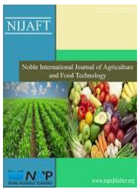
Noble International Journal of Agriculture and Food Technology
Vol. 02, No. 04, pp: 25-32, 2020

Published by Noble Academic Publisher
URL: www.napublisher.org



Original Article **Open Access**

OPTIMAL DESIGN OF THE WATER SPECIES CONTRIBUTING TO THE MAILLARD REACTION MECHANISM IN LEEK AND CABBAGE DRYINGS

Yasuyuki KONISHI[1], Masayoshi KOBAYASHI[2*]

[1]Hokkaido Industrial Technology Center, Hakodate, Hokkaido, Japan
[2*]Advanced Technology Institute of Northern Resources, Sapporo, Hokkaido, Japan

ABSTRACT: In order to design an optimal drying process for agricultural products, the dynamism of the Maillard reaction was quantitatively evaluated by using the leek (LK) and cabbage (CB) drying processes. The necessity to solve the problems both the extremely complicated mechanism of the Maillard reaction brings us to focus on the simplification of the complicated reaction networks and a role of the active water species involved in the agricultural products contributing to the reaction networks. For the reaction mechanism simplification, both a dehydration step of the reaction networks was focused and the color change step of its nonenzymatic browning reaction (Maillard reaction) was effectively used. A typical consecutive reaction model A→B→C (the rate constants are ka and kb ,respectively), where A was glucose-like materials contained in the LK and the CB, B was intermediates formed, and C was melanoidin-like materials as final products, was considered. The first reaction step was replaced by the dehydration reaction step of the LK and CB and the second step was replaced by the final material production step of the browning reaction. The relative humidity (RH) and the glucose (GC) were usefully employed as the modifiers (M1 and M2, respectively) each of which could regulate the character of the active water species formed on the LK and CB. The formed water species sensitively changed the values of ka and kb. The computer simulation of the reaction networks reconfirmed the validity of the simplified reaction model proposed. The amount of the reaction intermediates evaluated by the computer simulation was reconfirmed to be one of the important parameters for the optimum design of the drying processes. The experimental results obtained demonstrated that M1 and M2 could be used as a useful tool to design the optimum drying processes to produce the good taste products.

Keywords: Drying processes of foods, Maillard reaction, leek and cabbage, Simplified consecutive reaction model, Relative humidity, Addition of glucose.

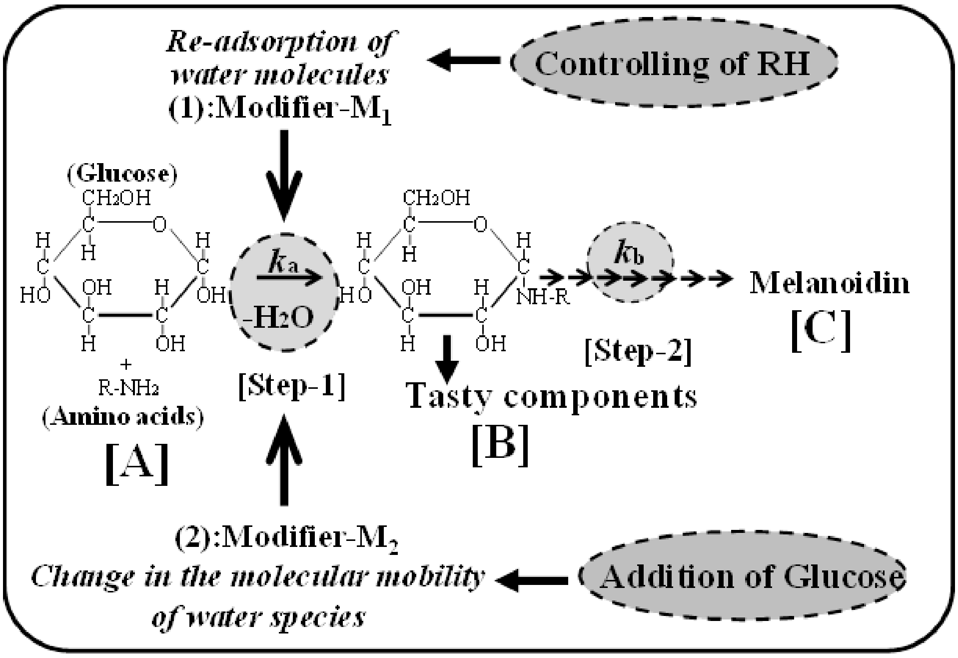
1. INTRODUCTION

In the drying processes of foods such as agricultural and seafood products, the active water species retained in the products have been recognized as one of the useful parameters to develop the high-quality drying techniques [1-8]. The drying processes work to reduce the water content of the foods and, at the same time, the color and flavor of the dried foods are changed by the Maillard reaction. As is well known, the Maillard reaction, a nonenzymatic browning reaction, is common in many foods. The Maillard reaction involves extremely complex passageways and produces many thousands of intermediates [9-11]. To propose a modified reaction model for 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 simplification might be useful rather than the complicated mechanism. In the present study, as a simplified schematic model of the Maillard reaction is proposed for the drying processes, using a leek (LK) and cabbage (CB) as examples, as shown in Figure 1.

Focusing on the (1) of step I (dehydration step) in Fig. 1, when the water content (relative humidity, RH which works as a first modifier, M_1, for the step I) in a drying air stream was increased, the gaseous water molecule would be readsorbed on the food surface. Since the readsorbed water would contribute to the chemical activity of the surface water species of the food, one may recognize that the readsorbed water molecule derived from the increase in RH strongly affected the rate constant (*ka*) of the dehydration reaction step I in Fig. 1. Focusing on the (2) of step I (changing the chemical mobility of water species), glucose (GC) as an additional reagent could be considered as a regulator (a second modifier, M_2) controlling the mobility of adsorbed water instead of the RH. Conclusively, the dehydration rate constant, *ka*, as an effective water species, would be influenced by the values of RH and GC.

In this study, in order to design an optimal drying process for agricultural products, the dynamism of the Maillard reaction is quantitatively evaluated using the LK and CB drying processes.

Figure 1. Simplified schematic model of Maillard reaction



2. MATERIAL AND METHODS

2.1. Materials

For the dehydration samples, commercially distributed leek (LK) and cabbage (CB) samples were used. The fresh LK samples were carefully washed with tap water and then cut into about 2 mm in thickness. The fresh CB samples were cut into 20×20 mm. As a branching pretreatment, the fresh CB samples were dipped in a boiling-water incubator for 3 min, rapidly cooled in a tap-water stream at about 15 ºC, and then dipped in a tank with various concentrations of glucose solution (0, 10, and 20 wt.% GC) at 15 ºC for 30 min. The initial water content of the LK and CB samples was W_D = 1000-1800 and W_D = 800-2400 %-d.b., respectively. The white part of the LK samples was chosen as a test sample for the stability of the color change, since the Maillard reaction rate was unstably influenced by the green part.

2.2. Dehydration Temperature and Humidity Regulation

The LK and CB samples were kept in a stainless steel net basket (175×175×40 mm). LK and CB dehydration was conducted at a temperature (T_D) range of 40-70 ºC and a relative humidity (RH) of 20-60 % for LK and 20 % for CB in dry 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 gauge transducer. The relative humidity was regulated by 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 = ±2.0 ºC.

2.3. 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 chromameter 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 set to a range of 0-100, with black indicated by smaller values and white by larger values. The value of a^* ranged from -60 to 60, with green indicated by negative values and red by positive values. The value of b^* ranged from -60 to 60, with blue indicated by negative values and yellow by positive values. The color parameter of ΔE^* was evaluated using the equation $\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$, which was also used to evaluate step II of the Maillard reaction in Fig. 1. The sensory score was counted by both the four human tasters and a commercial taste sensor (TS5000Z, Intelligent Censor Tech. Co.).

2.4. A sinplified model of the Maillard Reaction Mechanism

Based on the Maillard reaction model in Fig. 1, a nonenzymatic browning reaction model of the LK and CB drying processes can be expressed by Equation (1) as follows.

$$A \overset{k_a}{\rightarrow} B \overset{k_b}{\rightarrow} C \quad \cdots(1)$$

The notation *A* shows reactants (foods) such as glucose and/or amines, *B* shows intermediates such as Amadori products, *C* shows final products such as the brown pigments, and *ka* and *kb* are the rate constants for Eq. (1).

3. RESULTS AND DISCUSSION

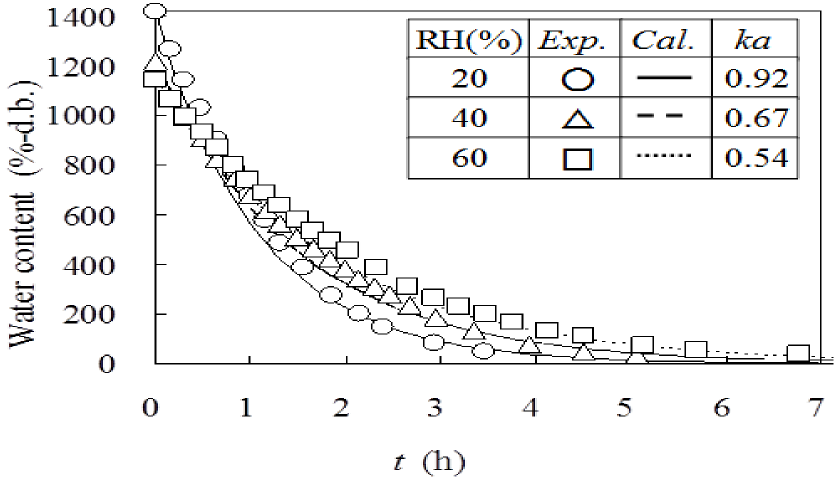
3.1. Maillard Reaction Controle By Humidity of Drying Air

The dehydration response curves of LK drying are affected by the relative humidity (RH as M_1) of the drying air. Figure 2 shows a comparison of the dehydration curves on the different RHs during the LK drying at 40 °C. One can recognize that the higher RH of the drying air becomes, the lower the dehydration rate is. In Eq. (1), *ka* can be determined using Eq. (2):

$$C_A = C_{A0} \cdot exp(-k_a \cdot t) \quad \cdots\cdot(2)$$

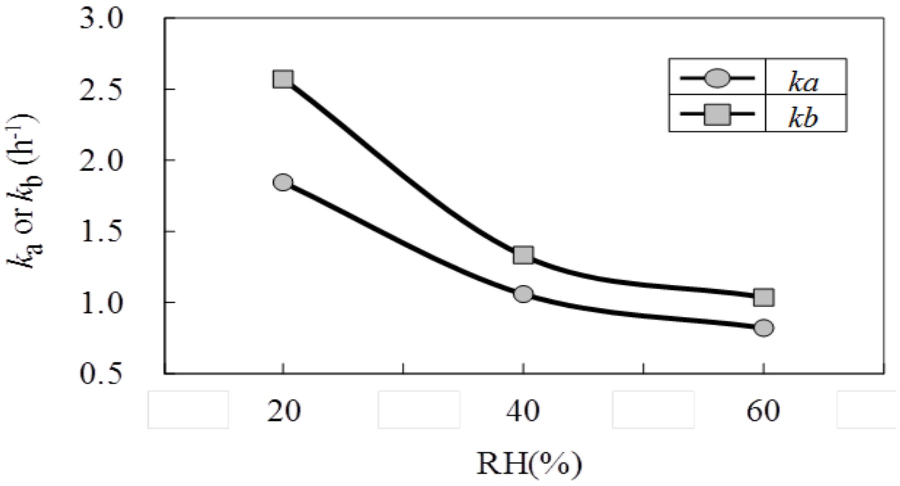
where C_{A0} is the initial concentration of *A* and *t* is the reaction time. The reactant component C_A is determined by the dehydration curve experimentally evaluated at the reaction time *t*.

Figure 2. Dehydration response curves as a function of RH and the calculated curves based on the Equation (1) (T_D=40 °C)



On the other hand, when our presumption that the component *C* in Eq. (1) corresponds to the color parameter of *ΔE** is accepted, *kb* could easily be determined from the response curves of the *ΔE** during the LK drying. This means that the response of the concentration of C (C_C), could be experimentally evaluated from the response of *ΔE**. The RH dependencies of the *ka* and *kb* values obtained at T_D = 60 °C are shown in Fig. 3. The Maillard reaction constants *ka* and *kb* are strongly influenced by the RH, and the *ka* and *kb* values become smaller under higher RH conditions as *ka* equals 1.8–0.81 h^{-1} and *kb* equals 2.6–1.0 h^{-1}.

Figure 3. RH dependency of *ka* and *kb* for Maillard reaction model of the LK-drying (T_D = 60 °C)

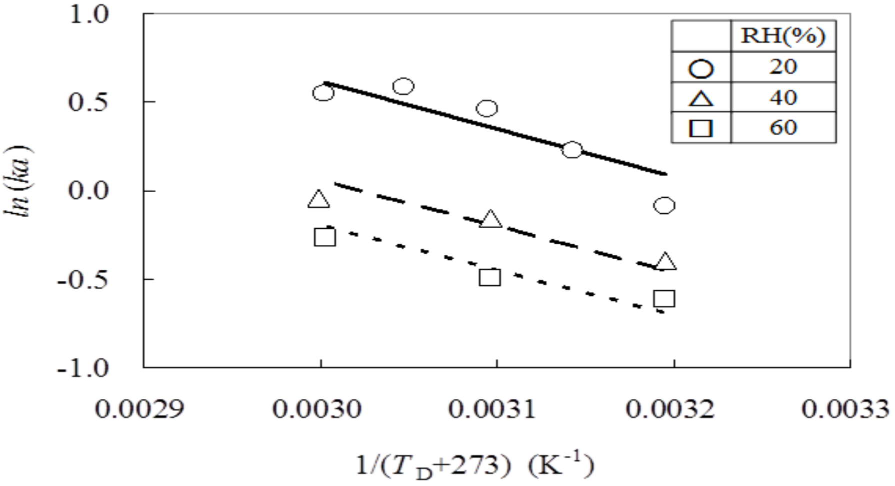


The *ka* values evaluated in Fig. 3 can be replotted using the Arrhenius equation, as demonstrated in Fig. 4. The *ln*(*ka*) values evaluated for each different RH were roughly distributed along each straight line, and the three slopes of straight lines evaluated at RH = 20, 40, and 60 % gave the same activation energy of the dehydration to be E_{ka} = 22.0±1.0 kJ/mol without depending on RH. This result strongly indicates that the increase in the RH of the drying air gave a reduction of *ka* without changing E_{ka}. Quantitatively evaluating the correlation between *ka* and RH, Equation (3) can be proposed:

$$ka = \left\{ \frac{k \cdot T}{h} \times exp\left(\frac{\Delta S}{\alpha_1 \cdot RH + \beta_1} \cdot \frac{1}{R} \right) \right\} \times exp\left(\frac{-E_{ka}}{R \cdot T} \right) \quad \text{....(3)}$$

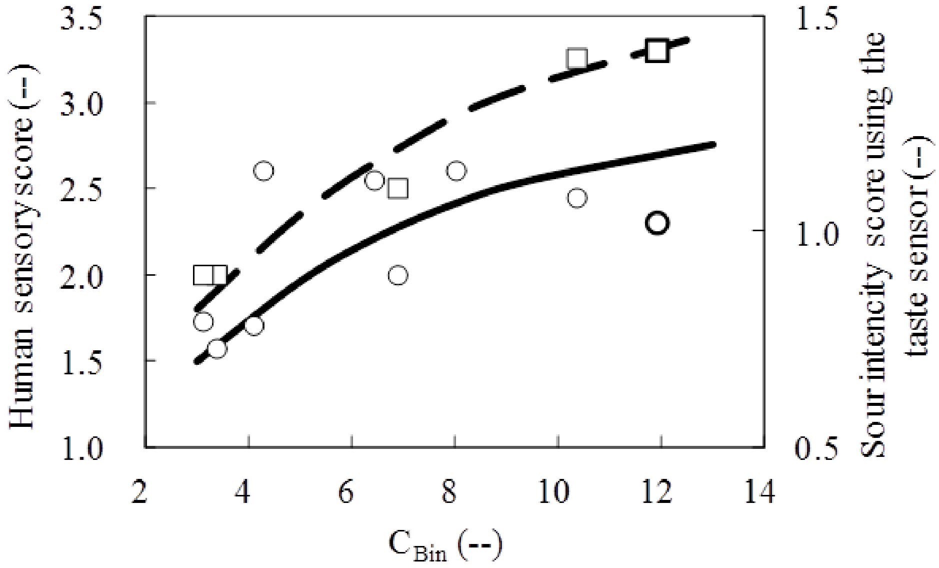
Where *t* is temperature (= T_{D}+273.15)(K), *h* is the Plank constant (J·s), *S* is entropy (J/K), E_{ka} is the activation energy of *ka* (kJ/mol), *R* is the gas constant (mol/kJ·K), and *k*, α_1, and β_1 are constants. Assuming that *ΔS* gives a constant value without depending on the drying temperature, from a calculation of the correlation between *ln*(*ka*) and $1/(\alpha_1 \cdot \mathrm{RH}+\beta_1)$ under different T_{D}s, the α_1 and β_1 values were determined to be 1.0 and 1.4, respectively. By using the *ka* and *kb* values obtained, it is possible to simulate the response curves for the components C_A, C_B, and C_C.

Figure 4. Arrhenius plot of *ka* as a function of RH



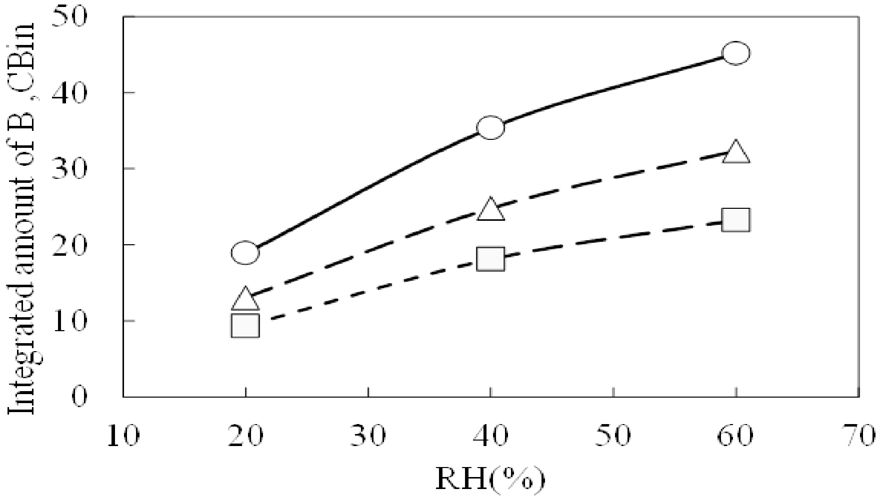
From the simulated curves of C_B, one can evaluate the integrated amount of the B component (C_{Bin}), which would strongly be influenced by the RH. The C_{Bin} contributes to a flavor value of the dried LK product, as shown in Figure 5. Fig. 5 shows sourness intensity scores from both human and commercial taste sensors for the dried LK products as a function of C_{Bin}. One can recognize that the higher the C_{Bin}, the higher the flavor score. This result means that the amount of C_{Bin} contributes to the quality of the dried products.

Figure 5. The taste score as a function of the integrated amount of C_B, C_{Bin}.; LK



Our interest is focusing on the quantitative relation between the amount of the C_{Bin} and RH. The C_{Bin} could easily evaluated by the computer simulation. The relation between the C_{Bin} and RH was demonstrated in Figure 6. The results obtained clearly demonstrated that the higher RH values gave the higher intermediates and the higher drying temperature gave the higher amount of the C_{Bin}. These results clearly demonstrated that the RH regulation would be employed as a useful tool for one of the optimum drying operation for the optimum production of the drying product.

Figure 6. The integrated amount of C_B (C_{Bin}) as a function of RH; LK

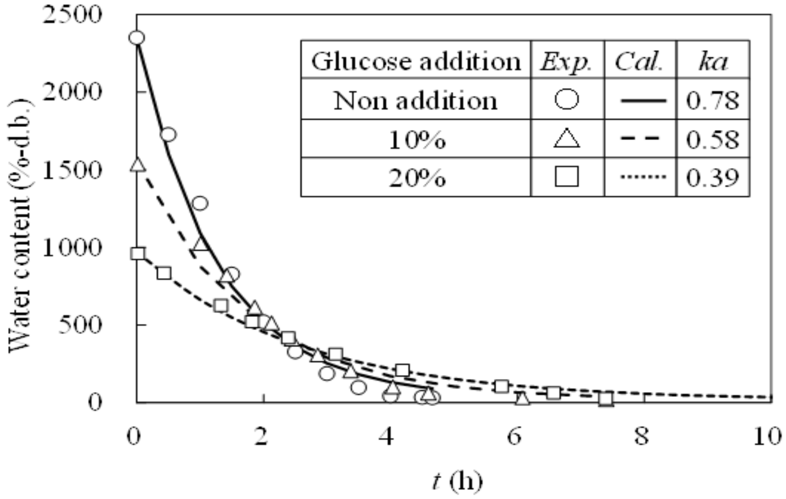


3.2. Maillard Reaction Mechanism Controle Due to the Glucose Addition in the CB-Dehydration

Glucose (GC) as a modifier (M_2) would strongly contribute to reducing the CB dehydration reaction rate as an inverse parameter, as shown in Fig. 1, because GC works as a reagent, reducing the molecular mobility of water species in the CB. Figure 7 demonstrates the experimental dehydration response curves of the CB samples, each of which was dipped in a glucose solution of a different concentration. The initial water content (W_D) of CB at $t = 0$ was reduced to 2250 %-d.b. depending on the concentration of the glucose dipping solution (GC = 0 %), 1540 %-d.b. at GC = 10 % and 960 %-d.b. at GC = 20 %. These results clearly demonstrate that the GC addition contributes to reducing the amount of water species in the CB.

Focusing on the dehydration response curves in Fig. 7, one may recognize that the time to reach an apparent equilibrium water content (W %-d.b. = 0), designated as t_{We}, became greater with increasing GC, such as t_{We} = 5.5 h at GC = 0 %, t_{We} = 6.5 h at GC = 10 %, and t_{We} = 11 h at GC = 20 %. These results indicate that the higher the glucose concentration, the lower the dehydration rate during the CB drying process.

Figure 7. Dehydration response curves as a function of GC and the calculated curves based on the consecutive reaction model. T_D = 55°C ; CB



As in the case of the LK drying in Fig. 2, assuming that the C_A-decreasing response for the CB drying corresponds to the dehydration response curves, the *ka* for CB drying was also evaluated using Eq. (2). The *kb* values of Eq. (3) were also evaluated by using the response curve of the ΔE^* as an accumulated product C_C during the CB drying. A computer-optimization fitting to the experimental response curves can easily be used to evaluate the optimal values of *ka* and *kb*. Figure 8 shows a comparison between the calculated and experimental response curves of C_A and C_C at T_D = 55 °C. For the C_B response curves, only the calculated values are exhibited.

Figure 8. Fitting of the computer simulation response curves to the experimental data based on the consecutive reaction model; CB; (GC= (A) 0, (B) 10 and (C) 20 wt%); RH = 20 %, T_D = 55ºC

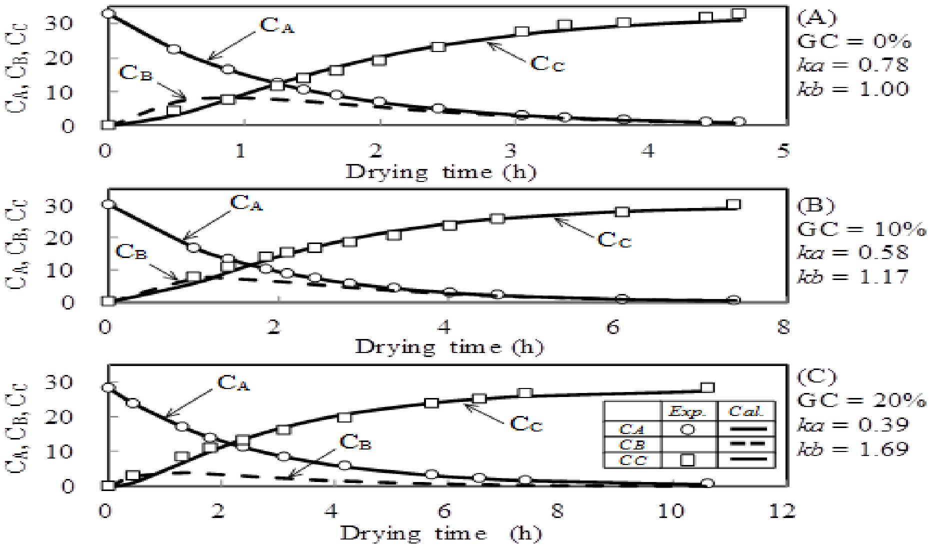


Figure 9 shows an Arrhenius plot of the *ka* evaluated from the dehydration response curves of CB drying. The *ln*(*ka*) values evaluated for each different glucose concentration were roughly distributed along a straight line, and the two slopes of the straight lines at GC = 10 % and GC = 20 % showed the activation energy of dehydration to be 34.3 ±1.0 kJ/mol without depending on GC.

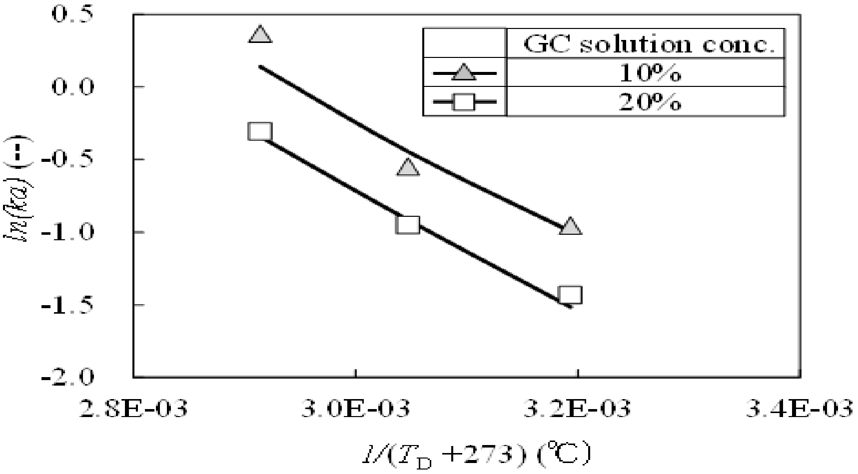
When a consideration similar to Eq. (3), derived from LK drying, is accepted, then Equation (4) can be proposed for CB drying modified by a glucose solution.

$$ka = \left\{ \frac{k \cdot T}{h} \times exp\left(\frac{\Delta S}{\alpha_2 \cdot GC + \beta_2} \cdot \frac{1}{R} \right) \right\} \times exp\left(\frac{-E_{ka}}{R \cdot T} \right) \quad ....(4)$$

Assuming that ΔS gives a constant value without depending on the drying temperature T_D, the α_2 and β_2 values were determined to be 1.0 and 300, respectively.

These results show that the first step in approximating the Maillard reaction of LK and CB drying presented in this study can be accepted, including the modification treatments of both RH (Modifier 1) and GC (Modifier 2).

Figure 9. Arrhenius plot of *ka* as a function of GC; CB



4. CONCLUSIONS

Explaining the dynamic behavior of the LK and CB dehydration processes, a simplified reaction model, $A \xrightarrow{ka} B \xrightarrow{kb} C$, was proposed for the complicated Maillard reaction. To develop an optimal food drying process, the RH for the LK drying and GC for the CB drying were effectively used as modifiers (M_1 and M_2) to control the chemical activity of the water species retained in the food products. As the results, the M_1 and M_2 could regulate the values of *ka* without changing the activation energies. The experimental dynamic behaviors of C_A and C_C were consistently explained by the proposed simplified model. The computer simulation of the dynamic response curves reasonably showed that the larger amounts of the evaluated intermediate components (C_{Bin}) gave a better account of the human taste of the dried LK.

Nomenclature

a^*	Red/Green cordinate values measured with chromameter
A	reactant for the simplified reaction model
b^*	Blue/Yellow cordinate values measured with chromameter
B	intermediate for the simplified reaction model
C	product for the simplified reaction model
CB	Cabbage
C_A	concentration of reactant A
C_{A0}	concentration of reactant A evaluated before the drying
C_B	concentration of intermadiate B
C_{Bin}	integrated amount of C_B
C_C	concentration of product C
E_{ka}	activation energy of *ka* (kJ/mol)
E^*	color parameter identified by the color factors, L^*, a^* and b^*
GC	Glucose
h	Plank constant (J·s)
k	constant
k_a	first step rate constant of the simplified reaction model
k_b	second step rate constant of the simplified reaction model
LK	Leek
L^*	brightness of color measured by the chromameter
M_1	first modifier using the relative humidity for the leek drying
M_2	second modifier using the glucose for the Cabbage drying
R	gasconstant (=8.31447) (mol/kJ·K)
RH	relative humidity of the drying air (%)
S	entropy (J/K)
T	temperature (= T_D+273.15) (K)
T_D	drying temperature (ºC)
t	reaction time (h)
t_{We}	time to reach an apparent equilibrium water content (h)
W_D	initial water content (%-d.b.)

Greek letters

α_1	constant for the leek drying
α_2	constant for the cabbage drying
$ß_1$	constant for the leek drying
$ß_2$	constant for the cabbage drying

REFERENCES

[1] Y. Konishi and M. Kobayashi, "Quantitative evaluation of the design-parameters requested in a drying operation of beef and pork, AIDIC Conference Series, Vol. 9, pp177, (published by AIDIC & Reed Business Information S.p.A.)," 2009.

[2] Y. Konishi and M. Kobayashi, "Challenge to the food engineering due to a hybrid method of chemical engineering-proton NMR technique -Meat jerky design by the scientific parameters," *Chem. Eng. Trans.*, vol. 20`, pp. 217-222, 2010.

[3] Y. Konishi and M. Kobayashi, "Dynamism of the water species as a probe molecules in foods," *Chem. Eng. Trans.,* vol. 24, pp. 475-480, 2011.

[4] Y. Konishi and M. Kobayashi, "The new evidences derived from a consecutive reaction model for the maillard reaction," *Chem. Eng. Trans.,* vol. 27, pp. 307-312, 2012.

[5] Y. Konishi and M. Kobayashi, "Challenging evaluation of the hybrid technique of chemical engineering - proton NMR technique for food engineering, Advances in Chemical Engineering, Ed. Z. Nawaz and S. Naveed., pp69-92, published by InTech, Croatia," 2012.

[6] Y. Konishi and M. Kobayashi, "Oscillating self-organization of hydration water in foods derived by a forced temperature cycling," *Chemical Engineering Transaction,* vol. 32, pp. 1789-1794, 2013.

[7] Y. Konishi and M. Kobayashi, "Advantage of the hybrid method of chemical engineering-proton NMR technique for food engineering," *Food Science and Technology Research,* vol. 19, pp. 717-727, 2013.

[8] Y. Konishi and M. Kobayashi, "Dualism of thehydration water visualized in drying processes of foods," *Drying Technology,* vol. 34, pp. 883-891, 2016.

[9] T. P. Labuza, "Interpreting the complexity of the kinetics of the Maillard reaction, In “the Maillard reaction in Food, Nurition and Health” Labuza,T.P., Reineccuis,G.A., Baynes,J., and Monnier (Eds), Royal Society of Chemistry, London," 1994.

[10] W. Baltes, J. Kunert-Kirchoff, and G. Reese, *Model reactions on generation of thermal aroma compounds, In "Thermal Generation of Aroma", Pariament T.H. et al.,(Eds),* 1989.

[11] K. Eichner and W. Wolf, *Maillard reaction products as indicator compounds for optimizing drying storage conditions, “Maillard reaction in Foods and Nutrition”, In: Waller G.R., Feather M.S.(Eds), ACS Symposium Series, 215,* , 1983.