MRI Observation and Mathematical Model Simulation of Water Migration in Wheat Flour Dough During Boiling

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ABSTRACT: Existing cooking rate equations fail to describe the change of moisture content profile in starchy foods during cooking. There is a need for a new model. In this paper, an experiment on water migration during boiling was performed using a slab of wheat flour dough. The moisture content profile was measured by an MRI method. The result was compared with predictions made using mathematical models. The existing mathematical model was found to predict a much more rapid change than that measured by experiment. The accuracy of the prediction was considerably improved when a new model was applied : a mathematical model based on a new concept that water migration is driven by water demand.

Key Words: starch gelatinization, water demand, MRI, diffusion, starchy food

Introduction

THE BEHAVIOR OF THE CHANGE OF MOISTURE CONTENT PROfile in starchy foods during cooking and/or storage could be one of the major concerns for food process engineers in starchy foods production because moisture content profile in food directly affects qualities of food such as texture. Unfortunately, however, moisture content profile in starchy foods was scarcely measured because there was no appropriate tool available for such measurements.

Suzuki and others (1977) measured the cooking rate of rice grains using a plastometer. They suggested that moisture content profile in a rice grain during cooking could be described by a fully cooked shell and an uncooked core, although this moisture content profile was not validated by experiments. Bakshi and Singh (1980) measured the gravimetric change of rice grains during parboiling. Their data was analyzed by a simultaneous diffusion and reaction model. In this model, water used by starch gelatinization reaction was assumed to be immobilized, and this affected to facilitate water migration from the surface boundary into the food body. By a method of nonlinear fitting, they predicted water diffusivity and reaction rate constant of starch gelatinization. Unfortunately, these physical constants were not validated by experiment.

Recently Gomi and others (1996) measured water diffusivity in rice starch/water mixture with a selected moisture content using PFG-NMR (pulsed field gradient nuclear magnetic resonance) method, over a range of temperature. When compared with the result of their experiment, the water diffusivity predicted by Bakshi and Singh (1980) was found to be considerably underestimated. Gomi and others (1998), then applied PFG-NMR to observe the rate of starch gelatinization during heating. They concluded that the rate constant of events taking place during the early stages of starch gelatinization (order-disorder transition) was about a hundred times larger than the reaction rate of starch gelatinization predicted by Bakshi and Singh (1980).

Recently there emerged the magnetic resonance imaging (MRI) method, which enabled the observation of moisture content profile in starchy foods. The change of moisture profile in a cereal grain (wheat) during cooking was first measured by Staply and others (1997) using MRI. Takeuchi and others (1997) observed the change of moisture profile in a rice grain during boiling. They found that the moisture migration in a grain was to be very slow, and found that there emerges a sharp moisture profile in the interspace between the surface and the center of a rice grain.

Examination of the newly measured constants, water diffusivity in the starch/water mixtures and starch gelatinization rate, lead to the conclusion that the existing diffusion model fails to predict the rate of water migration in a starchy food. So we need a new model. In order to produce a new model we will need more precise experiments which may be afforded by some experiment using a food body in simple shape such as a slab. Since there is no way to mold a slab by cereal grains, we used a slab made of wheat flour dough. Moreover, we believe that the factor which governs water migration in a starchy food, may be the process of starch gelatinization associated with water diffusion. This situation may be applied to cooking cereal grains as well as spaghetti or udon, a Japanese noodle.

In the present paper, 1-dimensional water migration was realized in a model food using a slab of wheat flour dough. The change of moisture profile in the slab during boiling was observed by MRI. The result was analyzed by a new mathematical model.

Materials and Methods

WHEAT FLOUR CONTAINING 8.5% WEIGHT GLUTEN (NISHIN SEifun Co., Tokyo, Japan) was used as received. 45 ml of distilled water was added to 100 g of flour gradually, and mixed softly to make a dough. After it was slowly kneaded about 5 min by hand, the dough was formed into a ball and wrapped in wrapping film to prevent it from drying. With this procedure we could repeatedly obtain the sample dough with similar texture. This may be because 1) The wheat flour dough used contained less protein. 2) The flour was mixed with water but without salt gently for short time. This may prevent the sample dough from growing a strong network. After standing for 4 h at 5 °C, the dough was flattened and rolled out to even thickness using a rod. Then the sample was embedded in an aluminum frame (inner size: 50 mm × 80 mm, 3-mm thick) to form a slab. The moisture content of the sample was 0.72 kg water/ kg solid (0.42 wet basis), which was measured by a gravimetric method.

The slab sample with the aluminum frame was put into boiling water for a specified time, and was quickly quenched in cold water in order to stop further cooking. After wiping the surface of the sample slab with paper, a piece of rectangular block (about 7 mm × 10 mm) was cut out of the sample slab. The piece was wrapped in polyethylene film and placed at the bottom of an NMR sample tube (9 mm i.d.) (Figure 1).

Two-dimensional spin echo images of protons in a vertical slice perpendicular to the boiled surface of the sample piece were observed using an NMR spectrometer (Bruker AM200WB, 4.7 T) with an imaging accessory. The number of encoding steps was 256 for both frequency and phase encoding except for the 120 min boiling (128 encoding steps). The pixel size of the image was about 150 mm, the slice thickness was 2 mm. The signal acquisition was averaged over 2 times.

Results and Discussion

Results of experiment

The 2-dimensional spin echo images (echo time τ = 14.24 ms) of wheat flour dough boiled for a specified period are shown in Figure 2. The 1-dimensional signal intensity profile along the cross-section a-a' is also shown in the figure. As the cooking proceeded, the brighter region spread out from the surfaces to the central region. At 120 min boiling an almost uniform profile was obtained. The swelling of the sample slab, detected by the images, was found to be negligibly small until 60 min boiling, while 42% swelling was observed at 120 min boiling. The thickness of the sample slab before boiling was found to be 3.8 mm by the use of the spin echo image.

The signal intensity of the proton spin echo images shown in Figure 2 does not directly indicate the moisture population in wheat flour dough because the intensity of the spin echo is greatly affected by the proton transverse relaxation. In order to obtain moisture content information from NMR signal intensity, we measured proton transverse relaxation time (T_2) at each pixel in the image. A series of 5 images, each with a different echo time (τ) ranging from 14 ms to 22 ms, was taken at 20 °C. The image intensity (I_i) with echo time τ_i was fitted to the following equation:

$$I_i = I_0 \exp(-\tau_i/T_2) \qquad (i = 1, 2, \cdots 5) \tag{1}$$

and a T_2 value for each pixel in the image was given. Then the T_2 value was converted to the moisture content by using a calibration equation (Takeuchi and others 1997) as follows:

$$T_2 = \exp[4.386 \cdot m/(1+m) + 0.6028] \tag{2}$$

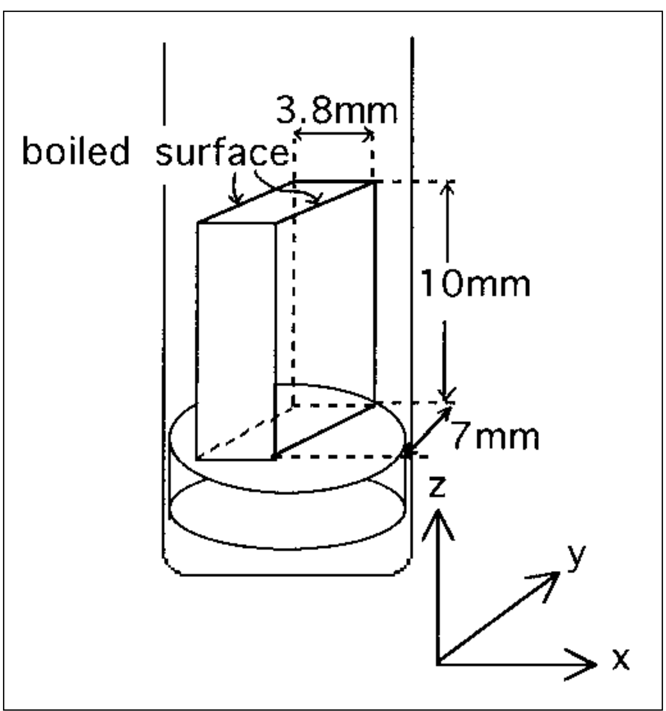

Figure 1—The sample for MRI measurement. Two dimensional spin echo image was measured in a vertical slice perpendicular to the boiled surface of the sample piece.

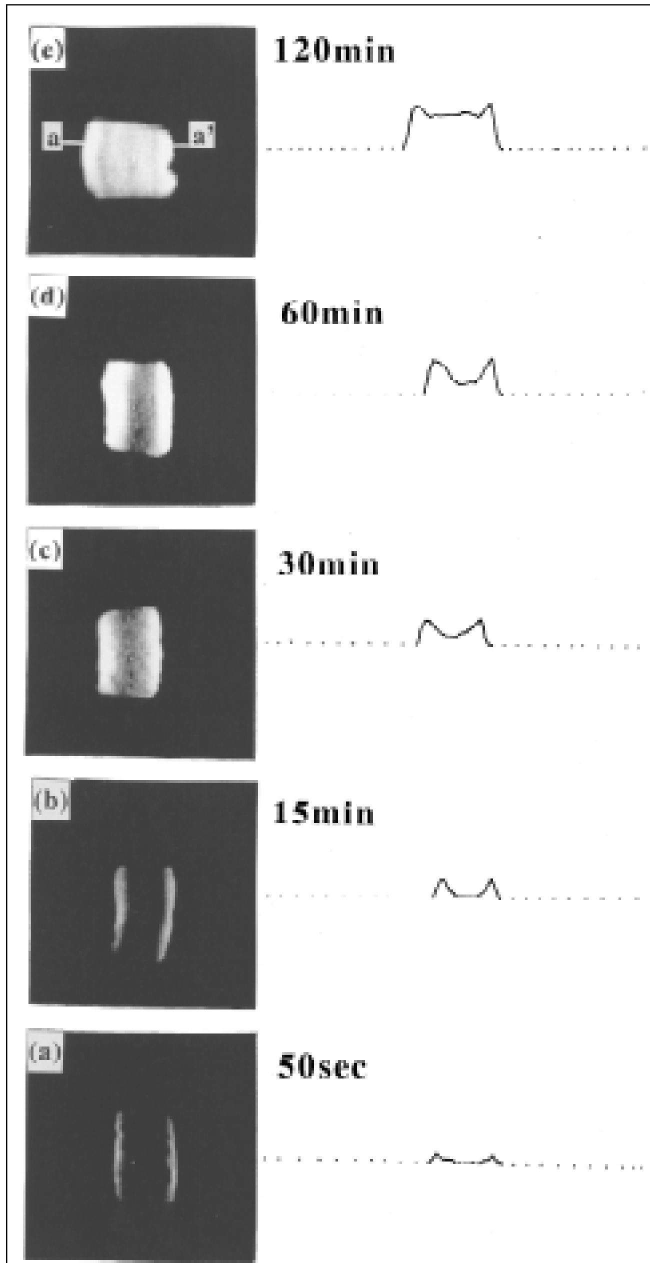

Figure 2—The two-dimensional spin echo images (echo time τ = 14.24 ms) of wheat flour dough boiled for a selected minutes. (a) 50 sec, (b) 15 min, (c) 30 min, (d) 60 min, (e) 120 min. The one-dimensional signal intensity profile along the cross-section a-a' is also shown.

where m is moisture content (kg water / kg solid). A T_2 shorter than 10 ms could not be identified in this experiment, since the signal-to-noise ratio declined considerably when the echo time was reduced below 12 ms.

The 1-dimensional moisture content profile across the slab of wheat flour dough, which was obtained through the procedure described above, is shown in Figure 3. Five images for each pixel were used in the sample. Data variation is shown in Figure 3. The pixels that seem to have T_2 shorter than 10 ms were regarded as remaining at the initial moisture content in Figure 3.

In order to check the accuracy of the moisture content profile, the moisture profile in Figure 3 was integrated from the surface to the center. The integrated amount of water was compared with the value obtained using a gravimetric method. The profile of 30 min boiling, 60 min boiling, and 120 min boiling, were checked, and it was found that the moisture content obtained by MRI was 3 to 10% lower than that measured by a gravimetric method. This assured that MRI method worked well.

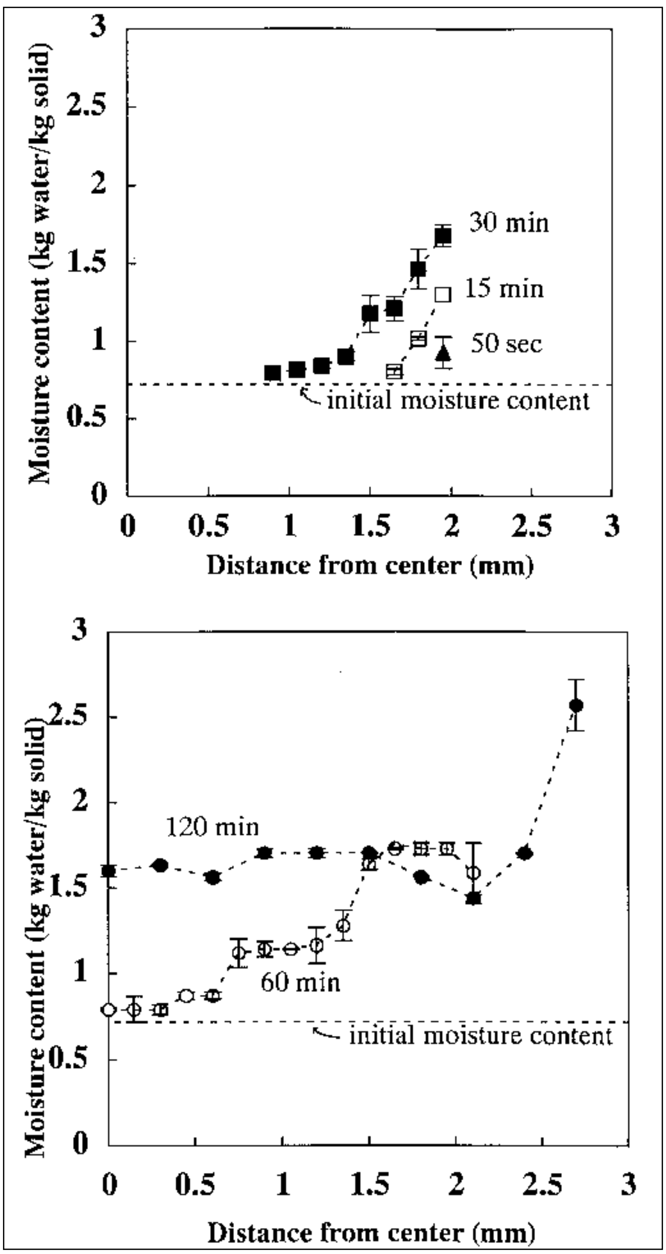

Figure 3—The change of one-dimensional moisture content profile in the slab of wheat flour dough during boiling

The features of the change in moisture profile during boiling shown in Figure 3 may be summarized as follows:

(1) The moisture migration in the wheat flour dough was found to be very slow. Even after 30 min boiling, the moisture content at the center of the slab remained at the initial level, while the moisture content reached an equilibrium value of 1.7 kg water/ kg solid (0.63 wet basis) at the surface.

(2) An anomaly in moisture profile was observed at 60 min boiling. A nearly flat moisture profile emerged in 3 regions: at the center, near to the surface and in the intermediate part of these 2 regions. These flat regions were tied with a sharp gradient curve of moisture profile.

(3) When the slab was boiled for 120 min, the moisture content inside the slab leveled off to an equilibrium of 1.7 kg water/ kg solid. On the other hand, it was extremely swollen at the surface and its moisture content was raised to 2.57 kg water/ kg solid (0.72 wet basis). This may be caused by some destruction of structures at the surface. This means the most surface region in 120 min boiling needs to be distinguished from that in inner region.

In the following section, cooking rate equations to simulate these features of moisture profile are examined.

Theoretical Consideration

Starch gelatinization kinetics

Water migration into starchy food during cooking is greatly affected by starch gelatinization. When observed by differential scanning calorimetry (DSC) (Lund and Wirakartakusumah 1984) or by NMR (Gomi and others 1998), starch granules are gelatinized rapidly to reach a specified extent of gelatinization within 1 or 2 min. This upper limit in the extent of gelatinization may be termed as the terminal extent of gelatinization (TEG) which depends on temperature and moisture content. TEG in wheat starch/water system was measured by DSC in the temperature range from 60 °C to 100 °C (Watanabe and Fukuoka 2000). The results of the experiment were examined to give the empirical equation:

$$TEG = \frac{3.15m/(1+m) - 0.946}{1+\exp[-0.1792(\theta - 69.1)]} \qquad (TEG \le 1) \qquad (3)$$

where m is moisture content (kg water/ kg solid) and θ is heating temperature (°C).

Water diffusivity

Fick's first law of diffusion is widely used in the existing mathematical models for analyzing water migration in food. The proportionality constant is diffusivity (diffusion coefficient; D).

$$j = -D\rho_s \frac{dm}{dx} \qquad (4)$$

Although it is well known that water diffusivity in food is, in general, not constant but deeply depends on moisture content and temperature, the actual dependence is very often unavailable. Fortunately, Gomi and others (1996) measured water diffusivity in rice starch/water mixtures at a range of temperatures and moisture contents using a PFG-NMR method. Since they found that 2 different diffusivities were observed in the partly gelatinized phase, they classified the samples into 2 categories in order to avoid complexity; one is nongelatinized samples in which temperature was kept below 60 °C. The other is fully heat-

ed samples, which were first heated at 95 °C for 60 min, then cooled and the diffusivity was measured at each of the selected temperatures. Gomi and others (1996) proposed the following empirical equation for each category:
for nongelatinized starch/water mixtures

$$D_{non} = D_{free} 0.127(m/(1+m) - 0.33)\exp[778/(\theta + 273)] \quad (5)$$

for fully heated starch/water mixtures

$$D_{full} = D_{free}(1.31m/(1+m) - 0.486) \quad (6)$$

where D_{free} is the diffusivity of water molecules which migrate freely in liquid phase without being restricted by any foreign obstacles such as solute or solid structure. The temperature dependence of D_{free} [m^2/s] is given by:

$$D_{free} = 2.32 \times 10^{-6}\exp[-2070/(\theta + 273)] \quad (7)$$

PFG-NMR is a method which measures a kind of tracer diffusivity in a distinctively defined diffusion time (the time during which diffusion of interest is observed). The diffusivity measured by PFG-NMR often shows significant dependence on diffusion time. This means the diffusion of targeted molecules is restricted by obstacles such as solute molecules or by any solid structure of the system. In these cases, the diffusivity decreases as the increase in diffusion time. This means the progress in averaging the restriction. When the length of water migration during a diffusion time t [s] (which may be evaluated as $\sqrt{6D\tau}$) exceeds the size of repeating structure in the sample, then the measured diffusivity may reach a constant value which may be regarded as an effective diffusivity, or a structure averaged diffusivity. This diffusivity may be intrinsically similar to the diffusivity which may be measured by methods other than PFG-NMR.

Since diffusivity of water molecules in rice starch/water mixture in 100 °C is in the order of 2×10^{-9} m^2/s and diffusion time used in PFG-NMR is about 0.5 s, then $\sqrt{6D\tau} \cong 80$ μm. This may exceeds the size of rice starch granules (10 μm), which may be the size of repeating structure in rice starch/water mixture. This endorses the diffusivity data in rice starch/water by Gomi and others (1996). Using this data, Gomi and others (1996) obtained Eq. (6).

Before we applied Eq. (6) to wheat flour dough, water diffusivity in wheat starch/water mixture and in wheat flour/water mixture was measured by PFG-NMR. Some of the results of this experiment is shown in Figure 4, although the detail of the experiment may be reported elsewhere (Fukuoka and Watanabe 2000). In Figure 4, water diffusivities in fully heated starch/water and flour/water mixtures, measured at 20 °C by PFG-NMR, are plotted against moisture content in wet basis. From this figure, we can see that water diffusivity in fully heated wheat flour dough can be roughly approximated by the solid line which gives diffusivity in fully heated rice starch/water mixture (Gomi and others 1996). Since similar relationship is available for nongelatinized starch/water mixture (Fukuoka and Watanabe 2000), the dependence of moisture content and temperature on water diffusivity in wheat flour dough is estimated using Eqs. (5) and (6) in the present paper.

Another point worth to be noted is that the microscopic migration of water molecules is hard to be measured by PFG-NMR when the water molecules are in some liquid phase which is dispersed in dried up medium, as is often encountered in dehydration processes. For this reason, the initial moisture content in wheat flour dough was chosen as high as about 40% (wet basis) in the present experiment. Although we have no concrete model for partly gelatinized phase in starch/water system, if the flux of water migration in the partly gelatinized phase can be described as the addition of the flux in fully gelatinized phase and that in nongelatinized phase, using TEG as the weighing factor, then:

$$\begin{aligned} j &= TEG \cdot j_{full} + (1 - TEG) \cdot j_{non} \\ &= TEG \cdot \left(-D_{full}\frac{dm}{dx}\right) + (1 - TEG) \cdot \left(-D_{non}\frac{dm}{dx}\right) \\ &= -\left\{TEG \cdot D_{full} + (1 - TEG) \cdot D_{non}\right\}\frac{dm}{dx} \\ &= -D_{av}\frac{dm}{dx}. \end{aligned}$$

Therefore, in this paper, a TEG weighing average of D_{non} and D_{full} as given in Eq. (8) is used for a water diffusivity in a partly gelatinized wheat flour dough.

$$D_{av} = TEG \cdot D_{full} + (1 - TEG) \cdot D_{non} \quad (8)$$

Moisture content gradient driven diffusion model

A water concentration gradient driven diffusion model may be constructed for a slab of wheat flour dough using the following assumptions:

(a) One-dimensional moisture migration takes place through a slab of dough (2L = 3.8 mm thick). Solid density does not change during boiling: swelling is negligibly small.

(b) The temperature in the slab is homogeneous (100 °C).

(c) The governing equation for water migration is as follows:

$$\frac{dm}{dt} = \frac{d}{dx}\left[D[m,\theta]\frac{dm}{dx}\right] \quad (9)$$

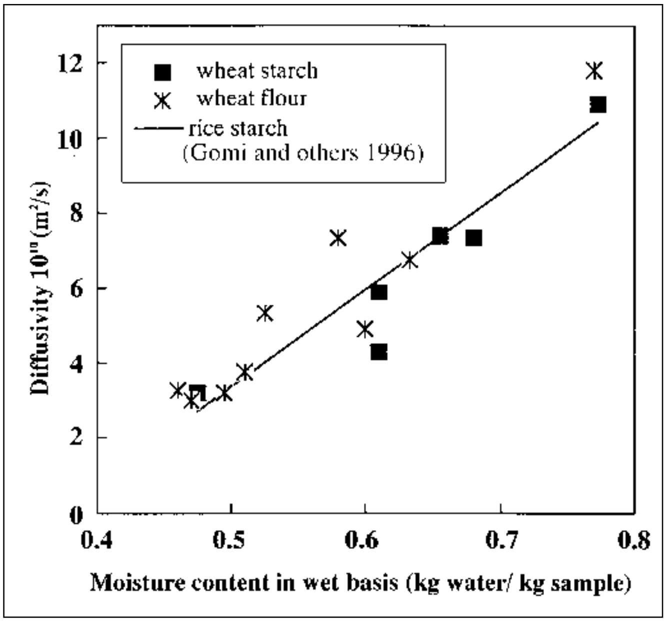

Figure 4—Water diffusivity in starch (flour)/water mixture plotted against moisture content in wet basis. The wheat starch/water and wheat flour/water mixture were prepared by heating the samples for 10 minutes at 90 °C and quenched. The diffusivity were measured at 20 °C by PFG-NMR. Both of the data points can be roughly approximated by the solid line which gives diffusivity in fully heated rice-starch/water mixture (Gomi and others 1996).

(d) At time t = 0, the moisture content in the slab is constant: $m = m_0$.

(e) The moisture content at the surface is assumed to be constant: $m = m_1$, where m_1 is the final moisture content in the slab.

(f) Water diffusivity is given by Eq. (8).

(g) TEG is given by Eq. (3).

The initial and final moisture content, $m_0 = 0.72$ (kg water/ kg solid) and $m_1 = 1.7$ (kg water/ kg solid) obtained from the experiment were used in this calculation. The moisture content profile obtained numerically solving Eq. (9) is shown in Figure 5, which indicates that this model overestimates the rate of water migration. The calculation estimates that the moisture content at the center reaches 1.5 kg water/ kg solid at 17 min boiling while the experiment suggests that it takes more than 60 min.

In addition, the moisture profiles given in Figure 5 are all monotonous curves without any irregular combination of flat and steep portions such as can be seen in Figure 3.

The conclusion to be drawn so far is that a mathematical model that is based on the idea that water migration is driven by moisture content gradient fails to mimic the change of moisture content profiles measured by MRI, and there must exist some mechanism that suppresses water migration to delay the rise of moisture content in the slab of wheat flour dough and form some flat and steep structures in the moisture profile.

Water demand gradient driven diffusion model

Takeuchi and others (1997) found that only a little change was observed in the MRIs when a rice grain was partly boiled and quenched, and then MRI was taken before and after it was kept for 24 h at room temperature. Since there existed a gradient in moisture content in the partly boiled and quenched rice grain, this observation forced us to discard the idea that water migration was driven by a gradient in moisture content. Then, in the present paper, we try to choose water demand (WD) as an alternative, the gradient of which may drive water migration; water migrates from a low WD site to a high WD site. The flux of water migration may be written as follows when water self diffusivity is adopted as the proportionality coefficient:

$$j = D\rho_s \frac{d(WD)}{dx} \tag{10}$$

Combining Eq. (10) with an equation of continuity, a water demand guided diffusion equation is given as follows:

$$\frac{dm}{dt} = -\frac{d}{dx}\left[D\frac{d(WD)}{dx}\right] \tag{11}$$

In a starch/water system, there may exist a maximum moisture content (m_{clg}) beyond which the system does not hold water even though it is in an excess water environment. The difference between this maximum moisture content and the existing moisture content may be regarded as the amount of water that the starch/water system can potentially accept. This difference may be defined as water demand:

$$WD = m_{clg} - m \tag{12}$$

Defining water demand by Eq. (12) helps us to have a concrete idea of what water demand is like. In order to go further to complete the discussion, the maximum moisture content, m_{clg}, needs to be characterized. In the present study, m_{clg} was postulated to be governed solely by the extent of starch gelatinization: m_{clg} may be a function of TEG. The simplest form of the function may be a linear function. Another may be an exponential function.

$$m_{clg} = m_0 + (m_1 - m_0)TEG \tag{13}$$

$$m_{clg} = m_0 \exp(TEG \cdot \log(m_1 / m_0)) \tag{14}$$

where m_0 and m_1 are the m_{clg} values when TEG = 0 and TEG = 1, respectively. Water demand, WD, for 100 °C calculated using Eqs. (3), (12) , (13) and (14) are shown in Figure 6, where $m_0 = 0.72$ and

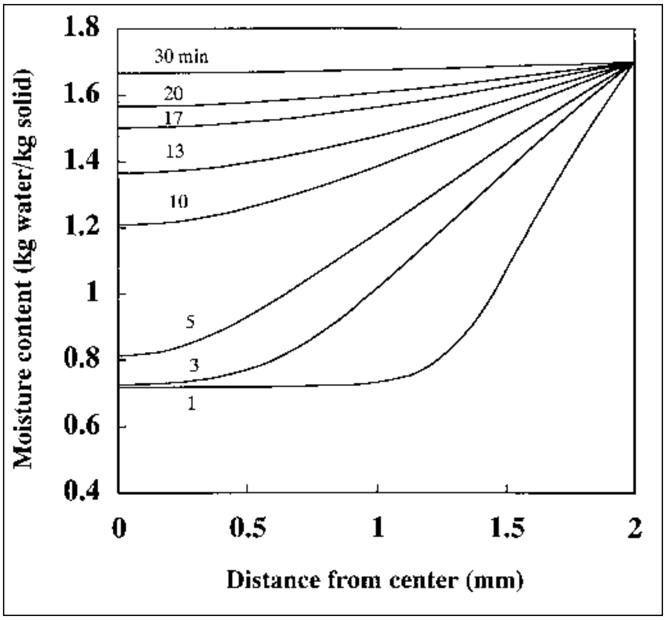

Figure 5—The change of moisture content profile numerically calculated using Eq. (9) : water content gradient driven diffusion model

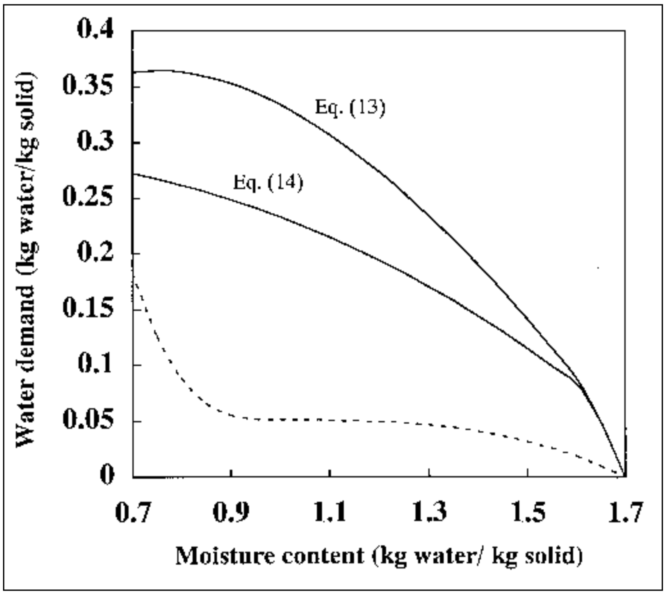

Figure 6—The water demand (WD) functions. The solid lines are calculated using Eqs. (13) and (14), respectively. The dotted line is a suggested alternative for WD function, which improves the simulation.

$m_1 = 1.7$ were used which were obtained in the experiment described above.

Now that WD is available, the change of moisture content in the wheat flour dough during boiling can be simulated by solving Eq. (11) numerically. The result of calculation using the exponential function for m_{clg} is shown in Figure 7. Figure 7 suggests that the water demand guided diffusion equation has a potential to describe the characteristic feature of moisture migration experimentally observed in the present study, because Figure 7 shows a steep moisture profile in the intermediate distance from the center, and the rise of moisture content is partly suppressed when compared with Figure 5. The simulation shown in Figure 7 needs more improvement because observed rise of moisture profile was much slower. Since the gradient in water demand is the driving force for water migration, less steep form in WD is preferable; the choice of Eq. (14) is the opposite (Figure 6). Then, the dotted line shown in Figure 6 which has low WD values was tested as the water demand function. The simulated change of moisture content profile using this dotted line WD is shown in Figure 8, which is greatly improved and satisfying, when compared with that shown in Figs. 5 and 7.

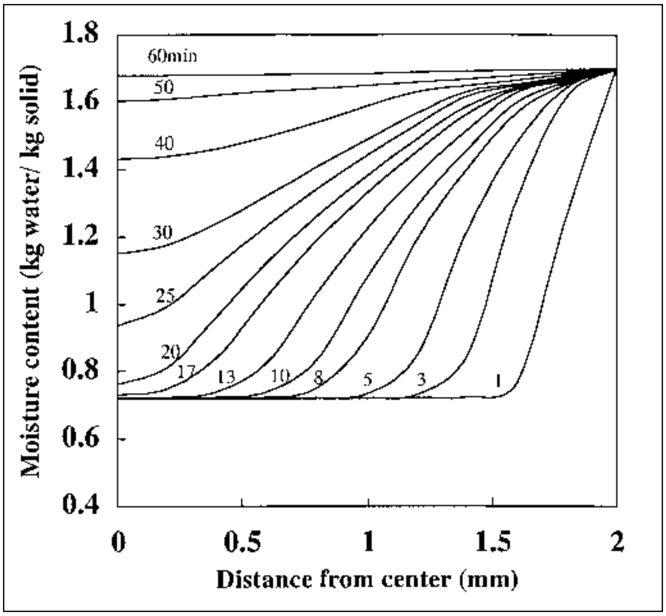

Figure 7—The change of moisture content profile in the slab of wheat flour dough predicted using water demand gradient driven model. Equation (14) is used for WD function.

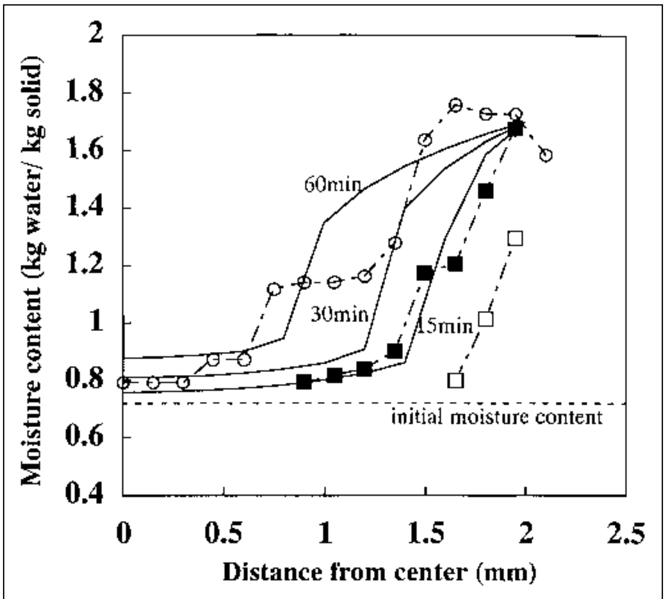

Figure 8—The change of moisture content profile in the slab of wheat flour dough calculated using water demand gradient driven model. The keys tied with a chain line is measured values as are shown in Figure 3.

Conclusions

THE CHANGE OF MOISTURE CONTENT IN STARCHY FOODS DURing boiling as measured by experiment was found to be very slow. An anomalous moisture content profile was observed before the profile leveled off: nearly flat moisture profile emerged at the center, near to the surface and in the intermediate part. A new mathematical model, based on the new concept that water migration is driven by water demand, was proposed to mimic the change in moisture content profile. The new model improved the simulation, although the anomaly in moisture content profile was left unresolved.

Nomenclature

θ	Temperature (°C)
ρ_s	Density of solid in food (kg/m^3)
τ	Time of echo (ms)
D	Water diffusivity (m^2/s)
I_i	Image intensity with echo time τ_i
I_0	Constant
j	Flux of water [kg water/(m^2 s)]
L	Half thickness of the slab (m)
m	Moisture content (kg water/kg solid)
m_{clg}	Ceiling moisture content (kg water/ kg solid)
m_0	Initial moisture content (kg water/ kg solid)
m_1	Final moisture content (kg water/ kg solid)
t	Time (s)
T_2	Proton transverse relaxation time (ms)
TEG	Terminal extent of gelatinization
WD	Water demand (kg water/ kg solid)
x	Position (m)

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