Proceedings of European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Innovated Food Design Visualized in the Nonlinear Analysis of Multi-functional Water Species Based on the Specified Physicochemical Parameters

Yasuyuki KONISHI,[a] Masayoshi KOBAYASHI[b]

[a]*Research and Development Department, Hokkaido Industrial Technology Center, 379 Kikyo-cho, 041-0801 Hakodate, Hokkaido, Japan*
[b]*Chemical Engineering Department, Advanced Technology Institute for Northern Resources, 8-6 Tonden-2Jo-2chome, Kitaku, 002-0852 Sapporo, Hokkaido, Japan*

Abstract

An innovated food design was challengingly studied in the course of the nonlinear analysis of multi-functional water species by using a drying process of Japanese squid at 30 ~ 60°C. An optimal design of the drying process requested was effectively visualized by using four physicochemical parameters as a function of the three multi-functional water species. The three water species were clearly distinguished as species-A_1 (weakly restricted-water species), species-A_2 (strongly restricted-water species) and species-A_2' (unfrozen-water species), all of which were exactly characterized by the four physicochemical parameters. The four parameters were individually evaluated as effective diffusivity (*De*), activation energy of *De* (E_D), correlation time (τ_C) derived by a proton NMR technique, and bacterial growth rate coefficient (*m*). Species-A_1 was described by a higher *De*, lower E_D, lower τ_C, and higher *m*. Species-A_2 was characterized by widely distributed values of *De*, E_D, and τ_C, and *m*=0. Species-A_2' was suddenly recognized in the course of temperature decrease at -15°C, accompanying a hysterisis of the Arrhenius plot of $1/\tau_C$ and new activation energy for the rotation rate of water molecule. All the dehydration curves obtained were sufficiently simulated by a proposed water tank model.

keywords: Three water species, bacterial growth coefficient, effective moisture diffusivity (*De*), activation energy of *De*, hysterisis of correlation time

Nomenclature

$A_I - A_{III}$	*constants designated by Eqs.* (*10*)-(*12*) (-)
De	*effective moisture diffusion coefficient* (m^2/h)
De^0	*frequency factor of moisture diffusivity* (m^2/h)
E_D	*activation energy of moisture diffusivity* (kJ/mol)
$E\tau_C$	*activation energy of water molecule rotation* (*kJ/mol*)
f_S	*proportion of strongly restricted-water* (=*1 – fw*) (-)
f_W	*proportion of weakly restricted-water* (-)

k_S *dehydration constant for strongly restricted-water* (h^{-1})
k_W *dehydration constant for weakly restricted-water* (h^{-1})
I *nuclear spin quantum number of water proton* (=0.5) (--)
L_a *half distance of a-axis of the rectangular sample* (m)
L_b *half distance of b-axis of the rectangular sample* (m)
L_c *half distance of c-axis of the rectangular sample* (m)
m *bacterial growth rate coefficient* (h^{-1})
r *proton-proton distance of water molecule* (=0.16nm)
T *squid sample temperature for the proton NMR technique* (°C)
T_2 *spin-spin relaxation time of water proton* (s)
T_D *drying temperature* (°C)
t *drying time* (h)
W *moisture content at the drying time t* (%-d.b.)
W_0 *initial moisture content at the time of PUP operated* (%-d.b.)
W_D *initial moisture content of drying flesh sample* (%-d.b.)
We *equilibrium moisture content* (%-d.b.)
W_{R1} *moisture content ratio of region I at* W_0 >120%-d.b. (%-d.b.)
W_{R2} *moisture content ratio of region II at* W_0 <120%-d.b. (%-d.b.)

Greek letters

$\beta_1 - \beta_3$ *constants* (h^{-1})
$\beta'_1 - \beta'_3$ *constants* (m^{-2})
π *the ratio of the circumference of a circle to its diameter* (=3.14)
γ *gyromagnetic ratio of proton* ($=2.675\times10^8$ $rad \cdot T^{-1} \cdot s^{-1}$)
τ_C *correlation time of water proton* (s)
$\hbar$ *modified Plank's constant* ($=6.63\times10^{-34}$ $J \cdot s$)
ω_0 *resonance frequency* ($=3.14\times10^9$ s^{-1})

1. Introduction

For optimal design of food to store it for a long time, an appropriate drying process and freezing process are strongly requested. In the two processes, as is well known, moisture distributed in the food matrix is one of the most important substrates which sensitively regulate to quality of food. The state of the moisture is multi-functionally and dynamically varied depending on a kind of foods and moisture content of foods. A large number of researchers have studied the moisture states in the foods indicating variety of the states such as gaseous water (Waananen and Okos, 1996), free water (Rockland and Nishi, 1980; Caurie, 1971), weekly restricted water, strongly restricted water, unfrozen water, multilayered water and bound water (Rockland and Nishi, 1980). Konishi and Kobayashi (1999; 2001(a); 2001(b)) demonstrated two different moisture content regions of food (regions I and II) in which variety of water species was distributed such as mobile liquid-water and gaseous water, by using a drying operation of a fish past sausage used as a model food. The two species were clearly distinguished at a specified moisture content of 100%-d.b., indicating the mobile water to be weekly restricted water species at W_0>100%-d.b.(region I) and the gaseous water to be available at W_0<100%-d.b.(region II). The effective diffusivity (De) of the two species demonstrated a characteristically different behavior as a function of moisture content of the sausage. *De* of the mobile water was fallen in the range of 1.3×10^{-6} ~ 2.1×10^{-6} m^2/h and the gaseous water gave $De=1.3\times10^{-6}$ m^2/h at T_D=35ºC. The activation energies (E_D) of the effective moisture diffusivity for the two species were also evaluated as 16.5kJ/mol for the mobile water and 9.6kJ/mol for the gaseous water. From these evidences obtained, one can recognize that the dried foods are effectively used to examine a variety of multifunctional water species and characterized by the two parameters, *De* and E_D.

To quantitatively distinguish the multifunctional water species distributed in food body matrix, proton NMR method has commonly been used and demonstrated interesting evidences. Yano, Tanaka, Suzuki and Kanzaki (2003) demonstrated, using two ^{1}H-NMR relaxation methods, two different characteristic behavior of water species depending on the two different freezing temperature regions, -1 ~ -5ºC(region-A) and -13 ~ -28ºC(region-B), by employing a bamboo shoot, potatoes, and a cod. In the region-A, the amount of the mobile water was a rate determining factor for the freezing behavior whereas, in region-B, the mobility of water molecule was an important factor. The results obtained strongly suggest that the moisture state is sensitively changed depending on the freezing temperature region. One may recognize that the proton NMR method is a useful tool to evaluate the moisture state in food, and the correlation time (τ_C) derived from the NMR method is an important parameter.

In the course of food design process, as is well known, bacterial growth brings difficult problems to keep the food in a good quality. The bacterial growth rate is strongly influenced by moisture content and the state of water molecule (Heiss and Eichner, 1971), suggesting that the state of water species strongly contributes to the bacterial growth rate coefficient (*m*) in food.

For the design of food quality in the course of drying operation, computer simulation technique can effectively be used to evaluate dehydration curves obtained. Overhults, White, Hamilton and Ross (1973) simulated the dehydration response curves for a soybean drying process at 37.8 ~ 104.4ºC using an exponential equation developed by Page (1949). Shepherd and Bhadwaj (1988) examined a single-term diffusion model to describe the thin layer drying characteristics of the whole pigeon pea. Ezeike and Otten (1991) proposed a two-term exponential model for the drying of unshelled melon seeds. In our previous papers (Konishi and Kobayashi, 2001(a) and 2001(b); Konishi, Horiuchi and Kobayashi, 2001(a) and 2001(b)), a water tank model was proposed as a mathematical model to describe the dehydration curves of a fish past sausage. The generalized application of the models proposed to various kinds of foods is, however, still unclear.

The objectives of this study are, employing a Japanese squid as a model food, (1) to distinguish the multifunctional water species by using specified physicochemical parameters as effective diffusivity (*De*) and activation energy of the diffusivity (E_D), (2) to apply a proton NMR method for the evaluation of the multifunctional water species using correlation time (τ_C), (3) to demonstrate a further discrimination of the multifunctional water species by using the bacterial growth rate coefficient (m), and (4) to simulate the dehydration curves obtained using the water tank model.

2. Experimental Procedure

For a model sample, a Japanese common squid (50mm square and 8±1.5mm in thickness, initial moisture content of 300 ~ 360%-d.b. (dry base, W_D)) was used. Through all the drying operation, drying air with a flow rate of 0.7m/s was introduced into a drying room passing through a rectifiable compartment with regulating the humidity. The drying temperature was electrically controlled within ±2ºC at given temperatures. The sample was placed in a stainless steel net basket (10 meshes) that was mechanically hung from a strain gage transducer in the dryer. During the drying process, a poultice-up process (designated as PUP) was operated to keep the moisture distribution in the squid sample uniform. For the PUP, the samples were stored in an incubator for 36h, the temperature of which was regulated at 2°C. The PUP was operated at a given moisture content (W_0) in the range of 15 ~ 360%-d.b. The sample weight was continuously recorded by the output of a strain-gage transducer using a data-logger. Thirty, 40, and 50°C were chosen as the drying temperatures (T_D). In the present drying conditions, it was previously reconfirmed that all the drying operations for the squid were within a falling-rate period.

For the readsoption of water molecule to make a variety of W_0, the dried sample was stored into a humidifier for a given time; the temperature and humidity of the humidifier were regulated at 23.5±0.5ºC and 90±5% respectively. The W_0 for the water-readsorbed sample was controlled by the storage time in the humidifier.

The bacterial count of the squid sample was measured by a plate culture method using Tryptone Soya Agar (Oxid) at 30°C for 48h after the PUP given at specified W_0.

For the characterization of moisture species in the squid, a nuclear magnetic resonance (NMR) technique was used to measure the ^{1}H-NMR spectra and a spin-spin relaxation time (T_2) of water proton. The squid samples which were cut into the pieces of 2×2×10mm were inserted into an NMR sample tube (9mmϕ × 15mm in length). ^{1}H-NMR spectra were obtained by a JEOL A-500 FT-NMR spectrometer operating at 500MHz for protons. The observed frequency width was 20kHz. 90º pulse width was 12.5μs and the number of pulse repetitions was 8. The proton chemical sifts were measured by using a slight amount of water containing deuterium oxide as an external reference. All the NMR measurements were performed at 23.5±0.5ºC. The spin-spin relaxation times were obtained by the CPMG method.

The value of T_2 obtained is related to the correlation time (τ_C) by using *Eq*.(1).

$$\frac{1}{T_2} = \frac{\gamma^4 \cdot \hbar^2 \cdot I(I+1)}{5r^6}\left(3\tau_c + \frac{5\tau_c}{1+\omega_0{}^2 \cdot \tau_c{}^2} + \frac{2\tau_c}{1+4\omega_0{}^2 \cdot \tau_c{}^2}\right) \quad \text{..................(1)}$$

where T_2 is the spin-spin relaxation time of the water proton (s), γ is the gyromagnetic ratio of a proton (=2.675×10^8 rad·T^{-1}·s^{-1}), $\hbar$ is the modified Plank's constant (=6.63×10^{-34} J·s), I is a nuclear-spin quantum number of a water proton (=0.5), r is the proton-proton distance of a water molecule (0.16nm), ω_0 is the resonance frequency of NMR (=3.14×10^9 s^{-1}), and τ_C is the correlation time of a water proton (s). Using this equation, τ_C values at any given T_2 can be evaluated.

Further detailed experimental procedures and the evaluation details of *De* have been presented elsewhere (Konishi, Horiuchi and Kobayashi, 2001(a); Konishi and Kobayashi, 1999(a)).

3. Results and Discussion

3-1.Dynamic Behavior of Dehydration Curves in a Drying Process

Fig.1(A) shows a dehydration response curve (curve-(*a*)) obtained under a continuous drying operation for the squid (W_0=306%-d.b.) at T_D=50ºC. The graphical differentiation of the curve-(*a*) proposes a dehydration rate and the rates evaluated at any elapsed time can be plotted as a function of the time as shown by curve-*a*' in Fig.1(B). In the course of the curve-(*a*) in Fig.1(A), eight PUP operations were introduced at points (*b*) ~ (*i*) which were characterized by different moisture content as W_0=220 ~ 40%-d.b. Each of the eight PUP operations produces a new dehydration curve and the graphical differentiation of the new curves obtained gives a newly specified dehydration rate. The dehydration rates evaluated at the eight points (*b*) ~ (*i*) in Fig.1(A) were shown by curves-(*b'*) ~ -(*i'*) in Fig.1(B). As can be seen from the comparison between the curve-(*a'*) and the curves-(*b'*) ~ -(*i'*) in Fig.1(B), all the curves-(*b'*) ~ -(*i'*) gave the dehydration rates higher than the curve-(*a'*) in Fig.1(B). One can recognize a stepwise increase of the dehydration rates. These increases are resulted from the stepwise increase in the moisture content of the squid surface layer due to the PUP operation. The acceleration degree of dehydration rate after the PUP was strongly influenced by the W_0-values at the points (*b*) ~ (*i*) located on the curve-(*a*) in Fig.1 (A). As has been mentioned in the previous section, the dehydration operation is limited in a falling rate period. In

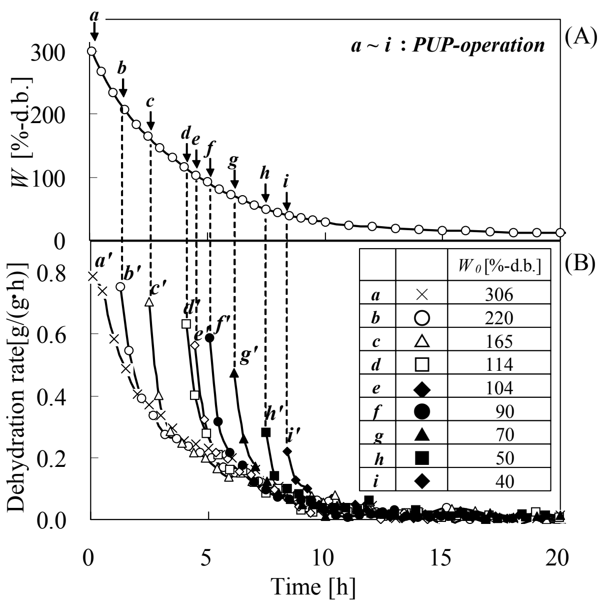

Fig.1 Acceleration behavior of drying rate derived from PUP-operation for the squid (T_D=50°C)

this period, the effective moisture diffusivity (*De*) can be evaluated by using Eq.2 (Jason, 1958).

$$\frac{W-We}{W_D-We}=\left(\frac{8}{\pi^2}\right)^3 exp\left(\frac{-\pi^2\cdot De\cdot t}{4}\cdot\left(L_a^{-2}+L_b^{-2}+L_c^{-2}\right)\right)\ldots\ldots\ldots\ldots(2)$$

where W is the moisture content at the drying time t, We is the equilibrium moisture content, W_D is the initial moisture content of a drying fresh sample, t is the drying time, and L_a, L_b, and L_c are the half-distances of the sample width.

At the initial points of the curves-(*a'*) ~ -(*i'*) in Fig.1 (B), the values of *De* were evaluated and plotted as a function of W_0 as shown in Fig.2. The *De* obtained showed a characteristic behaviour exhibiting two regions as a constant value region at W_0>120%d.b. (designated as region I) and a gradual increase region at W_0<120%d.b. (designated as region II). From the two regions, one may recognize two different water species, water species-A_1 which contributes to an identical *De* [=1.8(±0.2)×10^{-6} m^2/h] without depending on W_0 in region I and water species-A_2 which is characterized as a gradual increase from De=0.6×10^{-6} to De=1.7×10^{-6} m^2/h with increasing W_0 in region II.

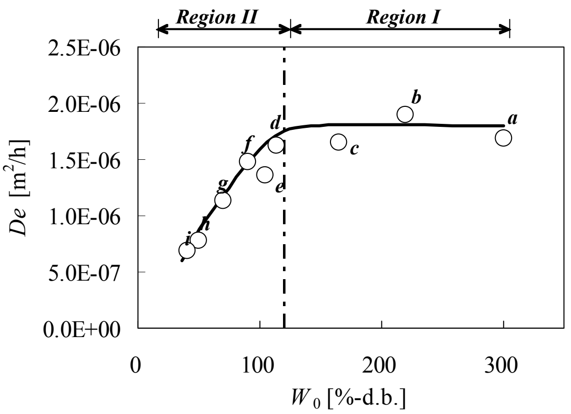

Fig.2 *De* as a function of W_0 for the squid (T_D=40°C).

De can be characterized by activation energy of diffusion using a simple Arrhenius-type relationship:

$$De = De^0 exp\left[\frac{-E_D}{R\cdot(T_D+273)}\right]\ldots\ldots\ldots\ldots(3)$$

where De^0 is frequency factor (m^2/h), E_D is activation energy of effective moisture diffusivity (kJ/mol), R is gas constant (8.314J/K·mol), and T_D is drying temperature (ºC).

The Arrhenius plots of *De*-values obtained at T_D=30, 40 and 50ºC give a good straight line and E_D's are evaluated at various moisture contents. The E_D obtained clearly demonstrates again two regions, identical value of 17(±0.2) kJ/mol in the region I and gradual increase value from 25 to 35kJ/mol with increasing W_0 in the region II. Based on the results of *De* and E_D in the two regions, one may recognize that species-A_1 is mobile water with uniformed and characterized by higher *De*-values and lower E_D-values, and species-A_2 is restricted water with widely distributed *De*- and E_D-values.

3-2.Mutifunctional Water Species Distinguished by the Bacterial Growth Behavior

As has been mentioned in the previous section, water species-A_1 effectively contributes to the moisture diffusion in region I whereas, in region II, water species-A_2 is available for the characteristic moisture diffusion indicating the restricted water molecule in the squid muscle. The two water species can be distinguished again by bacteria growth behavior. The bacteria observed on the squid skin were recognized mainly as staphylococcus and micrococcus. Noting the bacterial contamination of the squid skin, one can easily evaluate the bacteria growth which is sensitively influenced by both the moisture content (W_0) and a relative humidity of supplied drying air flow (RH). Fig.3 illustrates a bacteria count as a function of W_0 and RH. As one can recognize from the five curves obtained, the bacterial growth was completely limited at both W_0<120%-d.b. (region II: species-A_2 to be available in this region) and RH = 30% (designated as RH_{30}). This limitation clearly demonstrates the bacterial growth to sensitively be regulated by the W_0 and the RH. In other wards, the water species-A_2 should work to prevent bacterial contamination and the RH_{30} gives a critical relative humidity to completely control the bacterial contamination even at the region of species-A_1 (at W_0>120%-d.b.: region I). Since the bacterial count was measured as a function of time at various W_0, the bacterial growth rate coefficient (m) can be evaluated as m = 0 at RH = 30, m = 0.24 at RH = 55, m = 0.34 at RH = 65, m = 0.43 at RH = 75 and m = 0.55h^{-1} at RH = 85% within the region of species-A_1. In the regions of species-A_2 (at W_0<120%-d.b.) and RH<RH_{30}, the value of m exactly becomes zero indicating no bacterial growth. The two factors, species-A_2 and RH_{30}, thus can effectively be used as an operating parameter to preventing food from the bacterial contamination.

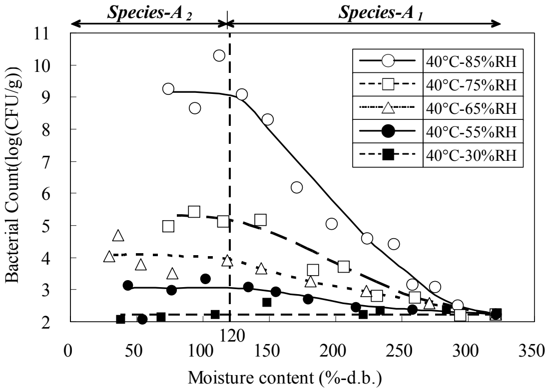

Fig.3 Bacterial count as a function of moisture content and the relative humidity.

3-3. Nonlinear Behavior of the Correlation Time of Water Proton

As is well known, water molecules of food are commonly restricted from the food body matrix. The degree of the restriction is strongly influenced from the matrix structure of food and the conditions of circumstances especially moisture content and temperature. To evaluate the degree of the restriction for the water species, the proton NMR method can effectively be used. In the present study, the correlation time (τ_C) was chosen to distinguish multifunctional water species. The value of τ_C is dynamically varied depending on a kind of water species as species-A_1 to be 4.8×10^{-9}

s and species-A_2 to be $1.0\times10^{-8}\sim1.2\times10^{-7}$ s. From the difference of the absolute value of τ_C between the two species, one can exactly recognize species-A_1 to be a weekly restricted-water and species-A_2 to be strongly restricted-water.

Since $1/\tau_C$ means a rotation rate of water molecule, the value can be expressed by an Arrhenius equation. Fig.4 illustrates the Arrhenius plot of $1/\tau_C$. The locus of the plot gave an anomalous behavior depending on the locus of temperature decrease or temperature increase indicating a typical hysterisis. In the course of temperature decrease from 30 to -30°C, the value of $\ln(1/\tau_C)$ steeply decreased at -10°C and, in the locus of temperature increase course from -30 to 30°C, it linearly increased up to 0°C and fell on the line of the previous curve obtained in the temperature decrease course. This hysterisis behavior was exactly reproducible, and it was reconfirmed that the reversibility of the linear relation between 0 and -25°C in the course of temperature increase was completely examined, indicating an activation energy of the rotation to be 40(±2)kJ/mol. One may call this water species as species-A_2' different from species-A_1 and -A_2. The species-A_2' was, in the course of the temperature decrease from 30 to -30°C, suddenly recognized at the temperature range between -10 and -25°C, suggesting a happening of a self organization of unfrozen water molecule. This nonlinear behavior of the Arrhenius plot for the rotation rate of the water species was commonly observed for other foods as salmon, scallop and sardine. Species-A_2' is thus recognized as the self organization of the species-A_2' newly formed from species-A_1 and -A_2. For further detailed discussion on the anomalous hysterisis behavior, more visualized experimental data based on the physicochemical analysis should be needed in future.

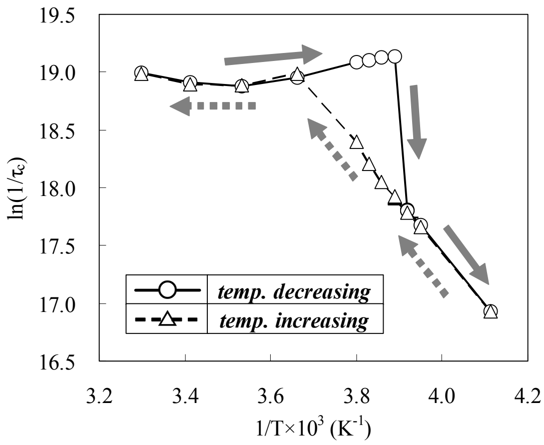

Fig.4 Hysterisis behaviour of the Arrhenius plot of $1/\tau_C$

3-4.Model Description and Computer Simulation of the Dehydration Curves

As mentioned in the above section, the squid-drying period consists of a falling rate period, which indicates the dehydration rate to be limited by moisture diffusion from the internal to the surface layer. Fig.5 illustrates the experimental dehydration curves as a function of the moisture content. To simulate the dehydration curves, a water tank model (Konishi, Horiuchi and Kobayashi, 2001(b)), which was previously applied to the drying process of the fish past sausage, could be

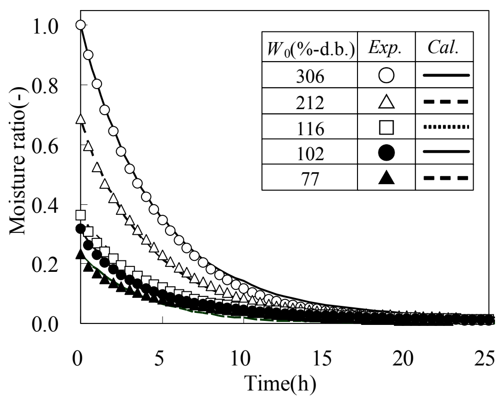

Fig.5 Comparison of the calculated curves and the experimental curves at 40ºC

used. Fig.6 is a schematic of the tank model proposed. In the region I, the dehydrated moisture is separately supplied from the two water tanks consisting of weakly restricted water for the first tank (#1) and strongly restricted water for the second tank (#2), whereas, in the region II, the dehydration moisture is supplied from third tank (#3) of moisture which is same as the second tank (#2).

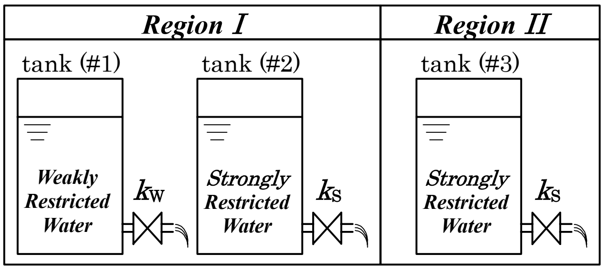

Fig.6 Schematic explanation of the tank model.

For a mathematical description of the tank model, the following assumptions are proposed:

(1) The dehydration process from the sample squid is adequately approximated by effluent moisture from two tanks #1 and #2 for the region I and the effluent moisture from tank #3 which is same as tank #2 for the region II.
(2) The rates of effluent moisture from tanks #1, #2 and #3 are controlled by three dehydration constants, k_W, k_S and k_S respectively.
(3) k_W and k_S are described as a function of diffusion coefficients, De_W and De_S, respectively.
(4) The temperature dependencies of k_W and k_S obey the activation energies of De_W and De_S, respectively.
(5) De_W and De_S, which are given at the initial stage of drying with specified initial moisture content (W_0), can effectively contribute to the characteristics mode of the dehydration curves obtained.

In the region I, the mathematical descriptions are given by the following equations:

$$\frac{-dW_{R1}}{dt} = \frac{-dW_W}{dt} + \frac{-dW_S}{dt} \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$\frac{-dW_W}{dt} = k_W \cdot W_W \quad \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

$$\frac{-dW_S}{dt} = k_S \cdot W_S \quad \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

when the drying started at the region II:

$$\frac{-dW_{R2}}{dt} = k_S \cdot W_S \quad \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

where W_{R1} and W_{R2} are the moisture ratio for the regions I and II, respectively; W_W and W_S are the moisture ratios for the weekly restricted water (species-A_1) and strongly restricted water (species-A_2), respectively.
For the three tanks, boundary conditions,
when W_0>120%-d.b.(region I), are

$W_S = A_I$ and $W_S = A_{II}$ at $t = 0$

when W_0<120%-d.b.(region II), are

$W_S = A_{III}$ at t = 0

$W_W = 0$ and $W_S = 0$ at $t = \infty$

The solutions of Eqs.(4) and (7) become

Region I **:** $W_{R1} = A_I \, exp(-k_W \cdot t) + A_{II} \exp(-k_S \cdot t)$……(8)

Region II **:** $W_{R2} = A_{III} \, exp(-k_s \cdot t)$…………………(9)

where A_I, A_{II} and A_{III} are rewritten by

$$A_I = \frac{W_0 - We}{W_D - We} \cdot f_W \text{ ……………….(10)}$$

$$A_{II} = \frac{W_0 - We}{W_D - We} \cdot f_S \text{ ……………….(11)}$$

$$A_{III} = \frac{W_0 - We}{W_D - We} \text{ ……………….(12)}$$

where f_W and f_S are the proportions for the amounts of the weakly restricted and strongly restricted water, respectively. Both f_W and f_S are experimentally obtained as follows.

$f_W = 6.1(\pm 2.8) \times 10^{-6}\ W_0 + 0.89(\pm 0.07)$………………(13)

$f_S = 1 - f_W = 0.89(\pm 0.07) + 6.1(\pm 2.8) \times 10^{-6}\ W_0$…………..(14)

Since the drying period is the falling rate period, the drying rate is limited by moisture diffusion from the internal to the surface layer of squid. The dehydration constants in Eqs. (8) and (9) can thereby be expressed as a function of moisture diffusivity:

$k_W = \beta_1' \cdot D\, e_w$………(15)

$k_S = \beta_2' \cdot De_s$………(16)

where β_1' and β_2' are constants (m^{-2}), which are given by the drying conditions.

Using Eq.(3), the two dehydration constants can be rewritten by the assumption of the activation energies for species-A_1 and -A_2 to be same:

$k_W = \beta_1' \cdot De_W = \beta_1' \cdot De_W^0 \cdot \exp(-E_D/(R \cdot (T_D+273)) = \beta_1 \cdot \exp(-E_D/(R \cdot (T_D+273))$……(17)

$k_S = \beta_2' \cdot De_S = \beta_2' \cdot De_S^0 \cdot \exp(-E_D/(R \cdot (T_D+273)) = \beta_2 \cdot \exp(-E_D/(R \cdot (T_D+273))$……(18)

where E_D is the activation energy for both species-A_1 and -A_2.

By using Eqs. (17) and (18), Eqs. (8) and (9) are rewritten by

$$W_{R1} = \left(\frac{W_0 - We}{W_D - We}\right)\cdot\left[f_W \cdot exp\left(-\beta_1 \cdot exp\left(\frac{-E_D}{R\cdot(T_D+273)}\right)\cdot t\right) + f_S \cdot exp\left(-\beta_2 \cdot exp\left(\frac{-E_D}{R\cdot(T_D+273)}\right)\cdot t\right)\right] \quad \text{.......................................(19)}$$

$$W_{R2} = \left(\frac{W_0 - We}{W_D - We}\right)\cdot f_S \cdot exp\left(-\beta_3 \cdot exp\left(\frac{-E_D}{R\cdot(T_D+273)}\right)\cdot t\right)\Bigg] \quad \text{....................................(20)}$$

Since the activation energy is experimentally evaluated as E_D=1.8kJ/mol, β_1, β_2 and β_3 can easily be estimated by using a simple optimization technique for fitting to the two W_{R1} and W_{R2} curves obtained after the PUP at W_0=306 and 102 %-d.b. at 40ºC.

β_1 = 306(±90) h^{-1}
β_2 = 75(±22) h^{-1}
β_3 = 16900(±3000) h^{-1}

By using these values, one can evaluate the values of k_W and k_S as 0.19-0.39 and 0.053-0.228h^{-1}, respectively, at W_0=306 ~ 77%-d.b. and T_D=35-50ºC. These values obtained fall in the range of dehydration constants reported in the previous works as 0.186-0.450h^{-1} for pigeon pea (Shephered and Bhardwaj, 1988) and 0.023-0.086h^{-1} for ear corn (Sharaf-Eldeen, Blaisdell and Hamdy, 1980).

Using Eqs. (19) and (20), all the dehydration curves obtained could be simulated. The simulated curves are presented in Fig.5 by the solid and broken curves. The results clearly indicate good agreement with the experimental curves suggesting that the proposed water tank mode can usefully be applied to the squid drying process same as the fish past sausage.

4. Conclusions

The four physicochemical parameters chosen for the squid, De, E_D, τ_C, and m, individually characterized the three water species, -A_1, -A_2 and -A_2'. On De, it was evaluated as 1.8×10^{-6} for the water species-A_1 and $0.6\sim1.7\times10^{-6}$ m^2/h for species-A_2. On E_D, they were 17 for species-A_1 and 25~35kJ/mol for species-A_2. On τ_C, they were 4.8×10^{-9} for species-A_1 and $1.0\times10^{-8}\sim1.2\times10^{-7}$ s for species-A_2. On m, they were 0.24~0.55 for species-A_1 and 0h^{-1} for species-A_2. On the water species-A_2', an unusual histerisis behaviour for the Arrhenius plot of $1/\tau_C$ was exactly appeared indicating two different locus's depending on the temperature decrease from 30 to -30°C or the temperature increase from -30 to 30°C. The activation energy ($E\tau_C$) of the water molecule rotation rate was evaluated to be 3kJ/mol for the temperature decrease course and 40kJ/mol for the temperature increase course, indicating a self organization formed from the species-A_1 and -A_2 as unfrozen water molecule even at the temperatures lower than -10°C.

All the four parameters can individually be chosen depending on the food quality requested. The populations of species-A_1, -A_2, and -A_2' can easily be regulated by controlling W_0, T, and the relative humidity of supplied drying air (RH) as an operating parameter. The growth rates of staphylococcus and micrococcus for the squid sample were completely limited by the species-A_2 or by an RH lower than 30% (designated as critical relative humidity, RH_{30}) at less than 10^3 CFU/g without depending on W_0. One could recognize that the RH_{30} was usefully employed as an optimal operation in the drying process without bacterial contamination. All the unknown parameters to simulate the dehydration curves were reasonably evaluated for the design of optimal drying operation.

Acknowledgements

This work has been financially supported by the Cooperation of Innovation Technology and Advanced Research in Evolution Area (City Area) for the Japanese Ministry of Education, Culture, Sports, Science, and Technology. The authors wish to thank Professor Yuji Kawai, Hokkaido University, for the useful supports on the bacterial contamination analysis, and Professor Koichi Miura, Kitami Institute of Technology, on the proton NMR analysis.

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