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Studies on drying of sugar solutions and stabilization of dried foods by sugars

Sachie Fujii

2014
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General Introduction

Drying is a very important unit operation in food industries, which is carried out for volume/weight reduction suitable for distribution and storage. When foods are dried properly, dried food products become very stable and have a very long shelf life.

Various types of drying operation are available. Among them freeze drying (FD) is known to be a method for producing high-quality dried foods. However, the running cost is so expensive that it is only possible to employ FD for high-value-added foods such as functional (health-promoting) foods. Hot air drying such as spray drying is commonly employed for producing food powders from liquid foods. For agricultural products such as vegetables and fruits, and semi-solid foods such as pasta and pasta-like foods (Udon, Somen and etc.), hot air drying at relatively low air temperatures is used in order to prevent deterioration of food qualities.

Various physical, chemical and biochemical changes occur during drying. Such changes are flavor loss, color change, texture change, enzyme inactivation, oxidation, nutritional value degradation, and etc. It is known that the rate of such changes depend on both temperature and water content.

Water activity $a_w$ is an important parameter that affects the product stability. Water activity $a_w$ as a function of water content is usually described as equilibrium water content vs. $a_w$, which is called a “water sorption isotherm” (Figs. 1 and 2). Figure 1 shows a typical water sorption isotherm of food materials. Since at low water activity regions
(a_w<0.2) most reactions become extremely low, foods become highly stable. It is therefore important to know isotherms of food materials as a function of temperature.

Fig. 1  Typical food sorption isotherm (experimental data for sucrose).

Fig. 2  Effect of temperature on food sorption isotherm. Usually, water content at a given a_w decreases with temperature. Or the a_w value increases at a given water content with temperature.
For storage (shelf life) even a small reduction of water activity \( a_w \) is effective since higher \( a_w \) values are need for microorganisms to grow. Bacteria usually require at least \( a_w = 0.91 \) whereas fungi at least \( a_w = 0.7 \). Water content values of foods at \( a_w = 0.7 \) are summarized in Table 1.

**Table 1** Water content (kg-water/kg-solid) of foods at \( a_w = 0.7 \).

<table>
<thead>
<tr>
<th>Food</th>
<th>Water Content (kg-water/kg-solid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuts</td>
<td>0.04 - 0.09</td>
</tr>
<tr>
<td>Whole milk powder</td>
<td>0.07</td>
</tr>
<tr>
<td>Cocoa</td>
<td>0.07 - 0.10</td>
</tr>
<tr>
<td>Soybeans</td>
<td>0.09 - 0.13</td>
</tr>
<tr>
<td>Dried whole egg</td>
<td>0.10</td>
</tr>
<tr>
<td>Skim milk powder</td>
<td>0.10</td>
</tr>
<tr>
<td>Dried lean meat and fish</td>
<td>0.10</td>
</tr>
<tr>
<td>Rice</td>
<td>0.12 - 0.15</td>
</tr>
<tr>
<td>Pulses</td>
<td>0.12 - 0.15</td>
</tr>
<tr>
<td>Dried vegetables</td>
<td>0.12 - 0.22</td>
</tr>
<tr>
<td>Wheat flour, pasta</td>
<td>0.13 - 0.15</td>
</tr>
<tr>
<td>Dried soup mixes</td>
<td>0.13 - 0.21</td>
</tr>
<tr>
<td>Dried fruits</td>
<td>0.18 - 0.25</td>
</tr>
</tbody>
</table>

Data were taken from Mossel and Pflug; Crit. Rev. Environ. Control, 5, 1-139 (1975).

Water contents of dried foods range between 0.07 and 0.25. Since dried fruits contain a large amount of sugars, the water activity is lower than other foods such as wheat flour.

A typical drying curve of a liquid food droplet is shown in Fig. 3. At the beginning of the drying process, the constant drying rate period may exist where the sample temperature is equal to the wet-bulb temperature. When the surface is dried (critical water content, this period ends. The drying rate decreases with time, which is called a “falling rate period”. This period is important for many reactions since the sample temperature rises with time.
Fig. 3  Typical drying curve of a liquid food droplet.

Since drying is a combined heat and mass transfer operation, drying rates must be known to predict the temperature of the sample during drying. Generally the water diffusion inside the food material governs the drying rate. The water diffusion coefficient decreases with decreasing water content especially for liquid foods. At low water contents the water diffusion coefficient of liquid foods becomes quite low. Although the water diffusion coefficient as a function of water content and temperature is needed for drying simulations, the data are not readily available. In addition, there are not many reliable, standard methods for determining the water diffusion coefficient.

In addition to liquid foods and semi-solid foods, agricultural products such as vegetables and fruits are distributed to food processing companies as dried products. The purpose of
such food drying processes is not only to reduce the volume and weight of the products
but also to improve the product stability (shelf life) whereas the product quality must be
maintained during and after drying. Again it is important to know how to dry the product
properly and how to choose suitable additives.

In this study first we have investigated the drying behavior of sugar solutions (Chapter
1). Sugars (carbohydrates) are typical constituents of foods, and are also known to be
good stabilizing additives for foods and pharmaceutical drugs. The water diffusion
coefficients and the desorption isotherms were determined for temperatures between 282
and 353K. The drying behavior of sucrose solution was compared with that of pasta-like
semi-solid foods in order to understand the drying mechanism at low temperatures.

In Chapter 2, enzyme retention during drying of sugar solutions containing enzyme was
examined based on the diffusion model. The enzyme retention was simulated by using
the water diffusion coefficient and the enzyme inactivation rate constant as a function of
water content and temperature. Protective effects of sugars on enzyme inactivation were
investigated. A method for obtaining high enzyme retention was discussed.

Chapter 3 presents the inactivation of a food microorganism, baker’s yeast during drying
at low temperatures where thermal inactivation does not occur. Factors affecting
dehydration inactivation were examined. Protective effects of sugars on the inactivation
of yeasts during drying and storage were investigated.
Effects of pretreatments on drying of agricultural products (sliced potatoes and carrots) on drying behavior and the product quality were experimentally investigated (Chapter 4). Steam blanching and soaking in a sugar solution were chosen as pretreatment methods. Water loss and solid uptake during soaking in a sugar solution were determined. The drying behavior as well as the change of the shape during drying was examined. The cell structure of re-hydrated dried samples was investigated in order to understand protective effect of sugar solutions.
Chapter 1  

Water diffusion and desorption behavior during low-temperature drying

1. Introduction

Although hot air convective drying of foods is carried out at high temperatures especially for spray drying of liquid foods, low temperature drying is needed for some foods. For example, pasta and pasta- like foods are dried at low temperatures in order to avoid formation of cracks on the surface of the product (Andrieu and Stamatopoulos, 1986; Inazu et al., 2002). Heat-labile biomaterials such as proteins, enzymes and microorganisms might be dehydrated at low temperatures as well.

One of the interesting and important applications of low-temperature drying is a Japanese traditional pasta-like food “somen”, which has been traditionally produced in winter in the open air by drying at temperatures of 273-283 K. although current commercial production is carried out in a drying room or a drying chamber, the drying air temperature is kept still low (lower than 293 K) and the air is not dehumidified. The exact drying mechanism of somen at low temperatures is still not clarified.

Various biopharmaceuticals have been developed and commercialized, which are quite expensive and very unstable. They are freeze-dried when necessary. However, vacume drying at low temperature is claimed to be an alternative method for unstable biopharmaceuticals (Anonymous, 2004).
In order to design and optimize the low-temperature drying process data on diffusion coefficients and desorption isotherms are necessary. However, such data for temperatures below 303 K are not readily found in the literature.

In this study we investigated the water diffusion and the water desorption behavior for liquid foods for temperatures between 283 K and 323 K. The isothermal drying experiments were carried out in order to obtain isothermal regular regime drying curves, from which the apparent water diffusion coefficients as a function of water determined from the equilibrium water contents at constant relative humidities (water activities).

2. Materials and methods

2.1 Materials

Sugars employed in this study are sucrose and maltodextrin (MD) (dextrose equivalents DE = 11, Pindex #2, Matsutani Chemical Industry). A medium flour (Tokushima Seifun) was used (the gluten content is ca. 8 - 10 wt%).

2.2 Sample preparation

A sugar solution (ca. 20 - 40 wt%) was heated with agar-agar (1 wt%) until the homogeneous solution was obtained. The solution was then injected into an aluminum dish (diameter = 50 mm, depth = 1 mm) to prepare slab shaped samples (Yamamoto, 2004; Yamamoto et al., 2005).

A dough was prepared by kneading a mixture of flour (100 g), NaCl (0.5 g) and water (50 g). The dough was packed in a plastic foil and left for 2 h at room temperature. Then,
the dough was processed with a pasta machine in order to obtain thin sheets of different thicknesses (0.3 – 0.9 mm). The sheet was cut into a small piece (40 mm × 40 mm) as a model somen sample for desorption or drying experiments.

The solid weight of the sample was determined by drying at 363 – 373K for 2 – 4 hours in a drying oven.

2.3 Desorption isotherm

Samples were stored in a sealed container in the presence of saturated salt solutions of known water activities (Troller and Christian, 1978). The samples were weighed periodically. It is not easy to confirm the equilibrium of these samples as they change the physical properties with time (i.e., crystallization, rubber-glass transition, etc.). So we decided to terminate the experiment when the weight loss became 2% at maximum in 12 h (usually 2 - 3 d).

The isotherm data were fitted by a three parameter Guggenheima - Anderson - de Boer (GAB) model (Van den Berg, 1984; Rahman, 1995).

\[
X = \frac{Ck_\alpha wW_m}{(1-k_\alpha w)(1-k_\alpha w+Ck_\alpha w)}
\]  

(1.1)

\(W_m\) implies the water content equivalent to a monolayer coverage. \(C\) and \(K\) are constants related to the binding energies.

The excess heat (net heat) of adsorption \(Q_s\) was determined from the temperature dependence of isotherms (Labuza et al., 1985; Rahman, 1995).
\[ Q_s = R_G \frac{\ln(a_w/a_{wref})}{(1/T_{ref})-(1/T)} \]  
(1.2)

\( a_{wref} \) is the value at a temperature of \( T_{ref} \).

2.4 Drying experiment

Isothermal drying experiments were performed in a constant-air temperature box (Yamamoto 2004; Yamamoto et al., 2005). Silica gels or saturated salt solutions were placed in the box to control the relative humidity (RH). The air temperature was controlled so that the sample temperature is maintained at an assigned temperature. The air temperature in the drying box was somewhat higher than the assigned value at the beginning of the experiment, and then, lowered gradually with the progress of the drying. The weight and the temperature measurements were done separately.

2.5 Water diffusivity

The diffusion coefficient of water in liquid foods, \( D(\chi) \), which depends strongly on the water content \( u \) can be determined from the regular regime isothermal drying curve (Bruin and Luyben, 1980; Coumans, 1987; Schoeber, 1976; Yamamoto, 2001). The diffusion coefficients were determined as a function of \( \chi \) from the isothermal drying rates experimentally measured.

3. Results

3.1 Desorption isotherms

Fig. 1.1 shows the desorption isotherms of sucrose as a function of temperature. The water content at a given water activity \( a_w \) increases with lowering temperature. The desorption isotherm at 283 K for \( a_w < 0.5 \) is almost rectangular (irreversible isotherm...
shape). It was impossible to fit this curve with the GAB equation. The isotherms for MD showed similar tendencies although the temperature effect is less compared with the sucrose data (Fig. 1.2). On the other hand, the temperature did not affect the desorption isotherms of hand-made somen significantly as shown in Fig. 1.3. The equilibrium water content in low water activity (monolayer coverage), $W_m$, increased with a decreasing temperature especially for sucrose whereas the values did not change significantly with temperature for pasta-like foods. The values of excess heat of adsorption $Q_s$ were determined from the temperature dependence of desorption isotherms according to Eq. (1.2). As shown in Fig. 1.4, a very sharp increase of $Q_s$ was observed for sucrose when the water content is decreased from 0.5 to 0.1. MD also showed a similar trend in lower water content region ($X < 0.3$). The $Q_s$ did not change appreciably for somen.

Fig. 1.1 Desorption isotherms of sucrose.
Fig. 1.2  Desorption isotherms of maltodextrin (MD).

Fig. 1.3  Desorption isotherms of somen and flour.
3.2 Drying curves

The drying curves of sucrose at different temperatures are shown in Fig. 1.5. The drying rate was quite low at 293 K, and the water content did not reach 0.4 even at \( \tau' = 60000 \) where \( \tau' \) is the normalized drying time on the basis of a shrinking coordinate (Schoeber, 1976; Coumans, 1987; Yamamoto, 2001, 2004; Yamamoto et al., 2005).

As shown in Fig. 1.6, the drying curves for somen at RH = 33% with respect to the normalized time were described by a single curve, indicating that the drying is controlled by the water diffusion inside the material. The product specification of dried somen is that the water concentration is ca. 0.1 – 0.13 kg-water/kg-total.
3.3 Equilibrium water content

So far we have shown that the sucrose solution is difficult to dry at low temperatures because of the high equilibrium water content (Fig. 1.7a) and very low water diffusivity (data not shown). On the other hand, the equilibrium water contents of somen are much
lower than those of sucrose even at low temperatures (Fig. 1.7b). The water diffusivity of somen is higher than that of the sucrose solution at lower temperatures. Consequently, it is possible to dry thin somen noodles to the water content of 0.1 kg-water/kg-solid at temperatures below 283 K and RH = 20 – 50 %.

Fig. 1.7  Relationship between equilibrium water content and temperature as a function of RH. (a) sucrose, (b)somen.
4. Discussions

We have shown that the drying rates of somen (pasta-like flour based foods) at low temperatures are much higher than those of sucrose and maltodextrin. This is mainly because of the lower equilibrium water content and higher water diffusivity of somen compared with those of sucrose.

One of the difficulties in measuring the desorption isotherm is how to determine the equilibrium. For example, sucrose solutions in this study formed very stable supersaturated glassy solutions. However, after a few weeks some crystals were observed on the surface. So the equilibrium here is based on the time scale that we chose. The isotherm data for model somen samples are similar to those for flour powders.

In the production of somen a small amount of oil (ca. 0.8 %) is added to the dough prepared with medium flour. It is therefore important to know how the oil affects the drying rates of somen at low temperatures. Another important point is the effect of the gluten content on the drying rate. Although the water sorption isotherms of flour having different gluten contents were quite similar as shown in Fig 1.3, physical properties of wheat flour dough such as water-holding capacities may depend on the gluten content as shown by Yahata et al. (2006).
5. Conclusions

The drying rates at low temperatures for a pasta-like food (somen) were higher than those for sucrose. This is because the amount of water, which is bound to the solid tightly, was much smaller compared with that for sucrose. The excess heat of adsorption at lower water contents was quite large for sucrose and maltodextrin whereas it was quite small for somen.
Chapter 2

Enzyme Retention during Drying of Sugar Solutions

1. Introduction

Because protein or enzyme solutions are heat sensitive and easily denatured at high temperatures, freeze drying is often employed for drying of proteins. However, when the proper drying conditions and suitable additives (stabilizers) are chosen, it is possible to dry protein solutions with minimum denaturation by hot air convective drying such as spray drying (Masters, 1979; Namaldi et al., 2006; Joshi et al., 2011).

Numerous papers have been published on the drying of enzymes or proteins. It is important to know how enzyme activities are lost during drying for prediction of enzyme retention at the end of the drying. Single droplet drying experiments have been carried out by several researchers for enzyme retention studies (Rahman et al., 1971; Yamamoto and Sano, 1992, 1994; Yoshii et al., 2005). A model was also developed for single droplet drying that can simulate enzyme retention as well as the water content and sample temperature during drying (Kerkhof and Schoeber, 1974; Wijlhuizen et al., 1979; Luyben et al., 1982; Liou, 1982; Liou et al., 1985; Meerdinger, 1983), and the model was applied to the experimental results (Yamamoto and Sano, 1992, 1994; Liou, 1982; Liou et al., 1985; Meerdinger, 1983). This model consists of the diffusion equation, the heat balance equation, the mass and heat transfer at the interface, and the inactivation equation (see the Appendix). A different version of single droplet drying and review papers have been published (Lorenzen and Lee, 2012; Mezhericher et al., 2010; Che and Chen, 2010).
Based on these simulations, the typical drying and enzyme retention behavior of liquids containing an enzyme is shown schematically in Fig. 2.1. Because the sample temperature was low during the constant drying rate period, the enzyme activity was retained. After the constant drying rate period, the sample temperature increased and the enzyme activity began to decrease. However, because enzymes become highly stable at low water concentrations (Troller and Christian 1978; Svensson, 1977; Monsan and Combes, 1984; Franks, 1993). The enzyme activity reached a steady value.

![Fig. 2.1  Enzyme retention during drying.](image)

Researchers have also investigated the enzyme retention of spray-dried powders by changing drying conditions such as inlet temperature and additives (Namaldi et al., 2006; Joshi et al., 2011). One such study showed that the final enzyme retention did not decrease...
monotonously (Namaldi et al., 2006) although the above-mentioned simulation simply predicted that higher air temperature results in lower enzyme retention.

Amorphous sugars are known to protect proteins (Schebor et al., 1997; Yu, 2001; Mazzobre et al., 1997). Glass transition and crystallization are considered to be important factors affecting enzyme stability. However, it is still not clear how to choose a suitable additive for drying of enzymes.

In this study, enzyme inactivation during hot air drying of amorphous sugar solutions was investigated based on the diffusion model. Various carbohydrate solutions containing a small amount of an enzyme were used as sample solutions. The water content, sample temperature, and remaining enzyme activity were simulated on the basis of the above-mentioned diffusion-based drying model. The remaining enzyme activity and the drying time relationships were examined in terms of the water concentration and temperature histories.

2. Experimental
Carbohydrates employed in this study were monosaccharides (glucose, xylose), disaccharides (sucrose, maltose, trehalose), and oligosaccharide (maltodextrin [MD] with a dextrose equivalent of 11, molecular weight ca. 6,000, obtained from Matsutani Kagaku Kogyo, Itami, Japan).

When aqueous solutions of these sugars were employed for the slab drying experiment without an enzyme, the solutions were gelled with agar–agar (1 wt% concentration).
When the enzyme retention during drying was measured, the solution was gelled with sodium alginate. The procedures are based on those reported by Liou (1982) and modified so that the amount of sodium alginate could be reduced. The enzyme used was β-galactosidase from Aspergillus oryzae (Amano Enzyme, Nagoya, Japan) and its activity was measured according to the standard method with o-nitrophenyl galactoside as the substrate.

The drying experiment with a gelled slab was performed in a constant-air temperature box. Silica gels were placed in the box to remove the water vapor. The sample temperature Td was recorded continuously from the output of a thermocouple inserted into the gelled slab. The slab was suspended from an electronic balance to measure the weight. The air temperature TA was controlled so that the drying rate in the regular regime at an assigned temperature could be obtained. TA in the drying box was somewhat higher than the assigned value at the beginning of the experiment. Then, TA was lowered gradually as drying progressed. Such temperature control programs were not employed for the drying of gelled slabs containing the enzyme at TA > 70°C. The gelled slab was dissolved in a 1M K2HPO4 solution for the enzyme assay.

3. Computer simulations

The average water content X, the sample temperature Td and the average enzyme retention XE are calculated as a function of time t on the basis of the following equations (Yamamoto and Sano, 1992, 1994; Kerkhof and Schoeber, 1974; Wijlhuizen et al., 1979; Luyben et al., 1982; Liou, 1982; Liou et al., 1985; Meerding, 1983).
Diffusion equation with the shrinking coordinate

\[
\frac{\partial X}{\partial t} = \frac{\partial}{\partial z} \left( \rho g \frac{\partial^2 X}{\partial z^2} \right) \tag{2.1}\n\]

\[
\rho C_p \frac{dT_d}{dt} = \left( \frac{v + 1}{R} \right) \left\{ h_g (T_a - T_d) - j_{w,j} \Delta H_y \right\} \tag{2.2}\n\]

Inactivation rate equation

\[
\ln \rho_{E0} / \rho_E = - \int_0^t k_d dt \tag{2.3}\n\]

The initial and boundary conditions are:

\[
t = 0; \ 0 < z < Z; \ X = X_0 \tag{2.4}\n\]

\[
t > 0; \ z = 0; \ \rho g \frac{\partial X}{\partial z} = 0 \tag{2.5}\n\]

\[
t > 0; \ z = Z; \ \rho g \frac{\partial X}{\partial z} = -j_{w,j} \tag{2.6}\n\]

\[
j_{w,j} = k_g (a_{w,j} \rho_{sat} - \rho_{w,j}) \tag{2.7}\n\]

The assumptions are

1) uniform shrinking due to the loss of water,

2) no temperature distribution in the sample, and

3) water movement in the droplet by molecular diffusion.

The above equations are discretized to obtain the numerical solution.

The water content profile in the droplet is integrated to give \( \bar{X} \). \( D = f(X, T) \) was calculated by the following equation (Yamamoto and Sano, 1992, 1994).

\[
D = D_0 \exp\left[-16/(1+16X)\right] \tag{2.8}\n\]

\( D_0 = 2.2 \times 10^{-10} \) for MD (DE=11), \( 6.0 \times 10^{-10} \) for sucrose.
The activation energy for diffusion $E_D$ was given by

$$E_D = \frac{(1.0 \times 10^5 + 1.9 \times 10^5 X)}{1 + 10^X}$$

(2.9)

$a_w$ was calculated by the GAB equation (Eq. (1.1)) where $K = 0.98$, $W_m = 0.085$ and $C = 30$ for sucrose and $K = 0.90$, $W_m = 0.07$ and $C = 30$ for MD.

The temperature dependence was not considered in the calculation. From the drying rates of agar-gel slabs the mass transfer coefficient was determined to be $k_g = 0.2$ m/s. The heat transfer coefficient was calculated on the basis of the Chilton-Colburn analogy.

The inactivation rate data (Yamamoto and Sano, 1992, 1994) were fitted by the following equations:

$$k_d = k_{65} \exp[-(E_d/8.3)(1.0/T - 1.0/338)]$$

(2.10)

$$k_{65} = \exp(-13.4 + 7.02W)$$

(2.11)

$$E_d = 4.0 \times 10^5 - 2.5 \times 10^5 \exp[-2.5W/(1 - W)]$$

(2.12)

For the other physical properties used in the calculation, see (Liou, 1982; Liou et al., 1985; Sano and Keey, 1982).

4. Results and discussion

In our previous study (Yamamoto and Sano, 1992), the average water content $X$, the droplet temperature $T_d$, and the relative enzyme activity $X_E$ as a function of drying time for several carbohydrates were measured. It was found that the enzyme activity $X_E$ remained at the initial value until $T_d$ began rising to the air temperature $T_A$. Because the inactivation rate $k_d$ decreased very sharply with decreasing water concentration, quite
high $X_E$ values at the end of the drying were retained.

However, it was also difficult to investigate the protective effect of different carbohydrates from the single droplet drying experiment because higher temperature and/or larger droplet size is needed in order to observe much lower remaining activities to examine the protective effect in detail. Therefore, we decided to use slab-shaped samples for the drying in this study.

Fig. 2.2 shows typical drying and enzyme retention behavior of a sucrose solution containing the enzyme. The enzyme activity was lost quickly when the solution without sugar (sucrose) was incubated at 70°C. The enzyme became stable when it was dissolved in a sugar solution (18.2%, $X_0=4.5$). When the sugar solution was dried at 70°C, the initial enzyme activity was retained until 140 s. Although further drying reduced the enzyme activity, the final relative activity was 0.85. The initial enzyme activity was maintained at 65°C until the end of the drying (data not shown).
Fig. 2.2  Relationships between the remaining enzyme activity (enzyme retention) $X_E$ and drying time $t$ at $T_A = 70^\circ$C. $R_0 = 1$ mm, $X_0 = 4.2$. Curve A: enzyme solution without sugar in the airtight sample dish incubated at $70^\circ$C. Curve B: enzyme solution with sugar in the airtight sample dish incubated at $70^\circ$C.

Similar experiments were carried out with various sugars (Fig. 2.3). The enzyme stability in the sugar solution without drying was different from sugar to sugar, whereas the enzyme retention during drying was quite high, with exception of maltodextrin.
Enzyme retention during drying of various sugar solutions. Glass transition temperature (Rahman, 1995), $T_g = 30 - 40 \degree C$ for glucose (molecular weight $M_w = 180$), $T_g = 10 - 13 \degree C$ for xylose ($M_w = 152$), $T_g = 57 - 70 \degree C$ for sucrose ($M_w = 342$), $T_g = 77 - 79 \degree C$ for trehalose ($M_w = 342$), $T_g = 87 - 95 \degree C$ for maltose ($M_w = 342$), $T_g = ca. 160 \degree C$ for maltodextrin ($M_w = ca. 6,000$). Filled circles are the data obtained with the airtight sample dish.

In order to investigate the low enzyme retention of maltodextrin solution, the model simulation was carried out for experiments at higher temperatures ($82 \degree C$). First, the data with sucrose solution were compared with the simulated results (Figs. 2.4 and 2.5). The enzyme retention $X_E$, water content, and temperature $T_d$ data were in good agreement with the simulated results within acceptable experimental error. The agreement between the simulated and experimental temperature of the slab was not very good in the early stage of drying because it was not easy to precisely measure the real slab temperature by the thermocouple.
Fig. 2.4 Enzyme retention of sucrose solution at $T_A = 77^\circ\text{C}$. Initial moisture content $X_0 = 4.2$, initial slab thickness $R_0 = 3\text{ mm}$. $\bullet =$ average water content $\bar{X}$, $\diamond =$ slab temperature $T_d$, $\square =$ enzyme retention $X_E$. Solid curves are simulated results by the model.

Fig. 2.5 Enzyme retention of sucrose solution at $T_A = 82^\circ\text{C}$. Initial moisture content $X_0 = 4.2$, initial slab thickness $R_0 = 3\text{ mm}$. $\bullet =$ average water content $\bar{X}$, $\diamond =$ slab temperature $T_d$, $\square =$ enzyme retention $X_E$. Solid curves are simulated results by the model.
Because the inactivation rate constant as a function of water concentration \((k_d - W)\) was only available for sucrose, the simulation for MD was carried out with the data for sucrose. The experimental and simulated results for MD are shown in Fig. 2.6. The simulated results well described the experimental data.

![Graph](image.png)

Fig. 2.6 Enzyme retention of maltodextrin solution at \(T_A = 82^\circ\text{C}\). Initial moisture content \(X_0 = 4.2\), initial slab thickness \(R_0 = 3\) mm. ◯ = average water content \(\bar{X}\), □ = slab temperature \(T_{d}\), © = enzyme retention \(X_E\). Solid curves are simulated results by the model.

We checked the effect of the enzyme inactivation rate constant \(k_d\) at low water concentrations on the final retention by changing \(k_d\) at \(X = 0\). As shown in Fig. 2.7, the enzyme retention curves \((X_E - t)\) did not change appreciably. From Figs. 2.8a and 2.8b it is easily understood that the enzyme retention in this case was strongly dependent on the \(T_d - X\) relationships. In other words, when the water content was reduced to a certain critical value before the sample temperature approached the air temperature, quite high
enzyme activity was retained. Therefore, high-molecular-weight sugars such as MD resulted in lower enzyme retention although it still had a protective effect because the enzyme activity in the solution was completely lost within 600 s at 70°C. Fig. 2.8b shows that the inactivation rate constant $k_d$ for MD calculated based on the average water content was greater than $10^{-3}$ in the range $0.5 < X < 3$ where the enzyme was quickly inactivated. However, $k_d$ decreased again sharply when $X < 0.5$. $k_d$ values were relatively lower for sucrose, which resulted in higher enzyme retention. It must be noted that because of the water content profile in the sample, the enzyme retention profile also existed (enzyme retention was higher near the surface) (Kerkhof and Schoeber, 1974; Wijlhuizen et al., 1979; Luyben et al., 1982; Liou, 1982; Liou et al., 1985; Meerding, 1983).

![Simulated enzyme retention of MD solution at $T_A = 82^\circ$C.](image)

Fig. 2.7 Simulated enzyme retention of MD solution at $T_A = 82^\circ$C.
Fig. 2.8 Calculated $T_d - X$ and $k_d - X$ curves at $T_A = 82^\circ$C. $T_d - X$ curves were constructed from $T_d - t$ and $X - t$ curves in Figs. 2.5 and 2.6. The inactivation rate constant $k_d$ was calculated based on the $T_d - X$ and Eqs. (2.10) – (2.12).

It is a common practice to add carbohydrates (sugars) or polyols to protein solutions to increase stability (Troller and Christian, 1978; Svensson, 1977; Monsan and Combes, 1984). One explanation for this protective effect is the lowering of the water activity $a_w$ (Troller and Christian, 1978). A reduction in the water concentration also results in the lowering of $a_w$. This may be a simple interpretation of why the inactivation rate $k_d$ decreased with decreasing $W$, although a more quantitative explanation has been presented (Monsan and Combes, 1984).

In freeze drying, it is known that a phenomenon called collapse leads to deterioration of the product. Franks (1993) pointed out the importance of the relationship between the glass transition temperature and water concentration, $T_g - W$, which may be correlated to the protective effect of carbohydrates.
The protective effect may vary from carbohydrate to carbohydrate in hot air convective drying. However, as shown in Fig. 2.8, drying rates due to low water diffusivities determined the final enzyme activity. Because drying of higher-molecular-weight carbohydrates is slower, the enzyme retention was lower than that of small sugars. Although the $k_d - W$ curve for MD may be different from that for sucrose, it does not significantly affect the enzyme retention behavior. This study has shown that quite high remaining enzyme activities can be obtained even in hot air drying.

Contradictory results are often observed for the enzyme retention of spray-dried products. Namaldi et al. (2006) found that the enzyme retention decreased with temperature up to a certain temperature and increased above that temperature. This may be due to accelerated drying due to droplet rupture (Sano and Keey, 1982). Once a hollow particle is formed, drying becomes faster and a higher enzyme retention is obtained (Wijlhuizen et al., 1979). Such accelerated drying is also possible by foaming the liquid before drying (foam drying) (Rahman, 1971).

Another concern regarding enzyme retention during storage is crystallization. It is known that amorphous sugar matrices can stabilize enzymes or proteins, whereas crystallization of sugars during storage inactivates enzymes (Rahman, 1995; Schebor et al., 1997; Mazzobre et al., 1997; Sano and Keey, 1982; Buera et al., 2005). Transformation of amorphous sugars to a crystalline state is a complicated phenomenon (Carstensen and Scoik, 1991).
5. Conclusion

We have shown that enzyme retention during drying of amorphous sugar and carbohydrate solutions containing a small amount of enzyme can be predicted by the diffusion model with the heat balance equation and the inactivation rate equation. Mono- and disaccharides protected the enzyme during drying, whereas a high-molecular-weight sugar, maltodextrin, resulted in lower enzyme retention. The experimental data as well as the model simulation showed that this low retention is due to low drying rates of maltodextrin because the temperature increases as the water content decreases very slowly.
Chapter 3  
**Effect of Sugar Solutions during Drying of Yeasts**

1. **Introduction**

   Food microorganisms such as lactic acid bacteria and yeasts play important roles in food processing and are also being produced as functional (health-promoting) foods (Knorr, 1998). Although dried baker’s yeasts and lactic acid bacteria are available on the market and many papers have been published on the drying of yeasts or lactic acid bacteria (Knorr, 1998; Josic, 1982; Bayrock and Ingledew, 1997; Buera, *et al.*, 1999; Rakotozafy, *et al.*, 2000; Laroche, 2003; Luna-Solano, 2000; Mille, *et al.*, 2005; Guyot, 2006; Debaste, *et al.*, 2008; Yamamoto, *et al.*, 2008; Lievense, *et al.*, 1992; Zayed and Roos, 2004; Ananta, 2005; Oldenhof, *et al.*, 2005; Li, *et al.*, 2006; Chavez and Ledeboer, 2007), the inactivation mechanism during and after drying is quite complicated and still not fully known. For example, low-temperature drying does not damage proteins (Yamamoto, 2004; Bruin and Luyben, 1980), whereas microorganisms are inactivated even during low temperature drying due to dehydration inactivation (Yamamoto, *et al.*, 2008; Lievense, *et al.*, 1992). Dehydration inactivation is unavoidable during not only hot air drying but during freeze drying (FD) (Buera, *et al.*, 1999). Although various factors are important, it is not understood which factor is dominant in dehydration inactivation. For example, contradictory results have been reported on the effect of drying rate as summarized by Lievense *et al* (1992).

   In this study, the inactivation behavior of baker’s yeast during low-temperature constant temperature hot air drying and FD was investigated. The average water content was measured as a function of time. The activity was determined by measuring the
fermentative ability.

Thermal stability of yeasts in water (suspension) was first examined as a function of temperature. Hot air convective drying experiments at constant air temperature and air humidity were carried out at low temperature (30°C) where thermal inactivation does not occur. The water content and water activity were measured during drying. Based on these experimental data, we examined the effect of drying rate and water content on dehydration inactivation during drying.

2. Experimental

2.1 Materials

Pressed baker’s yeast was purchased from Oriental Yeast (Tokyo, Japan). We confirmed that the yeasts were stable in terms of the activity (fermentative ability due to CO₂ production rate) in a refrigerator at 4°C for a few days. The activity was checked prior to use. CO₂ production rates of fresh yeasts were reproducible. Other reagents were of analytical grade.

2.2 Sample preparation

In order to prepare filtered yeasts, yeast was suspended in a solution of known concentrations of sugars (3 wt% sorbitol) or in water. After a 30 - 60min incubation, the suspension was filtered using a vacuum filtration device. The final (apparent) water content of the filtered yeast was similar to the pressed yeast (ca. 2.2 - 2.5 kg-water/kg-dry solid). The shape of the yeast sample was formatted to a thin sheet using a plastic template (17 mm × 17 mm × 0.7, 1 or 2 mm thickness). The solid weight of the sample was
determined by drying at 90 - 100 °C for 2 - 4 h in a drying oven.

2.3 Activity of yeast (fermentative ability)

The fermentative ability (fermentation activity) was determined by measuring carbon dioxide production rates. Fresh yeast samples were suspended in water. After the drying experiment, the yeast sample was first suspended in water for 5 min at 35°C. Then, the suspended yeast was fermented in a 3 wt% glucose solution. The amount of CO₂ produced was collected by displacing water trapped in an inverted graduated cylinder and measured as a function of time. The relative activity was defined as the CO₂ production rate of the dried (or heat-treated) yeast sample divided by that of fresh yeast.

2.4 Growth rate

The yeast suspended in a YPD (1 % yeast extract, 2 % polypeptone, 2 % dextrose) substrate solution was incubated in a 96-well microplate at 35 °C. The turbidity at 600nm was measured as a function of time. The calibration curve was prepared with yeast suspensions of different yeast concentrations, and the relative growth rate was determined. The concept behind this method was reported in the literature (Tsuchido, 1989).

2.5 Drying experiment

Isothermal drying experiments were performed in a constant air-temperature box (Yamamoto, 2004). Silica gels or saturated salt solutions were placed in the box to control the relative humidity. They were stored in the box for at least 12 h before the start of the drying experiment in order to assure the assigned relative humidity, which was regularly monitored by a digital humidity meter (Vaisala HM141 with an HMP45 probe, Helsinki,
Finland). The relative humidity (RH) in the drying box was maintained below 1% when the silica gels were used. The RH was 75 ± 3% when a saturated NaCl solution was used.

The air temperature was controlled so that the sample temperature was maintained at an assigned temperature. The constant rate drying curve was measured with an agar gelled water solution. The drying rate \( J \) (kg-water/[m²·s]) was calculated from the weight vs. time data as

\[
J = -d(W_w/A)/dt \quad \text{(3.1)}
\]

where \( W_w \) is the weight of water and \( A \) is the drying area (m²). This can be converted to

\[
dX/dt = d(W_w/W_s)/dt = -AJ/W_s \quad \text{(3.2)}
\]

where \( W_s \) is the solid weight of the dried sample. Based on Eq. (3.2) we can draw the drying curve for water in a hot air drying curve.

Freeze-drying experiments were carried out using a commercial laboratory freeze dryer (Eyela FD-1000, Tokyo Rikakikai, Tokyo, Japan). The chamber pressure was ca. 15 Pa and the trap temperature was \(-40^\circ\text{C} \) (233 K). The sample was frozen in a freezer at \(-40^\circ\text{C} \) for an hour. The activity of yeast samples was not affected by this freezing method (see Fig. 3.1b). The sample frozen with liquid nitrogen showed similar data. The sample was weighed at a specified drying time. The drying experiments were repeated three times, and the average water content was determined.

3. Results

3.1 Thermal stability of yeasts

The thermal stability of yeasts in water (suspension) was measured as a function of
temperature. The remaining activity after 1 hour incubation determined by the fermentative ability decreased sharply when the temperature was over 45°C (Fig. 3.1a). At 30°C the yeast sample suspension was stable up to 30 h (Fig. 3.1b). The yeast was also stable when stored at −40°C in a freezer. This was the sample preparation condition for the present FD experiment.

Fig. 3.1  Thermal stability of yeast in water.
3.2 Inactivation during drying

Because the yeast was very stable at 30°C as shown in Fig. 3.1, the air-drying experiments were carried out at 30°C in order to avoid thermal inactivation during drying. Typical drying experimental data are shown in Fig. 3.2, in which both the average water content and the relative remaining activity of the yeast sample as a function of time are presented. At the beginning of drying, a short constant drying rate period was observed. The water in the interstitial space between yeast particles evaporated during this constant rate period. Subsequently, the water inside the yeast cell diffused out and evaporated. The drying rate decreased with time. As this falling rate period started, the remaining activity decreased (Fig. 3.2). This decrease was found to be due to dehydration inactivation, because the yeast was stable at 30°C up to 1 h as shown in Fig. 3.1.

Fig. 3.2 Hot air drying curves of yeast and the relative remaining activity as a function of drying time. The air temperature was 30°C. The solid curve was calculated from the drying rate of an agar-gelled sample under the same conditions.
Typical FD experimental data are shown in Fig. 3.3. Similar to air drying, a constant drying rate period existed at the beginning, which corresponds to the primary drying phase due to the sublimation of ice. After this phase, the drying rate decreased (secondary drying phase). Dehydration inactivation occurred after the primary drying phase. The drying rate for the freeze-drying method was slightly higher than that for the air-drying method.

Fig. 3.3  Freeze drying (FD) curves of yeast and the relative remaining activity as a function of drying time. The solid curve was calculated from the drying rate of water under the same conditions. As a comparison, the water content data in Fig. 3.2 are also shown.

In order to examine the dehydration inactivation carefully, the remaining activity data were replotted against the average water content (Fig. 3.4). It is clearly seen from this figure that dehydration inactivation occurred when the water content decreased below 0.2
- 0.3 (kg-water/kg-solid).

The drying rate might affect the dehydration inactivation. Therefore, the drying experiments were carried out with different sample thicknesses. Figure 3.5 shows the freeze-drying curves with three different sample thickness values (0.7, 1 and 2 mm). As is clear from the figure, the drying rate became lower with increasing sample thickness. The remaining activity started decreasing at much higher water content for the 0.7 mm sample thickness, whereas the activity remained quite high for the 2 mm sample thickness (Fig. 3.6). These data indicate that the inactivation dehydration becomes more significant at higher drying rates. Air drying experiments of yeasts at 303K with different sample thicknesses showed a similar trend (data not shown).
Fig. 3.5  Effects of sample thickness on freeze drying (FD) curves of yeasts.

Fig. 3.6  Relative remaining activity of yeasts during freeze drying as a function of average water content.
The stability of the dried yeast samples was investigated. Dried samples with different water contents were incubated at 60°C for 1 h. As shown in Fig. 3.1, the fresh (wet) yeast samples lost water activity completely under this condition. As shown in Fig. 3.7, the stability of the dried yeast samples increased dramatically with decreasing water content. It is also shown that addition of sorbitol further increased the stability.

![Graph showing the effect of sorbitol on the remaining activity of dried yeasts.]  

**Fig. 3.7** Effect of sorbitol on the remaining activity of dried yeasts. Yeast samples (1mm thickness) pretreated with or without sorbitol were dried at 30°C. Dried samples at different drying times (different water content) were incubated at 60°C for 1 h, and the relative remaining activities were determined.

**4. Discussion**

Thermal inactivation is dominant during air drying of enzymes and proteins (Yamamoto, 2004; Bruin and Luyben, 1980). Therefore, most proteins or enzymes can be dried without damage at low temperatures.
However, as pointed out by many researchers (Bayrock and Ingledew, 1997; Lievense, et al., 1992), dehydration inactivation occurs in addition to thermal inactivation during drying of microorganisms. Osmotic pressure is another concern during drying and rehydration (Josic, 1982; Mille, et al., 2005).

Significant dehydration inactivation was observed for yeasts during air drying and FD, in which thermal inactivation does not occur. It is still not clear whether the drying rate affects the dehydration inactivation (Lievense, et al., 1992). The drying rate was varied simply by changing the yeast sample thickness. For freeze drying with increasing thickness, the drying rate decreased and the dehydration inactivation was suppressed. Air drying experiments showed similar trends. Air drying at higher relative humidities also resulted in higher remaining activities (data not shown). However, even at low drying rates, the activity decreased when the water content \( X \) reached 0.1–0.2 kg-water/kg-solid. There has been considerable discussion on a critical water content below which dehydration inactivation occurs or below which the activity is greatly or almost completely lost (Josic, 1982; Lievense, et al., 1992; Zayed, and Roos, 2004). It is generally considered that below the monolayer water content \( W_m \) the cells become unstable or lose activities (Josic, 1982; Zayed, and Roos, 2004). For baker’s yeasts, \( W_m \) was reported to be ca. 0.07 kg-water/kg-solid (Josic, 1982). Our study has shown that the water content \( X_D \) at which dehydration inactivation occurs is affected by the drying rate. When the drying rate was decreased, \( X_D \) became smaller. However, even during very low drying rate experiments such as in a desiccator, the activity dropped when \( X<0.1 \). This value corresponds to the \( W_m \) value mentioned above.
It was reported that even by freeze drying, inactivation of yeast is not avoidable (Buera, et al., 1999). Our study also showed that FD did not prevent dehydration inactivation. Several researchers employed fluidized bed drying, which resulted in rather high activity recovery (Bayrock and Ingledew, 1997; Mille, et al., 2005). A different method has also been proposed for drying of yeasts (Rakotozafy, et al., 2000). As pointed out by Chavez and Ledeboer (2007), because spray drying is by far the most economical way of drying liquids or suspensions, a method for obtaining dried food microorganisms of high activity is desirable. It is not easy to control the drying rate for spray drying, although our study indicates that low drying rates may result in higher activities of dried yeasts. Another method is to use a protectant such as sugars or polyols as shown in Fig. 3.7.

Several models have been proposed for the drying mechanism of microorganisms (Debaste, et al., 2008; Li, et al., 2006). For drying of enzymes, a diffusion equation, a heat balance equation, and an equation describing the evaporation and heat transfer at the interface along with a thermal inactivation rate equation provide the inactivation behavior during drying (Yamamoto, 2004; Bruin and Luyben, 1980). A similar model was applied to the drying of probiotic bacteria (Li, et al., 2006). However, the dehydration inactivation rate equation is not explicitly included in the model.
5. Conclusion

The fermentative ability of baker’s yeast dropped sharply when the incubation temperature was over 40°C. When the yeast sample was dried at 30°C where thermal inactivation is negligible, the dehydration inactivation of yeast occurred during both FD and air drying at 30°C after the primary drying phase (FD) and constant rate drying. The critical water content below which dehydration occurred was ca. 0.2–0.3 kg-water/kg-solid.

Higher drying rates increased the dehydration inactivation. The dried yeast samples became stable and maintained the activity at 60°C for 1 h. Addition of sorbitol before drying further improved the stability of dried yeasts.
Chapter 4  Effect of Pretreated with Sugar during Drying of Sliced Vegetables

1. Introduction

In addition to liquid foods and semi-solid foods, agricultural products such as vegetables and fruits are currently being dried and distributed to food processing companies. The purpose of such food drying processes is not only to reduce the volume and weight of the products but also to improve the product stability (shelf life) whereas the product quality must be maintained during and after drying.

Research and developments of new preservation methods are continuously carried out in order to improve the quality of the final product. For drying of vegetables and fruits, freeze-drying (FD) is known to be a good method, by which product shrinkage is eliminated or minimized, and a near-perfect preservation results are expected (Moreira et al., 1998). FD also prevents heat damage and produces products with excellent structural retention (Lin et al., 1998). However, as FD is a costly process, it is only suitable for high-value products (Lin et al., 1998).

More economical methods that can produce high quality dried products are required. Although conventional hot air drying is a cheaper method, it has several disadvantages such as non-uniformity of the dried sample, slower drying rates and lower quality of the resulting products. These, however, can be improved using a combination of different drying methods. Beaudry et al. (2004) compared combined osmotic dehydration of cranberries with microwave-assisted convective drying, convectional hot air-drying, freeze-drying and vacuum drying. Osmotic dehydration is a viable process for partial
removal of water in materials with cellular structure (such as fruits and vegetables). In recent years, osmotic dehydration has received considerable attention due to low operating temperature and reduced energy requirements (Robbers et al., 1997).

Several pre-treatments for hot-air drying are known to be effective for the improvement quality of the product. A blanching process is applied for vegetables to increase drying rate and decrease browning. During the blanching process enzymes such as polyphenoloxidases causing browning, and peroxidase, catalase and phenolase responsible for the development of off-flavors (Severini et al., 2004) are inactivated. Although blanching process improves the color properties, it cannot prevent shrinkage of final products. Some applications showed that pre-treatments of sugar solutions result in very good effect in respect of shrinkage of vegetable slices in production of vegetable-chips (Saito et al., 2002). Previous work has shown that non-reducing disaccharides such as sucrose and trehalose can protect biological systems from the adverse effects of freezing and drying (European Patent Application, 1999). Especially trehalose is known to have many advantages. For example, sweetness of a 10% trehalose solution is 45% as that of a 10% sucrose solution. Trehalose is a non-reducing sugar and therefore does not react with amino acids or proteins to cause Maillard browning. Consequently, deterioration caused by Maillard reaction such as loss of nutrition can be avoided in addition to protection of flavor and color (http://www.-cargill.com/sfi/treappl.htm). One of the problems is that trehalose tends to form crystals in the dried products, which is not favored. In order to avoid such crystal formations we examined the effect of addition of oligo-saccharides (maltosyltrehalose) into a trehalose solution. The isothermal drying experiments as well as the desorption isotherm measurement experiments were carried
out as a function of trehalose/maltosyltrehalose ratio in order to examine solid phase or crystal formation during drying.

Most of the dried products are usually rehydrated for cooking. Rehydration of foods has been studied by many researchers. Osmotic pre-treatments (with sucrose and sodium chloride solution) were reported to improve the rehydration characteristics. It was found that pre-treatment with mixture of salt solution (3%) and sucrose solution (6%) resulted in significant improvement in rehydration and reduced shrinkage (Jayaraman et al., 1990). The previous studies suggest that water loss and solid gain of cellular foods such as vegetables and fruits by applying sugar pre-treatments cause significant structural changes in the tissue structure of foods.

In this study effects of pretreatment of sliced vegetables with sugars on drying/dehydration behavior, and sorption properties and quality of dried vegetables were investigated experimentally. As model vegetables potato and carrot were chosen. Peroxidase activity was measured to confirm the effectiveness of steam blanching. Different sugar solutions in addition to trehalose and maltosyltrehalose were employed as a pretreatment sugar. The change of rehydration properties and microscopic structure of hot air dried vegetables were determined. Isothermal drying of sliced vegetables were carried out and both the drying curve and the dried product appearance were examined carefully.
2. Materials and methods

2.1 Materials

Vegetables (potato and carrot) were purchased at a local shop. They were washed under running water, wiped with blotting paper, hand-peeled and sliced using a manual slicer. The sliced samples were then cut in 20 mm diameter by means of a sampler having a sharp edge (20 mm diameter). The thickness of sliced samples was 0.5, 1, 1.5 or 2 mm, which was checked by using a digital linear gauge (Ono Sokki, DG 911).

Sugars employed in this study are trehalose (Trehaose, Hayashibara, Japan), maltodextrin (dextrose equivalents DE=11, Pinedex #2, Matsutani Kagaku Kogyo, Japan), sucrose and maltosyltrehalose - rich syrup (Hallodex, Hayashibara, Japan). This syrup contains 52% of maltosyltrehalose and the DE value is ca.14. Maltosyl trehalose (C_{24}H_{42}O_{21}, mol.wt 666) is a non-reducing tetrasaccharide, in which maltose is linked to trehalose. Trehalose (C_{12}H_{22}O_{11}, mol.wt 342) is also non-reducing disaccharide, which usually exists as the dehydrate.

2.2 Pretreatments

Steam was applied for 3 minutes for carrot, 4 minutes for potato as blanching based on the peroxidase inactivation experimental data and the texture of the sample (see Fig. 4.1). After blanching, the samples were cooled, drained and wiped with blotting papers. For pretreatments, potato and carrot slices were soaked in 20 wt% sugar (sucrose, trehalose, maltodextrin, maltosyltrehalose - rich syrup) solutions for 10 minutes before the drying experiment. The potato and carrot slices without blanching were kept dried and rehydrated as controls. For the isothermal drying experiment, the sliced samples were
coated with sugar powders and then blanched, as the second sugar treatment method.

### 2.3 Peroxidase activity measurement

1wt% guaiacol and 1wt% H₂O₂ solutions were dropped onto the surface of sliced vegetable samples (ca. 1 mL), and then the appearance after 5 minutes was captured by a digital camera.

### 2.4 Determination of water loss and solid gain during pretreatments

The samples after blanched were dipped in a sugar solution of a specified concentration for an assigned time. Water loss \((WL)\) and solid gain \((SG)\) were calculated from the following equations (Antonia and Murr, 2002):

\[
WL = \left(\frac{W_{wa} - W_w}{M_0}\right) \times 100 \quad (4.1)
\]

\[
SG = \left(\frac{W_s - W_{s0}}{M_0}\right) \times 100 \quad (4.2)
\]

where, \(WL\) and \(SG\) are water loss and solid gain in %, respectively. \(W_s\) is the solid mass at time \(t\), \(W_{s0}\) is the initial solid mass, \(W_w\) is the mass of water at time \(t\), \(W_{w0}\) is the initial water mass, and \(M_0\) is the initial mass (water + solid) of the fresh sample (prior to blanching).

### 2.5 Desorption isotherm

Samples were stored in a sealed container in the presence of saturated salt solutions of known water activities \((a_w)\). A constant temperature and humidity chamber (Enviros, KCL-1000, EYELA, Japan) was also employed for the measurement.

The samples were weighed periodically. It is not easy to confirm the equilibrium of these
samples as they change the physical properties with time (i.e., crystallization, rubber-glass transition, etc.). So we decided to terminate the experiment when the weight loss became less than 2% per 12 hours (usually two to three days).

The isotherm data were fitted by GAB model (Rahman, 1995; Timmermann, 2003).

2.6 Drying experiment

Isothermal drying experiments were performed in a constant-air temperature box. Silica gels or saturated salt solutions were placed in the box to control the relative humidity (RH). The air temperature was controlled so that the sample temperature is maintained at an assigned temperature. The air temperature in the drying box was somewhat higher than the assigned value at the beginning of the experiment, and then, lowered gradually with the progress of the drying. The weight and the temperature measurements were done separately.

2.7 Rehydration experiment

Dried vegetables are usually rehydrated before consumption by using boiled water. For this reason, the rehydration properties were evaluated by immersing the dried samples in distilled water with 373 K temperatures (boiled water) and experiments were repeated for water with 298 K (room temperature). Ratio between the sample weight and the water weight was ca. 1 to 100. After soaking, the samples were taken from the water. Then the excess water was removed with the help of tissue paper, and weighed at 5, 10, 15, 30, 60, 90, 120, 150, and 180 minutes for those at 298 K and at 0.5, 1, 2, 4, 6, 8, and 10 minutes for those at 373 K. Rehydration ratio did not change too much after 4 minutes for carrot samples and after 6 minutes for potato samples at 373 K. For this reason and also to avoid
cooking of samples, the measurements at 373 K were performed for only 10 minutes. Determinations were carried out in triplicate.

As a measure of the rehydration characteristics of the sample, the rehydration ratio (RR) was expressed relevant to the moisture content of the rehydrated sample after $t$ minutes of rehydration ($X_{rh}$) and the moisture content of the dried sample for the rehydration tests ($X_{dh}$).

Rehydrated ratio (RR) of the samples were calculated as follows (Pappas et al., 1998):

\[
RR = \frac{X_{rh} + 1}{X_{dh} + 1} \tag{3.3}
\]

The ratios between moisture content of rehydrated samples and moisture content of fresh samples were also calculated using the same equation by replacing the moisture content of the fresh sample ($X_{fh}$) instead of ($X_{dh}$) values to examine whether the rehydrated sample can gain enough moisture to reach its original moisture content or not.

### 2.8 Microscopic analyses

The microscopic pictures of vegetable slices were captured by a digital microscope by using x10 objective lens (PCSCOPE, Inabata Co. Ltd., Japan). The changes of the shape and the size of the cell structure were analyzed by using a PCSCOPE Analyzer software (Inabata Co. Ltd., Japan).
3. Results and discussion

3.1 Effect of blanching on peroxidase inactivation

Figure 4.1 shows the effect of blanching time on peroxidase inactivation. It is clear that steam blanching for three minutes completely inactivate peroxidase. Therefore, steam blanching for 3 minutes was chosen as the blanching condition.

<table>
<thead>
<tr>
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<th>potato</th>
<th>carrot</th>
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<td><img src="image2.png" alt="before" /></td>
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<tr>
<td></td>
<td><img src="image1.png" alt="after" /></td>
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<tr>
<td>Blanching for 3 min</td>
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<td></td>
<td><img src="image1.png" alt="after" /></td>
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<tr>
<td>Before reaction</td>
<td><img src="image1.png" alt="before" /></td>
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<tr>
<td>After reaction</td>
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<td><img src="image2.png" alt="after" /></td>
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Fig. 4.1. Effect of blanching time on peroxidase inactivation.
3.2 Mass transfer during pretreatments

Solid gain ($SG$) and water loss ($WL$) of carrot samples after pretreatments with different process time and sugar concentration are shown in Fig. 4.2. Both increasing process time and sugar concentration increased with $SG$ and $WL$ values. Generally $SG$ and $WL$ values treated with sucrose were higher than those treated with trehalose. Potato samples showed larger $SG$ and $WL$ values compared with those of carrot samples at the same conditions. For example while $WL$ value for the samples pretreated with sucrose that have 40 $\%$ concentration and 30 min was determined as 15.8 $\%$ for carrot samples, this value was determined as 52.7 $\%$ for the potato samples. $SG$ values for the carrot and potato samples treated in same way were determined as 14.5 $\%$ and 41.8 $\%$. These values were determined rather lower when trehalose pretreatments applied. Large $WL$ values indicate strong effect of osmotic dehydration. However, at the same time considerable amounts of sugars are up taken by sliced vegetables, which is not preferred. So, in the following experiments we chose a process (soaking) time of 10 min in a sugar solution of 20 $\%$ concentration.
Fig. 4.2  Water loss and solid gain of carrot samples during pretreatment with sugar solutions.

3.3 Desorption isotherm

Sorption isotherms for dried carrot and potato samples with different pretreatments are shown in Fig. 4.3. The sorption isotherm data were fitted by the GAB equation, and the GAB parameters determined are shown in Fig. 4.3 (a) and (b) for carrot and potato samples, respectively. As seen in this figure, sugar pretreatments lowered the equilibrium water content for the water activity ($a_w$) below 0.80. Especially trehalose pretreatment decreased the equilibrium water content for both carrot and potato samples.

The equilibrium water content at a given $a_w$ for the carrot samples treated with sugar
solutions were lower than those for the blanched and untreated samples especially when \( a_w = 0.75 \).

Figs. 4.4 and 4.5 show the desorption isotherm of trehalose and maltosyltrehalose (MT) –rich syrup (Hallodex), respectively. Trehalose solutions formed crystals after one day and the equilibrium water content is equal to that of trehalose-dihydrate irrespective of water activity \( (X = 0.11) \). On the other hand, the shape of the desorption isotherm of Hallodex is quite similar to a typical food isotherm. The GAB parameter values were close to those of maltodextrin (Yamamoto et al., 2004; 2005). This is not surprising as the DE of the two sugars are almost same.

When Hallodex was added to trehalose, the formation of crystals was inhibited (Fig. 4.6). When the Hallodex content is above 0.1 (kg-Hallodex /kg-total sugar), no crystals were observed and the sample was transparent even at low equilibrium moisture contents. The isotherm was similar to that of Hallodex.
Fig. 4.3 Sorption isotherms of dried vegetable samples: (a) carrot samples; (b) potato samples.
Fig. 4.4  Desorption isotherm of trehalose.

Fig. 4.5  Desorption isotherm of maltosyltrehalose-rich syrup (Hallodex).
Isothermal drying experiments with a trehalose-Hallodex mixture showed that when Hallodex content was ca 10 wt% of the total sugar weight, solid phase was not observed. The sample was transparent until the end of the drying. The drying curve was almost superimposable to that for Hallodex solution. The isotherm data and the drying data indicate that a trehalose-Hallodex mixture is suited as a pretreatment solution for sliced vegetable drying as the crystals may not appear on the dried product surface.

3.4 Drying experiment

Isothermal drying experiments at 303K were carried out for sliced potato samples with different pretreatment procedures. As shown in Figs. 4.7 and 4.8, the drying curves are different. With sugar solution pretreatment the sample was pre-dehydrated due to osmotic...
dehydration. The osmotic dehydration effects were more significant with the powder treatment. The drying curve with the HalloDEX pretreatment shows much higher drying rate compared with others especially at the beginning of the drying experiment. On the other hand, the drying curve with trehalose shows very low drying rates at later stage of drying where the average water content $X$ is below 0.2.

Fig. 4.7  Drying curves of sliced potato samples with or without pretreatments.

Fig. 4.8  Drying curves of sliced potato sample with different pretreatments.
The appearance of the dried product with different pretreatment procedures is shown in Figs. 4.9 and 4.10. Without any pretreatments potato samples showed quite significant irregular shrinkage. The color is much darker compared with other samples. Blanching itself is quite effective especially for the retention of favored color. All sugar treatments after the blanching resulted in better product shape and color. The color of the sample pretreated with trehalose is somewhat different from others. This may be due to crystallization of trehalose, which was not identified quantitatively.

Fig. 4.9 Appearance of dried sliced vegetables with different pretreatments: (a) non treatment, (b) blanching, (c) sucrose solution treatment after blanching, (d) trehalose solution treatment after blanching.
Other important properties of dried products are textures, taste and flavors. The dried products pretreated with a trehalose-maltosyltrehalose mixture solution were immersed in a hot water in order to test the quality. They were still crispy and not sweet.

In order to prevent crystallization of trehalose a mixture of trehalose and Hallodex was used as a pretreatment sugar solution. As shown in Fig. 4.6 and isothermal drying data (data not shown), this mixture can prevent crystallization of trehalose effectively.

As shown in Fig. 4.11, the drying curve for the trehalose-Hallodex mixture pretreatment is favorable. The drying rate is much higher at later stage of the drying ($t > 100$ min and $X < 0.2$).
3.5 Effects of pre-treatments on rehydration characteristics

The dried samples were soaked into water to measure the moisture regain to check their capability to rehydrate. Figs. 4.12 – 4.15 show the rehydration ratio and moisture change of samples during rehydration process.

The moisture regain behavior was affected by the pretreatments. The carrot samples that dried with sugar treatments after the blanching had a faster rehydration at 298 K than those with the blanching and without treatment as shown in Fig. 4.12. For example, initial moisture contents of potato samples were 0.067 kg-water/kg-solid (with no treatment), 0.038 kg-water/kg-solid (with the blanching), 0.0801 kg-water/kg-solid (with sucrose treatment after the blanching) and 0.0539 kg-water/kg-solid (with trehalose treatment after the blanching), respectively. After 30 minutes, velocity of absorbing water decreased
and after 90 minutes it stayed almost constant. At 30 minutes the moisture content of same samples became 6.32, 4.62, 7.88, and 6.53 kg-water/kg-solid, respectively. The same trend was observed for carrot samples although the rehydration of carrot samples was faster. Very sharp increase of moisture content was observed for 10 minutes, and after that the moisture content of carrot samples did not increase appreciably.

Fig. 4.12  Effects of pre-treatments on rehydration ratio of carrot samples at 298 K.

Fig. 4.13  Effects of pre-treatments on rehydration ratio of carrot samples at 373 K.
During rehydration, solid amount of samples decreased while their water content increased. For this reason their moisture contents (db) were calculated as very high after rehydration. Average moisture contents of fresh products were 6.6 kg-water/kg-solid for potato, and 30.92 kg-water/kg-solid for carrot samples.
The ratios between moisture content of rehydrated samples and moisture content of fresh samples were found smaller at 373 K than the values at 298 K both potato and carrot samples. These values of carrot samples were found 0.84 (with no treatment), 0.93 (with the blanching), 0.94 (with sucrose treatment after the blanching), and 0.99 (with trehalose treatment after the blanching) at 298 K, respectively. These ratios at 373 K were found 0.70, 0.82, 0.83, and 0.85 for carrot samples. The ratios for potato samples were calculated as 0.84, 0.95, 0.98, 1.04 at 298 K and 0.84, 0.86, 0.96, 1.02 at 373 K, respectively. It was found that moisture content of trehalose treated potato samples was higher than that for fresh samples after rehydration. Namely trehalose treated potato samples gained more water than their first water content.

In all applications, it was seen that there were initial rapid moisture gain periods followed by very slow moisture regain periods. Rehydration time decreased markedly by increasing water temperature from 298 K to 373 K. As seen in Figs. 4.13 and 4.15 the first period is much shorter for 373 K. For instance, carrot samples rehydrated at 298 K continued to regain water rapidly until 30 minute while at 373 K until 2 minute. As seen in Figs. 4.13 and 4.15 an increase in temperature of water from 298 K to 373 K increased rehydration ratio of samples treated trehalose.

3.6 Microscopic observation of pre-treated products

Rehydration can be considered as a measurement of the injury to the material caused by drying and treatment preceding drying (McMinn et al., 1997). For this reason microscopic observations of samples were attempted after pre-treatments, and rehydration. Unfortunately, microscopic examinations of completely dried samples could not be made
because of their brittle structure, and fragility.

As seen in Fig. 4.16 cell size of samples that were blanched, dipped into sucrose solution and dipped into trehalose solution were found smaller than those of the control samples. At the same time intercellular spaces increased with pre-treatments. This decrease in cell size and increase in intercellular space was large for sucrose, and small for trehalose among treated samples. According to analyses of micrographs average cell areas of samples that were 8042.29 $\mu$m$^2$ (with no treatment), 2037.70 $\mu$m$^2$ (with the blanching), 1688.70 $\mu$m$^2$ (with sucrose treatment after the blanching), and 4453.75 $\mu$m$^2$ (with trehalose treatment after the blanching), respectively. Average intercellular space of samples were 18.43, 37.71, 45.62, and 23.76 $\mu$m, respectively.

Fig. 4.16  Microscopic pictures of cell structure of carrot samples with or without pre-treatments (a: no treatment, b: blanching, c: sucrose treatment after blanching, d: trehalose treatment after blanching).
Pre-treatments with sugars resulted in an increase in moisture content during rehydration compared to the samples with no treatment and blanching. After rehydration microscopic structure of these samples were given in Fig. 4.17. Average cell areas of samples were measured as $1183.8 \, \mu m^2$ (with no treatment), $2281.57 \, \mu m^2$ (with the blanching), $2270.46 \, \mu m^2$ (with sucrose treatment after the blanching), and $2864.93 \, \mu m^2$ (with trehalose treatment after the blanching), respectively. According to these values reconstruction of cells for samples with trehalose-treatment is better.

Fig. 4.17  Microscopic pictures of cell structure after rehydration of dried carrot slices with or without pre-treatments (a: no treatment, b: blanching, c: sucrose treatment after blanching, d: trehalose treatment after blanching).

The micrographs were captured also for potato samples (Figs. 4.18 and 19). As seen in these Figures, the no-treated samples have starch granules spreading through surface with
their distinctively visible cellular structure. But in other applications starch granules cannot be observed because of blanching process that caused gelatinization of the granules. For potato samples decreasing of cell size occurred while intercellular space was increasing. Average cell size of potato samples were measured as 18199.42 μm² (with no treatment), 16091.23 μm² (with the blanching), 12581.42 μm² (with sucrose treatment after the blanching), and 14030.38 μm² (with trehalose treatment after the blanching), respectively. For potato also decreasing of cell size of trehalose-treated samples was found less than those samples treated using sucrose.

Fig. 4.18 Microscopic pictures of cell structure of potato samples with or without pre-treatments (a: no treatment, b: blanching, c: sucrose treatment after blanching, d: trehalose treatment after blanching).
As seen in Fig. 4.19, after rehydration cell size of samples were measured as 3129.53, 10887.02, 12934.04, and 18192.94 μm², respectively. According to these values reconstruction by rehydration was the worst for no treatment samples, and the best for treated samples using trehalose solution.

Reason of this better reconstruction by trehalose treatment can be explained that trehalose is stable in thermal processing systems and does not react with amino acids or proteins to commence Maillard Reaction and caramelization that may cause loss of flavor, color and texture change.
4. Conclusion

Effects of pretreatment methods on the drying curve, the rehydration properties, and the dried product quality of sliced vegetables (potatoes and carrots) were experimentally investigated.

Soaking of samples in a trehalose-maltosyltrehalose solution was found to be best suited as a pretreatment sugar solution after a three-minute steam blanching. The drying rate was accelerated with this pretreatment. The dried product showed better quality (less shrinkage and favored color). During the pretreatment process, the water content of the sample decreased significantly due to osmotic dehydration. Benefits expected and achieved from pretreatments are improved rehydration characteristics. Rehydration properties of the sample with sugar treatment are improved compared to the samples with blanching and no treatment.

According to microscopic measurements pretreatment of trehalose solution improved the reconstititutional properties of both carrot and potato samples more than pre-treatment of sucrose.

Sorption isotherms of the samples with trehalose treatment showed lower equilibrium water contents compared with the samples with no treatment.
Summary

In this study we have investigated the drying behavior of sugar (carbohydrate) solutions and protective effects of sugars on enzyme retention, inactivation of microorganisms and sliced vegetables during drying.

1. Drying rates of sugar solutions were controlled by the water diffusion and decreased very sharply with decreasing water content. Since the activation energy of diffusion became higher at low water contents the drying rates were quite low at such low temperature as 293K. The equilibrium water content at a given water content increased with decreasing temperature. For the drying of sugar solutions at low temperatures a long drying time with air of low relative humidity is needed.

2. When a sugar solution containing an enzyme is dried, the enzyme activity was retained at the beginning and decreases in the later period of drying. However, quite high enzyme retention was obtained when the sugar solution was dried to low water contents while the sample temperature did not approach the air temperature. This is because enzymes become stable with decreasing water content.

3. When baker’s yeast was dried at 303K, where the activity (fermentation ability) is completely retained in a solution, inactivation was observed in the late stage of drying. This inactivation, dehydration inactivation, was significant when the water content was lower than 0.2-0.3. Dried yeasts became stable especially
when the water content became low (<0.2). Furthermore, addition of sugar (sorbitol) improved the stability of dried yeasts.

4. When sliced vegetables were dried without any pre-treatments, significant shrinkage and color change were observed. Steam-blanching followed by soaking in a sugar solution resulted in better properties (less shrinkage and better color retention). Trehalose and sucrose were found to be good sugars for the pre-treatment. Osmotic dehydration occurred during soaking in the sugar solution. One of the disadvantages of using trehalose is that it forms crystals easily. Maltosyl-trehalose was another option, which does not crystalize during or after drying. Microscopic observation of rehydrated samples revealed that the cell structure was well remained when the sliced vegetables were pretreated by steam blanching and soaking in a sugar solution.

Sugars are important components of foods and play important roles in various different food processing. It is important to understand how sugar solutions are dried and how they work as additives or protectants of foods and food components. Further study is needed to investigate multi-component systems which contain sugars and other food components.
Nomenclature

$A$ effective drying area [m$^2$]

$a_{w}$ water activity [- -]

$C$ parameter in the GAB equation [- -]

$C_p$ heat capacity at constant pressure [J/kgK]

$D$ diffusion coefficient [m$^2$/s]

$D_0$ molecular diffusivity or diffusion coefficient at dilute solutions [m$^2$/s]

$d_s$ density of pure solid [kg/m$^3$]

$d_w$ density of water [kg/m$^3$]

$E_D$ activation energy for diffusion [J/mol]

$E_d$ activation energy for enzyme inactivation [J/mol]

$\Delta H_v$ latent heat of water evaporation [J/kg]

$h_g$ heat transfer coefficient in the gas phase [W/m$^2$K]

$J$ drying rate [kg-wate/m$^2$s]

$j_w$ mass flux [kg/m$^2$s]

$K$ parameter in the GAB equation [- -]

$k_d$ First-order inactivation rate constant [1/s]

$k_g$ mass transfer coefficient in the gas phase [m/s]

$M_W$ molecular weight [kg/kg-mol]

$Q_s$ excess (isosteric) heat of adsorption [J/mol]

$R$ slab (half) thickness of the sample, cylinder radius or sphere radius in the absence of water [m]

$R_0$ Initial slab thickness of the sample, initial cylinder radius or initial sphere radius in the absence of water [m]
\( R_G \) gas constant \[ \text{[J/mol K]} \]

\( R_s \) slab (half) thickness of the sample in the absence of water \[ \text{[m]} \]

\( \text{RH} \) relative humidity \[ \text{[\%]} \]

\( r \) space coordinate \[ \text{[m]} \]

\( T \) absolute temperature \[ \text{[K or °C]} \]

\( T_A \) Air temperature \[ \text{[K or °C]} \]

\( T_d \) Sample temperature \[ \text{[K or °C]} \]

\( T_g \) Glass transition temperature \[ \text{[K or °C]} \]

\( T_{WB} \) wet bulb temperature \[ \text{[K or °C]} \]

\( t \) time \[ \text{[s]} \]

\( U_A \) relative velocity of air \[ \text{[m/s]} \]

\( W, w \) water (moisture) concentration (mass fraction)

\[ = \frac{X}{1+X} \] \[ \text{[kg-water/kg-total]} \]

\( W_m \) water content equivalent to a monolayer coverage \[ \text{[kg-water/kg-dry solid]} \]

\( W_s \) weight of solid \[ \text{[kg]} \]

\( W_w \) weight of water \[ \text{[kg]} \]

\( X \) water (moisture) content \[ \text{[kg-water/kg-dry solid]} \]

\( X_0 \) X at \( t = 0 \) \[ \text{[kg-water/kg-dry solid]} \]

\( \bar{X}, X_a \) average water content \[ \text{[kg-water/kg-dry solid]} \]

\( X_c \) critical water content \[ \text{[kg-water/kg-dry solid]} \]

\( X_E \) relative (average) remaining activity of enzyme \[ \text{[-]} \]

\( X_e \) equilibrium water content \[ \text{[kg-water/kg-dry solid]} \]

\( X_D \) water content which dehydration inactivation of yeast occur \[ \text{[kg-water/kg-dry solid]} \]
\( X_S \) surface concentration \([\text{kg-water/kg-dry solid}]\)

\( z = \int_0^r \rho_s r^\nu \, dr \) Space coordinate in the shrinking system \([\text{kgm}^{-2}]\)

\( \nu \) geometrical factor; 0 for slab, 1 for cylinder, and 2 for sphere

\( \rho \) mass concentration \([\text{kg/m}^3]\)

\( \rho_s \) mass solid concentration \([\text{kg-solid/m}^3]\)

\( \rho_w \) water vapor concentration \([\text{kg/m}^3]\)

\( \tau' = t/(d_s R_s)^2 = t/(W_s/A)^2 \) \([\text{sm}^4/\text{kg}^2]\)

<Subscripts and Superscripts>

\( A \) air

\( a \) apparent value or average value

\( b \) bulk

\( E \) enzyme

\( i \) interface

\( \text{ref} \) reference value

\( s \) solid

\( \text{sat} \) saturated

\( W \) water

\( 0 \) value at \( t = 0 \) or initial value

\( \bar{\cdot} \) average value

\( ' \) gas phase
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List of Publications

1. Sachie Fujii, Noriko Yoshimoto and Shuichi Yamamoto; Enzyme Retention During Drying of Amorphous Sugar and Carbohydrate solution: Diffusion Model Revised. Drying technology, 31, 1525-1531 (2013)


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