Original paper

Numerical Modeling of Heterogeneous Moisture Diffusion in Milled Rice Grains: Diffusion Coefficient as a Function of Moisture, Temperature and Time

Jonathan PEREZ¹, Fumihiko TANAKA^{2*}, Daisuke HAMANAKA² and Toshitaka UCHINO²

¹Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, 6-10-1, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

²Faculty of Agriculture, Kyushu University, 6-10-1, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Received August 20, 2013 ; Accepted October 25, 2013

The heterogeneous moisture diffusion of milled rice grains at 25, 35 and 45°C was simulated in 3D using the finite element method. The objectives of the study were to investigate the effects of temperature on moisture absorption and to predict the heterogeneous moisture diffusion in milled rice grains. Major routes and cracks channeled and facilitated rapid moisture movement in the grain. High temperature increased the rate of moisture movement. The moisture diffusion coefficient expressed as a function of moisture, temperature and time adequately described the heterogeneous moisture diffusion characteristics in milled rice. The integration of the logistic function of time reduced the root mean square error (RMSE) values between the experimental data and the numerical solution. Moreover, the RMSE values were much lower than the values modeled with moisture and temperature only. Modeling moisture transfer using the major routes of moisture revealed an increase in the modified frequency factor of the moisture diffusion coefficient.

Keywords: Heterogeneous moisture diffusion, milled rice, finite element modeling, diffusion coefficient, 3D modeling

Introduction

The cooking of rice is initiated by two concurrent processes: the hydration process and the heating process. The purpose of grain hydration is to bring the moisture within the grain to an appropriate level to cause partial disruption in the crystalline structure of the starch. On the other hand, heating raises the temperature to a sufficient level to gelatinize the starch granules. Whether the cooking of rice is done at home or commercially, these two processes are required. Usually, the cooking process requires a longer duration because the starch granules need time to become hydrated in order to be gelatinized (van den Doel *et al.*, 2009). Thus, researchers and food processors alike are investigating ways to accelerate water uptake, thereby shortening the cooking time and reducing costs. Hence, this study aims to provide relevant data that will be useful in the design and optimization of the cooking

process.

Modeling of the moisture transfer in grains during soaking has attracted considerable attention. Mathematical modeling and simulation is one of the methods previously carried out to describe moisture transfer. There have been several attempts in the past to model moisture diffusion in rice grains. Bakalis *et al.* (2009) modeled the diffusion of moisture in rice using finite element analysis with Fickian diffusion. The result of their findings fit well when using a nonlinear dependency of the effective moisture diffusivity. van den Doel *et al.* (2009) also modeled moisture diffusion in rice using water demand. The results of their simulation were in agreement with MRI observations made during cooking. Bello *et al.* (2010) used partial differential equations and finite difference methodology to model the diffusion of moisture in rice. Landau transformations were used to address the diffusion

*To whom correspondence should be addressed.

E-mail: fumit@bpes.kyushu-u.ac.jp

of moisture with moving boundaries. Their findings revealed that the “differential” diffusion coefficient increased as the mean moisture content of rice increased with time. Perez *et al.* (2011) simulated the moisture diffusion and hygroscopic swelling in rice in three dimensions (3D) using Fick’s or Fickian diffusion and Peleg’s equation. The results of these studies were promising in understanding the hydration of rice. However, due to the complexity of grain geometry, which renders the diffusion process heterogeneous, it remains necessary to simulate the heterogeneous diffusion of moisture in milled rice in order to realistically reproduce the conditions occurring during moisture absorption. By definition, heterogeneous denotes variety and indicates non-uniformity. Ogawa *et al.* (2003) showed that the morphology of the starch particles in the grain is made up of different sizes. Voids and microcracks also served as microchannels for moisture migration. They also reported that the penetration of moisture in rice grain is unequal and heterogeneous.

Using commercially available software codes, the diffusion of moisture can be studied either homogeneously or heterogeneously. Perez *et al.* (2012) conducted 3D modeling of the homogeneous diffusion of moisture in milled rice using a diffusion coefficient modeled as a function of moisture and temperature. In the present report, moisture diffusion in rice is modeled heterogeneously and the diffusion coefficient is expressed as a function of moisture, temperature and time. In addition, several moisture transfer routes were studied and identified in the rice grain.

Materials and Methods

Preparation of samples and experimental set-up Rough rice samples harvested in the summer of 2012 were used in the experiment. The samples were de-husked using a laboratory-type dehusker (FC2K; Otake Agricultural Machinery Co. Ltd., Aichi, Japan). After de-husking, the brown rice samples were sorted using a grain quality inspector (RGQI20AS; Satake Co. Ltd., Hiroshima, Japan) to remove the immature, chalky and damaged kernels. The samples were then polished using a Magic Mill (SKM-5B; Satake Co. Ltd., Hiroshima, Japan) to produce white rice. Ten percent of the original weight of the brown rice samples was removed during the polishing process.

Fig. 1. Meshed and unmeshed 3D geometry of rice used in the modeling of heterogeneous moisture diffusion. In Fig. 1b, the light gray bounded regions (boundary one) indicate constant surface water content, while the dark gray bounded region (boundary two) was set to zero mass flux.

The initial moisture content of the samples was about 12.87 g H₂O/g dry matter (d. m.).

The experiment for the diffusion of moisture and observation of the major passageway of moisture was conducted inside a laboratory type incubator (BITEC300; Shimadzu Corp., Tokyo, Japan). Three temperature levels were assessed: 25, 35 and 45°C. An electric water bath (BO500; Yamato Scientific Co. Ltd., Tokyo, Japan) was used to heat the water during the experiment. The depth of the water was sufficiently deep to partially submerge the two 100-mL beakers and the Petri dish. The beakers were filled with 85 mL of distilled water while the Petri dish was half filled. The temperature of the water in the beaker and Petri dish was monitored with a digital thermocouple. A magnetic stirrer was also provided to facilitate uniform heating of the water.

Soaking of milled rice grains About 10 g of polished rice was placed in a screen pouch and then immersed in the water. The samples were removed from the soaking water at 10 min intervals. Excess water in both screen and samples was removed by centrifuging the samples in a centrifuge machine at 800 rpm for 5 min. After removing the excess water, the weight of the samples was measured. The samples were then returned to the water for further soaking. This process was repeated until the samples had been soaked for 80 min. The soaking experiment was replicated four times.

Examination of the principal pathways of moisture Cracked and fissure free polished rice samples were prepared for observation of moisture diffusion. A video microscope (VMS-170; Scalar Co. Ltd., Tokyo, Japan) connected to a laptop computer was used to capture images of the sample during the experiment. Images of individual grains during soaking were taken at two-minute intervals. The sampling was replicated six times at each soaking temperature.

Simulation of heterogeneous moisture diffusion The heterogeneous moisture diffusion in grains was simulated using COMSOL Multiphysics v4.3a (COMSOL Inc., Stockholm, Sweden). Perez *et al.* (2012) reported a coupled analysis on the homogenous moisture diffusion and hygroscopic swelling in rice. They modeled the moisture diffusion coefficient as a function of moisture and temperature. However, in the present report the diffusion coefficient was modified by integrating time as one of several factors in the model. Figure 1 shows the 3D model used in the study. The 3D geometry was discretized into numerous tetrahedral elements and the backward differential formula (BDF) was used to obtain the results. The total number of elements used was 65091. The number of degrees of freedom solved was 95908. The moisture diffusion flux was applied in the gray bounded regions (Fig. 1b). The selection was done manually based on previous experimental observation of the principal routes of moisture in grains.

The equations for the diffusion coefficient are presented below:

$$\frac{\partial M}{\partial t} = \nabla \cdot [D(M, T, t) \nabla M] \quad \text{.....Eq. 1}$$

The initial condition is given by:

$$\text{at } t = 0 \quad M = M_o \quad \text{.....Eq. 2}$$

The boundary conditions in the two different regions were:

Boundary one:

$$\text{at } x, y, z \in \text{surface}, t \geq 0 \quad M = M_s \quad \text{.....Eq. 3}$$

Boundary two:

$$\text{at } x, y, z \in \text{surface}, t \geq 0 \quad J = 0 \quad \text{.....Eq. 4}$$

The dependence of the diffusion coefficient to moisture, temperature and time is outlined using the following equations:

$$D = D_o \exp\left(-\frac{aE_s}{R_g T}\right) f(t) \quad \text{.....Eq. 5}$$

$$D_o = (b) \exp\left(\frac{c}{T}\right) \quad \text{.....Eq. 6}$$

$$f(t) = \frac{k}{1 + l e^{-mt}} + n \quad \text{.....Eq. 7}$$

The symbols used in the notations are as follows: M , moisture content; M_s , equilibrium moisture content; D , diffusion coefficient in m^2/s ; D_o , modified frequency factor of the moisture diffusion coefficient; E_s , activation energy in kJ/kg ; R_g , gas (water vapor) constant in kJ/kg-K is equivalent to 0.4615. Moreover, T is the soaking temperature in K, J is the moisture (mass) diffusion flux, t is the soaking time in seconds and a, b, c, k, l, m and n are numerical constants. Some of these constants bear specific units. For b, c and m , their units are as follows: m^2/s , K and $1/\text{s}$, respectively. The numerical constant a is equivalent to 0.5 (Bello *et al.*, 2010) while b and c are equivalent to 0.006375 and 1.75054, respectively.

The logistic function, $f(t)$, also known as the sigmoid function, has been widely used in a range of fields, i.e., in medicine, it was used in the modeling of tumor growth. It was also applied to the analysis of the autocatalytic reaction in the field of chemistry. According to the Fermi-Dirac statistics in physics, the logistic function was also used in the determination of the statistical distribution of fermions over the energy states of a system in thermal equilibrium. Thornley and France (2005) cited additional applications of the logistic function. Thus, in the present experiment, the logistic function was applied because microscopic cracks, which are not visible to the human eye, are believed to develop within the interior of the endosperm during soaking. The quantity and size of these microscopic cracks are thought to vary with time. These micro cracks soon widen and serve as channels for water migration. The formation of these cracks causes an abrupt rise in the amount of moisture in the grain. For this reason, we want to validate the applicability of the logistic function in the analysis of moisture diffusion in grains. The purpose of integrating the logistic function to the diffusion coefficient equation was to adjust for the abrupt rise in moisture caused by cracks and correct the

minor discrepancies in the fitting of the simulated data.

The equations of the activation energy and latent heat of vaporization of water are shown below as:

$$E_s(M, T) = (Q_{st})[1 + (75.5M^{-1.9})(T-273.15)^{-0.37}] \quad \text{.....Eq. 8}$$

The latent heat of vaporization of water is given by:

$$Q_{st} = 2500.8 - 2.23668(T - 273.15) \quad \text{.....Eq. 9}$$

The data used in the derivation of Eq. 8 was taken from Murata *et al.* (1996a, 1996b). This was accomplished by fitting Eq. 8 to the original data of the latent heat of vaporization of water of polished rice at the different temperatures listed in their report. The Q_{st} is the latent heat of vaporization of water in kJ/kg .

Results and Discussion

Regions of high moisture movement The diffusion of moisture in rice grains was monitored by capturing images of grains during soaking. Seven samples were tested at each temperature. Figure 2 shows a series of images of the moisture migration in grains at different temperatures. These images were used to validate key zones on the grain that conveyed and enabled moisture to penetrate towards the interior of the grain. In general, zones identified with high moisture movement were those at the apex and base of the grain. Initially, the grain was translucent and grayish in color but as time progressed, moisture penetration in the grain turned some boundaries in the grain to milky white color. The milky white color indicates a near and/or total moisture saturation. Probable reasons for this are the removal of the embryo, also known as the germ, and abrasion of the aleurone layer during milling. The embryo contains proteins, fatty acids, vitamins and enzymes. During milling, the embryo is detached from the starchy endosperm and the inner starchy portion of the endosperm is exposed. In addition, because aleurone cells continue to divide periclinally in the developing cereal endosperm the youngest cells are present in the sub-aleurone layer and the oldest cells in the central part of the endosperm. Moreover, in both small grain cereals and other panicoid species the sub-aleurone cells contain few starch granules, which tend to be smaller than those in the central endosperm cells (Shewry and Halford, 2002). Smaller sized starch granules more easily absorb moisture than bigger sized granules. Similarly, the abrasive action between the screen and the grain removes the fatty layer at the base of the grain. Over time, the development of cracks and fissures accelerated the diffusion of moisture. Most samples developed cracks at all soaking temperatures. Small arrowheads indicate the visible cracks that developed in the grain (Fig. 2). Depending on the sample, visible cracks were found to appear as early as two min and as late as 22 min. On the average, cracks appeared after 12 min. Single and/or multiple cracks were found to develop in some samples. The visible cracks are believed to develop from microscopic cracks that form in the interior of the grain.

The internal grain structure upon soaking in distilled water for

Fig. 2. Identified sites on the rice kernel with rapid moisture diffusion. a) 25°C, b) 35°C, c) 45°C.

5 min at room temperature was observed microscopically and is shown in Figs. 3a and 3b. The internal microstructure of the grain indicates that it is made up of an irregular crystalline structure. The composition of the crystalline structure showed two distinct grain sizes - coarse and fine grain crystals.

The coarse grains are glassy in appearance, smooth and are polygonal in shape. The fine grain crystals appeared rough in structure. In Fig. 3a, the internal microstructure did not have any signs of cracks while 3b showed some microscopic cracks, indicated by several arrowheads.

Effect of temperature on moisture diffusion The result of the soaking experiments is shown in Fig. 4. The characteristic moisture

Fig. 3. A view of the internal microstructure of a rice grain soaked in distilled water for 5 min at room temperature. The images were observed under a confocal laser scanning microscope (20X magnification). The samples were not stained in any staining or coloring agent. Fig. 3a shows the internal microstructure of the grain without microcracks while Fig. 3b indicates the presence of microcracks.

diffusion is presented in terms of the accumulated moisture on a dry matter basis versus the duration of soaking. Over time, these micro cracks become bigger, forming visible cracks due to accumulation of compressive and tensile stress within the grain. Perez *et al.* (2012) reported that these microscopic cracks begin to form after the von Mises stress reaches its peak, 3 – 5 min after soaking. The water absorption curves are characterized by an initial phase of a rapid escalation of moisture followed by an equilibrium phase. The initial phase of rapid moisture build up lasted for 20 min during the early stage of soaking. After this period, moisture absorption diminished as indicated by the flatter end of the curve. The rate of water absorption increased with increasing temperature, as suggested by the slopes of the moisture absorption curves that are becoming steeper with the increase in temperature.

Logistic function and its parameters Figures 5 and 6 show graphs of the logistic function and its time differential. The purpose of integrating the logistic function to the diffusion coefficient was to adjust the fitting of the predicted moisture diffusion curves. One of the reasons for inaccuracy in the fitting is due to the presence of cracks and inaccuracy of the model. Without the logistic function, the predicted moisture diffusion curve is rounded in the beginning and deviates somewhat from the experimental data, particularly during the first 15 min of moisture absorption. This inaccuracy is even more noticeable specifically at 25°C. The discrepancy between the numerical solution and the experimental data leads to a higher RMSE value. This can be observed in the report of Perez *et al.* (2012). By adding the logistic function, the fitting of the numerical solution more closely approached the experimental data. The best-fit solution was observed using the values of the parameters of the logistic function shown in Table 1. However, the best-fit solution resulted to unequal initial values in the logistic function, particularly at 25°C. The differences in the initial values were not so large and were tolerated during the simulation. This is due to the moisture absorption curve at 25°C that has a relatively more complex shape than the other temperatures. The complexity of the

shape of the curve is noticeable from its slope. Unlike the two other temperatures, the slope is less steep and a lag in the slope of the moisture absorption curve at 25 °C is visible. The complex shape of the curve is probably caused by the cracks in the grain, since this is likely to occur at this temperature level. The time differential curves indicate the inflection points of the logistic function. The inflection points were found to be at four minutes for 25 °C, while two minutes for the higher temperatures. This is also the time at which the von Mises stress is peaking during hygroscopic swelling. Microscopic cracks are believed to develop after this time (Perez *et al.*, 2012).

Numerical solution to the modeling of heterogeneous moisture diffusion The heterogeneous diffusion of moisture in milled rice was modeled in 3D using finite element analysis. In modeling the heterogeneous moisture diffusion in rice, the heat transfer in solids node in COMSOL Multiphysics v4.3a was used.

Equations 1 – 9 were translated to computer syntax in order for the software to understand and proceed with calculation of the numerical solution. The modeling was based on the experimental data obtained during observation of the moisture migration in milled rice. Results of the numerical analysis is shown in Figs. 4 and 7. The amount of accumulated moisture in the grain

Fig. 4. Amount of moisture accumulation in the grain during soaking.

Fig. 5. Graph of the logistic curve for the time function.

was compared with the experimental data. The fitting of the numerical solution was very close with the experimental data. The numerical solution adequately described the moisture diffusion characteristics at all three temperatures. From the lowest to the highest temperature, the RMSE values in the present experiment were 1.1808, 0.5940 and 0.5036 g H₂O/g dry matter. These values are comparatively lower than the RMSE values reported by Perez *et al.* (2012). In the previous report, the RMSE values at the same temperature level were 2.55, 1.19 and 1.27 g H₂O/g dry matter. Moisture movement was initiated at the two major sites of the grain. The spectrum of colors shows the different levels of moisture that is accumulating in the grain. Emanating from the apical region and at the base of the grain, the moisture gradually penetrated through the inner section of the grain. The time required to reach near saturation or equilibrium moisture content was found to be around 20 min. This observation is in agreement with the experimental data both in moisture diffusion curves and in images.

Effect of temperature on the modified frequency factor of the moisture diffusion coefficient The values of modified frequency factor of the moisture diffusion coefficient obtained from a series of trial and error experiments are shown in Fig. 8. In the simulation, the value of the modified frequency factor with the least RMSE value between the experimental data and the numerical solution was selected. A trendline of the exponential plot is also provided showing the values of parameters b and c and the coefficient of determination. From the lowest to the highest temperature, the

Fig. 6. Time differential of the logistic function, $f(t)$, showing points of inflection.

Table 1. Parameters of the logistic function for soaking time.

Parameters	Temperature, °C		
	25	35	45
k	1.166	1	0.930
l	23.50	7.454	7.030
m	0.01063	0.01242	0.01274
n	0.147	0.213	0.223

Fig. 7. Numerical solution for the moisture diffusion in milled rice grain at 35°C. Images depicted above are longitudinal slices of the 3D model.

Fig. 8. Dependence of the modified frequency factor of the moisture diffusion coefficient on the soaking temperature. An exponential plot of the modified frequency factor versus the inverse of the soaking temperature.

values were 2.316×10^{-5} , 1.780×10^{-5} and 1.603×10^{-5} . These values indicated an inverse relation to temperature. A similar trend was also observed by Perez *et al.* (2012). However, the previously reported values of the modified frequency factor of the moisture diffusion coefficient ranged from 1.371×10^{-6} to 6.849×10^{-7} . The reason for the differences in the values of the modified frequency factor is because of the assumption employed. In the previous report, the moisture diffusion in grains was assumed as homogenous, not heterogeneous. Apparently, the modified frequency factor was expected to have a bigger value because the entry of moisture did not start from all the boundaries of the grain but rather from the key zones or the so-called major moisture diffusion routes. The penetration of moisture in the grain mostly came from the two identified sites, which are at the apex and the base of the grain.

Conclusion

Moisture movement in rice has been demonstrated to be heterogeneous in nature. The complex grain geometry indirectly affected moisture movement. Certain boundaries of the grain's

geometry served as the major entry site for moisture. The development of cracks and fissures during soaking also increased the rate of moisture diffusion. The finite element modeling of the diffusion of moisture using a moisture diffusion coefficient expressed as a function of moisture, temperature and time adequately described the moisture diffusion characteristics. The result of the modeling was relatively more accurate than modeling the moisture diffusion coefficient as a function of moisture and temperature only. The newly developed technique described the heterogeneous moisture diffusion in rice excellently. The results are promising, but more studies are needed to validate this technique. Future testing with other commodities is recommended to assess the effectiveness of this method.

Acknowledgments The authors would like to thank the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) for the scholarship provided.

References

- Bakalis, S., Kyritsi, A., Karathanos, V.T., and Yanniotis, S. (2009). Modeling of rice hydration using finite elements. *J. Food Eng.*, **94**(3-4), 321-325.
- Bello, M.O., Tolaba, M.P., Aguerre, R.J., and Suarez, C. (2010). Modeling water uptake in a cereal grain during soaking. *J. Food Eng.*, **97**, 95-100.
- Murata, S., Tanaka, F., Tokunaga, J., Koide, S., and Amaratunga, K.S.P. (1996a). Study on sorption of grain kernels while soaking in water. *J. Jpn. Soc. Agric. Mach.*, **58**(2), 19-24.
- Murata, S., Tanaka, F., Tokunaga, J., Koide, S., and Amaratunga, K.S.P. (1996b). Water adsorption isotherms of polished rice. *J. Jpn. Soc. Agric. Mach.*, **58**(4), 29-34.
- Ogawa, Y., Glenn, G.M., Orts, W.J., and Wood, D.F. (2003). Histological structures of cooked rice grain. *J. Agric. Food Chem.*, **51**(24), 7019-7023.
- Perez, J.H., Tanaka, F., and Uchino, T. (2011). Comparative 3D simulation on water absorption and hygroscopic swelling in japonica rice grains under various isothermal soaking conditions. *Food Res. Int.*, **44**(9), 2615-2623.
- Perez, J.H., Tanaka, F., and Uchino, T. (2012). Modeling of mass transfer and initiation of hygroscopically induced cracks in rice grains in a thermally controlled soaking condition: With dependency of diffusion coefficient to moisture content and temperature – A 3D finite element approach. *J. Food Eng.*, **111**(3), 519-527.
- Shewry P.R. and Halford, N.G. (2002). Cereal seed storage proteins: structures, properties and role in grain utilization. *J. Exp. Bot.*, **53**(370), 947-958.
- Thornley, J.H.M. and France, J. (2005). An open-ended logistic-based growth function. *Ecol. model.*, **184**(2-4), 257-261.
- van den Doel, L.R., Mohoric, A., Vergeldt, F.J., van Duynhoven, J., Blonk, van Dalen, G., van As H., and van Vliet, L.J. (2009). Mathematical modeling of water uptake through diffusion in 3D inhomogeneous swelling substrates. *AIChE J.*, **55**(7), 1834-1826.