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New Evidences Derived from a Consecutive Reaction Model for the Maillard Reaction in Foods: Optimum Drying Operation of a Leek

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The Maillard reaction in foods has been studied by using a computer simulation technique. As a typical model system, the dehydration process of an ordinary leek was effectively used to demonstrate an optimum drying operation. The Maillard reaction rate of the leek has been measured as a color change using a commercially prepared color meter. To evaluate the color change of the leek, a color parameter of ΔE^* $(=((\Delta a^*)^2+(\Delta b^*)^2+(\Delta L^*)^2)^{1/2})$ was chosen because it followed a good linear relation with the dehydration response curve of the leek. The response curves of ΔE^* obtained in the dehydration operation were described by a typical consecutive reaction model A→B→C, where A is glucose-like materials contained in the leek, B is intermediates formed, and C is melanoidin-like materials as final products. The computer simulation fitting to both the experimental dehydration response curves of C_C and the ΔE^*-value response curves evaluated the maximum amount of C_B (C_{Bmax}).

The integrated amount of C_B (C_{Bin}) produced in the course of the dehydration process changed appreciably depending on the drying temperature and the humidity of the drying air. This took place because the water species dynamically shifted from species A_1 (weakly restricted water species in the A_1 region of W_0 = 1600~120 %-d.b.) to A_2 (strongly restricted water species in the A_2 region of W_0 = 120~20 %-d.b.) at the water content of W_0 = 120 %-d.b.

The sensory scores, evaluated by both the four human tasters and a commercially distributed taste tester as a function of C_{Bin}, gave a gradual increase curve indicating the larger C_{Bin} to be the higher taste score. A two-step dehydration, using the 70 ºC-operation in the water species A_1 region and the 40 ºC - operation in the water species A_2 region, was recognized as an optimized operation for the best sensory score product.

1. Introduction

As is well known, a non-enzymatic browning called the Maillard reaction is commonly recognized in a large number of foods. The Maillard reaction has extremely complex passageways and produces many thousands of products (Labuza, 1994; Baltes et al., 1989; Eichner and Wolf, 1983).

Labuza and his co-workers (Labuza, 1994; Baisier and Labuza, 1992) have rigorously studied the details of the Maillard reaction and reported a large number of useful evidences. The reaction mechanisms proposed were rather diverse because of the complexity of the process and changed dynamically due to the influences on the reaction sequences derived from the products (Hurrell, 1990; Eichner and Wolf, 1983) and kinds of foods (Labuza, 1994). To propose a modified reaction model for

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use as a tool in the actual design of food products, it would be advantageous to visualize a simplified reaction model as a first approximation. Responding to this need, a daring reaction model might be useful.

In the reaction passageways for the browning reaction, the water activity (a_w) strongly influences the browning reaction rate, indicating an important a_w region (a_w = 0.5 ~ 0.8). In our previous works (Konishi, Miura and Kobayashi, 2003; Konishi and Kobayashi, 2010; Konishi, Kobayashi and Miura, 2010; Konishi and Kobayashi, 2011; Konishi, Kobayashi and Kawai, 2011) using various foods such as fish past sausage, squid, salmon, scallops etc., we demonstrated that two different water species, A_1 and A_2, existed, and each of them contributes differently to the water mobility evaluated by the effective diffusivity (*De*) and the molecular mobility ($1/\tau_C$, s^{-1}) determined by the proton NMR technique. Since a_w can be expressed as a function of the correlation time (τ_C), the Maillard reaction rate would be influenced by τ_C. The τ_C means the restriction strength of the water species due to surrounding macro-molecules such as proteins. Therefore, τ_C strongly influences the browning reaction.

The aims of this work are (1) to discriminate the two water species, A_1 and A_2, retained in the leek, (2) to demonstrate a simplified reaction model for the Maillard reaction of the leek, (3) to reconfirm confidence in the reaction scheme proposed, and (4) to propose an optimal drying process that will produce a dried leek with a high score taste as a function of the two water species.

2. Experimental

2.1 Materials

Commercially distributed leeks were used as a dehydration sample. The fresh leeks were carefully washed with tap water and then cut 2 mm in thickness. The initial water content of the sample was W_D = 900~1600 %-d.b. The white part of the leeks was chosen as a test sample for stability in color change, since the Maillard reaction rate was unstably influenced by the green part.

2.2 Dehydration temperature and humidity regulation

The sample was inserted in a stainless steel net basket (175×175×40 mm). Dehydration of the leeks was conducted at a temperature range of T_D = 40 ºC~80 ºC and a relative humidity of RH = 20~60 % in drying air with a flow rate of 2.5 m/s. Using a data logger, the weight of the sample was continuously recorded by the output of a strain gage transducer. The relative humidity was regulated by using a commercially distributed humidifier with an accuracy of RH = ±5 %. The dehydration temperature was controlled by a programmed temperature controller with an accuracy of T = ±1.0 ºC.

2.3 Correlation time evaluation

The correlation time of the water proton for the water species retained in the leek was effectively evaluated by using the proton NMR technique. The details of the evaluating procedure and the conditions were presented in our previous paper (Konishi et al., 2010).

2.4 Effective water diffusivity evaluation

Using a graphical differentiation of the dehydration response curves, the effective diffusivity (*De*) of the water species was evaluated from the sample weight, which was continuously recorded using a strain gage transducer connected to a data logger. The details of the evaluating procedure of *De* were presented in our previous paper (Konishi et al., 2010).

2.5 Color and sensory count evaluations

To evaluate the color change of the leek, the sample was taken from the incubator at the given drying time and moved into a color meter cell of the Konica-Minolta CR-400. The color change of the sample was evaluated using the *L**a*b** system. To evaluate brightness, *L** was ranged as 0~100 and indicated black with smaller values and white with larger values. The value *a** was ranged as -60~60 and indicated green with minus values and red with plus values. The value *b** was ranged as -60~60 and indicated blue with minus values and yellow with plus values. The color parameter of *ΔE** was evaluated by using the equation $\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$ .The sensory count was conducted by both the four human tasters and a commercial taste sensor (Intelligent Censor Tech. Co. TS5000Z).

3. Results and Discussion

3.1 Discrimination of two water species, A_1 and A_2

Figure 1 demonstrates the dehydration response curves of the leek as a function of elapsed time and temperature change. The dehydration rate was evaluated from the graphical differentiation of the response curves and increased with rising temperatures from 40 ºC to 60 ºC. Although discriminating between water species A_1 and A_2 is difficult from the mode of the response curves, the differentiation of the curves obtained shows a clear distinction between the two water species at the water content of W_0=120 %-d.b. as shown in the figure by using the *De* evaluated. Figure 2 illustrates *De* as a function of W_0 at T_D=40 ºC, 50 ºC, and 60 ºC. The obtained values of *De* were divided into two regions, water species A_1 and A_2, at W_0=120 %-d.b., which is similar to the previous study on the behavior of the squid, salmon, scallops, *etc.* (Konishi and Kobayashi, 2010, 2011). In the water species A_1 region, *De* gives an almost identical value. In the water species A_2 region, *De* demonstrates a steep decrease with decreasing W_0. This reduction of *De* in the species A_2 region would be explained by a steep growth of the restriction strength of the water species because of the growth of τ_C in the progression of dehydration. The molecular mobility ($1/\tau_C$) of the water species is strongly influenced by dehydration, which causes a change in diffusibility (a pre-exponential factor of *De*).

The discrimination of water species A_1 and A_2 could also be recognized from the a_w~τ_C straight line. Figure 3 demonstrates a_w as a function of τ_C. The straight line clearly gives a reflection point at τ_C =10^{-8} s (designated as $C\tau_C$). The $C\tau_C$ corresponds to the W_0 = 120 %-d.b. as presented in Figure 2. From this reflection point at $C\tau_C$, one may see that the nature of the water species should change drastically at $C\tau_C$, indicating the marked difference in both the *De* value as the three-dimensional mobility and the $1/\tau_C$ value as the molecular mobility of the water species. These changes should have an influence on the Maillard reaction sequences and produce a diversity of by-products such as the growth of the number of flavours (Baltes et al., 1989). This idea will be reconfirmed in a future section.

3.2 Determination of an effective color parameter to evaluate the Maillard reaction

To choose a color parameter describing the components for the browning reaction, the parameter must be quantitatively evaluated by using the dehydration response curve of the sample. The color parameters also need to be examined effectively by using relative water content (1-W_R). W_R is a water ratio with a scale of 0~1.0. Figure 4 demonstrates the color parameters *RΔa**, *RΔE**, *RΔb**, and *RΔL**, each of which is expressed as a function of (1-W_R) by using Equations (1)~(4) presented as follows.

$$R\Delta L^* = \sqrt{(L^*_t - L^*_0)^2 / (\Delta L^*_{(max)})^2} \quad (1)$$

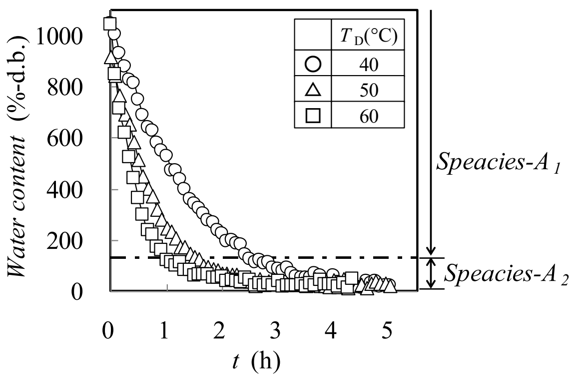

Figure 1: Dehydration response curves as a function of the drying temperatures (RH = 20 %).

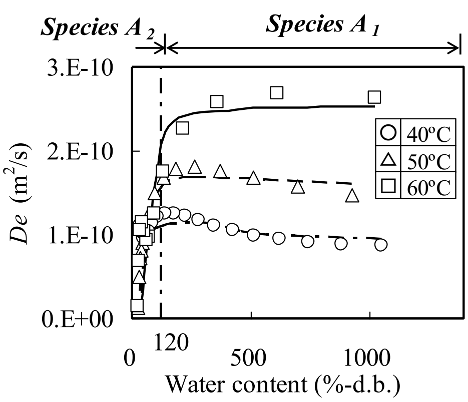

Figure 2: De as a function of the water content of the leek (RH=20 %).

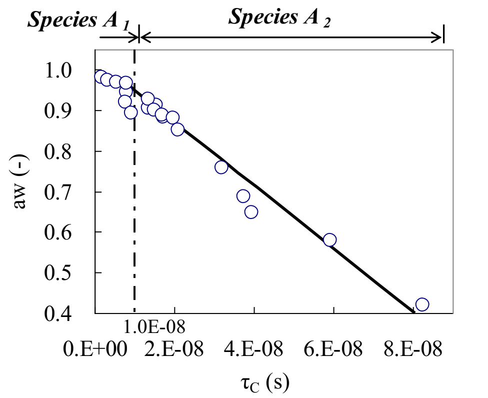

Figure 3 Demonstration of a_w as a function of τ_C.

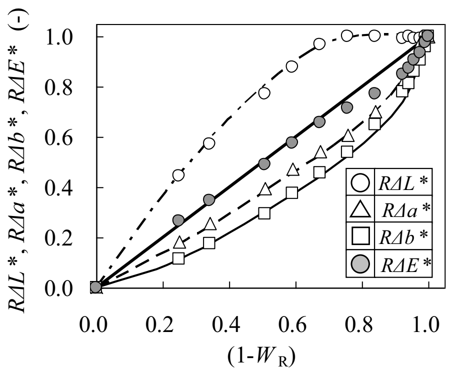

Figure 4 Color parameters as a function of the ratio of dehydrated water T_D=40ºC,RH=20%)

$$R\Delta a^* = \sqrt{\left(a^*_t - a^*_0\right)^2 / \left(\Delta a^*_{(max)}\right)^2} \quad (2)$$

$$R\Delta b^* = \sqrt{\left(b^*_t - b^*_0\right)^2 / \left(\Delta b^*_{(max)}\right)^2} \quad (3)$$

$$R\Delta E^* = \sqrt{\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2} \Big/ \Delta E^*_{(max)} \quad (4)$$

One can recognize the value of $R\Delta E^*$ (= $((\Delta a^*)^2+(\Delta b^*)^2+(\Delta L^*)^2)^{1/2}/\Delta E^*_{\mathbf{max}}$) to be exactly exhibited as a linear dependency against the value of (1-W_R). From the result, ΔE^* was chosen as a useful parameter to describe the final production of brown pigment.
Using the ΔE^*, the final products, melanoidins, can be visualised as a function of the reaction time. Figure 5 illustrates the response curves of ΔE^* evaluated as a function of browning products. The ΔE^*s evaluated at 40 ºC~60 ºC and RH=20 % clearly demonstrate an S-shape mode at the initial stage of the three response curves, which strongly suggests a multistep consecutive reaction mechanism.

3.3 A simplified model of the Maillard reaction visualized by the color change of the leek
The reaction model can be expressed by Equation (5) as follows.

$$A \xrightarrow{ka} B \xrightarrow{kb} C \quad (5)$$

The notation A shows reactants such as glucose and/or amine, B shows intermediates such as amadori products, and C shows a final product such as the brown pigment. The differential equations obtained from the material balance for the three components, C_A, C_B, and C_C, evaluated as concentration are easily solved and expressed as the Equations (6), (7), and (8).

$$C_A = C_{A0} \cdot exp(-k_a \cdot t) \quad (6)$$

$$C_B = C_{A0} \cdot \left(k_a / \left(k_b - k_a\right)\right) \cdot \left(exp(-k_a \cdot t) - exp(-k_b \cdot t)\right) \quad (7)$$

$$C_C = C_{A0} - C_{A0}\left[\left(k_b / \left(k_b - k_a\right)\right) \cdot exp\left(-k_a \cdot t\right)\right] - C_{A0}\left[\left(k_a / \left(k_a - k_b\right)\right) \cdot exp\left(-k_b \cdot t\right)\right] \quad (8)$$

C_{A0} is the initial concentration of A; and *t* is the reaction time. C_A is determined by the dehydration curve experimentally evaluated at the reaction time *t,* C_C is determined by the value of ΔE^* evaluated by the color meter, and C_B is evaluated from C_A-C_C. The rate constants, k_a and k_b, involve frequency factors, A_a and A_b, and activation energies, E_a and E_b, respectively.

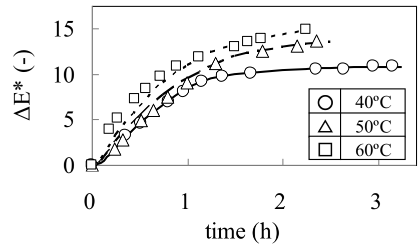

Figure 5: Demonstrating ΔE as a function of the dehydration time.*

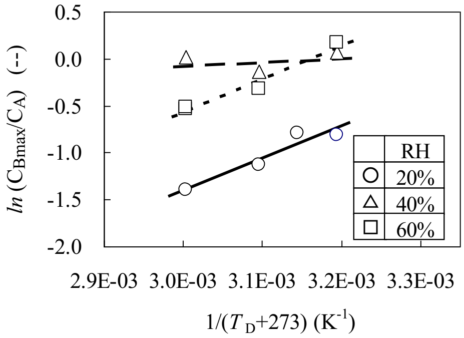

Figure 7: The Arrhenius plot of $C_B max/C_A$ as a function of RH.

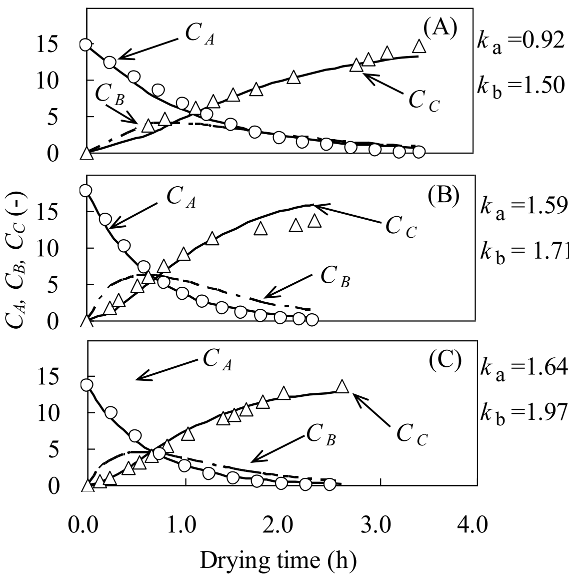

Figure 6: Fitting of the computer simulation response curves to the experimental data based on the consecutive reaction model (T_D = (A) 40 ºC, (B) 50 ºC, (C) 60 ºC), RH=20 %.

The curve-fitting application for the computer simulation using the two response curves of C_A and C_C can easily evaluate the dehydration response curves for the three components. The results are presented in Figure 6 as the results obtained at T_D=40 ºC, 50 ºC, and 60 ºC. Each concentration for the three components is evaluated as a modified concentration converted by the dimensionless values supposing C_{A0} (initial concentration) = $C_{C(max)}$ (maximum concentration of the final products).

3.4 New evidences derived from the Maillard reaction intermediates evaluated

Regarding the behavior of C_B, the computer simulation derived some interesting results. From Equation (7), Equation (10) is obtained by using Equation (9) supposed at the maximum value of B.

$$dC_{B(\max)}/dt = k_a \cdot C_A - k_b \cdot C_{B(\max)} = 0 \tag{9}$$

$$ln\left(C_{B(\max)}/C_A\right) = ln\left(A_a/A_b\right) + \left(\left(E_b - E_a\right)/\left(R \cdot \left(T_D + 273\right)\right)\right) \tag{10}$$

Figure 7 demonstrates ln($C_{B(max)}/C_A$) as a function of 1/(T_D+273) and RH. Comparing the three straight lines obtained, one can recognize that the lower temperatures and RH=40 % give the higher $C_{B(max)}/C_A$. Figure 8 illustrates the sensory score of the dried leek products as a function of the integrated amounts of C_B, C_{Bin}, produced in the course of reaction. The sensory scores obtained using both the four human tasters and the commercial taste sensor clearly demonstrates the higher C_{Bin} as the better sensory score. To get the higher sensory score, the C_{Bin} produced in the course of the Maillard reaction must be kept as much as possible. To achieve this, a two-step dehydration operation is proposed. As a first-step operation, the 70 ºC-dehydration in the water species A_1 region can be chosen because of the higher $C_{B(max)}$. In the second-step operation, the 40 ºC-dehydration in the water species A_2 region can be chosen because of the slow decay of the C_B as presented in Figure 9. The computer simulation curves obtained roughly agreed with the experimental response curves for C_A and C_C. The C_{Bin} evaluated fell on the best sensory score region of the curve as shown in Fig.8. When confirmed, the obtained value of C_{Bin} was about 11 % larger than the one-step operation of 70 ºC.

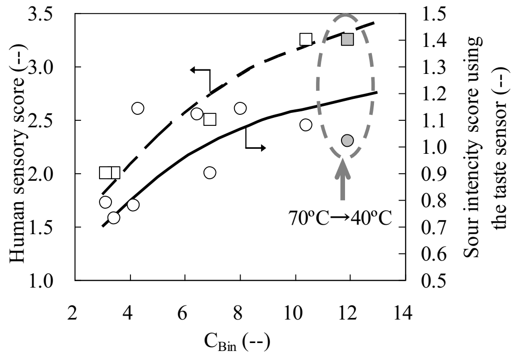

Figure 8: The taste score as a function of the integrated amount of C_B, C_{Bin}.

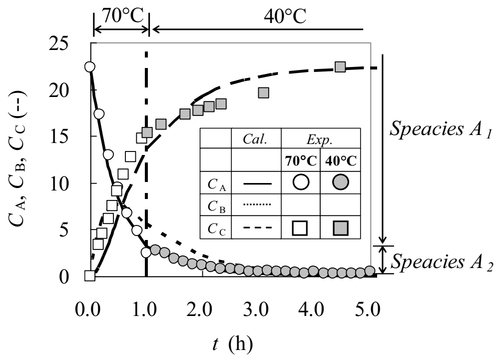

Figure 9: The two step dehydration response curves. RH=20 %

4. Conclusions

The simplified consecutive reaction model proposed consistently explained the Maillard reaction as it appeared in the course of dehydration of the leek. The two water species, A_1 and A_2, were clearly distinguished and both strongly contributed to the Maillard reaction passageways. All the experimental results obtained were reasonably explained by the model proposed. The amount of reaction intermediates evaluated as the precursors of the final browning products showed a strong relationship with the sensory score of the dried leek, indicating the larger amount of intermediates contributes to the better sensory score. To design a higher sensory score of dried leek products, a two-step dehydration operation was proposed, involving the 70 ºC-operation in the water species A_1 region, followed by the 40 ºC-operation in the water species A_2 region.

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