without need for experimentation) that the hardening of Yudane bread at various storage temperature conditions was retarded compared to the control.

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