

Study of Water in Dough Using Nuclear Magnetic Resonance

R. Roger Ruan,^{1,2,3} Xiaolan Wang,¹ Paul L. Chen,¹ R. Gary Fulcher,²
Peter Pesheck,⁴ and Sumana Chakrabarti⁴

ABSTRACT

Cereal Chem. 76(2):231–235

The amount and state of water play an important role in the preparation and properties of wheat flour doughs and their products. A new method for presentation and analysis of relaxation time measurements of protons in dough is described in this article. This new method acknowledges a continuous probability distribution of protons having different relaxation times in heterogeneous systems such as dough, which is dramatically different from the conventional discrete methods that rely on prior assumptions of a number of discrete relaxation components. In the present study, pulsed proton nuclear magnetic resonance was used to study the relaxation characteristics of dough systems at moisture levels of 12–45%. The relaxation curves obtained using a 90-degree pulse (Onepulse)

sequence and the Carr-Purcell-Meiboom-Gill pulse sequence were analyzed using a multiexponential discrete model and a continuum model. The discrete model produced three fractions of protons relaxing in three different time domains. The continuum model produced spectra of spin-spin relaxation time vs. amplitude, from which two to five peaks, depending on the moisture content, could be identified. At moisture contents of 23 and 35%, dramatic changes in relaxation time and amplitude were observed with both models. The continuum model provided additional information about the homogeneity of the morphology and physical state of the dough systems.

Water is an indispensable component of dough and baked products. It usually constitutes ≈40% (w/w) of bread dough and more than 35% (w/w) of baked bread. Water is added to flour during mixing, which is essentially a hydration process. Water is necessary for gluten development and plays an important role in all types of interactions and chemical reactions that occur during mixing and baking. The effect of water on dough rheology and handling and on product quality and stability has been well documented (Sidwell and Hammerle 1970; Tschoegl et al 1970; Webb et al 1970; Bushuk and Mehrotra 1977a; Dexter and Matsuo 1979; Sharma and Hanna 1992; Sharma et al 1993a,b; Sahi 1994). Understanding the properties of water in dough is of great interest and vital to the bakery industry.

In dough, water interacts with gluten and starch to form the so-called “bicontinuous networks”—the continuous water-containing gluten phase that is interpenetrated by the continuous “free” water-starch mixture phase. Water is not evenly distributed among the flour constituents in dough. Bushuk (1966) reported that ≈46% of the water in dough is associated with starch, 31% with protein, and 23% with pentosan gum, which is strongly influenced by the amount of protein and damaged starch. Besides the variations in distribution of water among the flour constituents, the physical properties of dough water differ from those of bulk water because of the interaction of water and these flour constituents. For example, the freezing point of water in dough is dramatically changed, and part of the water in dough becomes “unfreezable” as measured by differential scanning calorimetry (Bushuk and Mehrotra 1977b). Therefore, the study of water in dough is a very complex subject in which one must deal with the distribution of water among flour components as well as the variations in properties or state of water due to interactions between water and the flour constituents.

Nuclear magnetic resonance (NMR) relaxation times (i.e., spin-lattice relaxation time T_1 and spin-spin relaxation time T_2) have been used to indicate the state of water in doughs (Toledo et al 1968, Leung et al 1979, 1983, Richardson et al 1986, Belton et al 1995). A shorter T_1 or T_2 of water usually means lower mobility.

T_2 has been used by many researchers, probably because of the ease of T_2 measurement. Observed T_2 for bulk water is ≈2 sec. It is generally believed that water molecules in doughs are somehow “bound” to different sites of the flour constituents or in exchange with “bound” water and experience faster relaxation than in bulk water; thus, they have a much shorter T_2 than bulk water. Earlier studies of water-dough systems using NMR showed two fractions of water molecules in doughs, namely “bound” or less mobile and “free” or mobile water (Toledo et al 1968, Leung et al 1979). Toledo et al (1968) found that the “bound” water content, defined as that which remained liquid at -18°C , was 0.29 ± 0.01 g of water per gram of dry solid of the wheat flour dough; this value was independent of total moisture content for doughs of the same flour with moisture contents greater than 24.6%. Leung et al (1979) also reported that the less-mobile water fraction in flour doughs has a T_2 of ≈20 msec and accounts for ≈0.62 g of water per gram of dry solid; these values seem to be independent of flour strength and mixing time. They also pointed out that staling of bread crumb was accompanied by decreased T_1 and T_2 and that the decrease in T_1 and T_2 (water mobility) of bread crumb with storage time was independent of reduction in moisture content. This suggests that relaxation is largely structure-dependent and that physiochemical changes other than change in moisture content would cause relaxation time to change, probably by altering the structure or morphological characteristics of the systems. Recently, Hills et al (1990) suggested that interpretation of NMR relaxation measurements of food systems must involve chemical and diffusive exchanges between water protons and biopolymer protons. While the authors indicated that proton relaxation measurements could produce limited information on bound water and the number of sites or states, they proposed that relaxation measurements might serve as a useful probe of morphology and the state of the biopolymers or other species having exchangeable protons. They further concluded that the abundant water protons might act as an “amplifier” of the relatively few polymer protons and that therefore relaxation measurement could be used to study the state of biopolymers.

Interpretation of NMR relaxation measurements has been model dependent. Because of the complex or heterogeneous characteristics of food systems, many researchers use multiexponential models to analyze NMR relaxation data. Most of these models predict relaxation decay data based on specific model assumptions, for example, certain small integral numbers of discrete exponential decay components of different mobility (Leung et al 1979, Schmidt and Lai 1990). This does simplify the analysis; however, it may not produce satisfactory solutions to very complex, heterogeneous systems because the factors affecting spin-lattice and

¹ Department of Biosystems and Agricultural Engineering, University of Minnesota, 1390 Eckles Ave., St. Paul, MN 55108.

² Department of Food Science and Nutrition, University of Minnesota, 1334 Eckles Ave., St. Paul, MN 55108.

³ Corresponding author. Phone: (612) 625-1710. Fax: (612) 624-3005. E-mail: ruanx001@tc.umn.edu

⁴ Pillsbury Technology Center, 330 University Ave., Minneapolis, MN 55414.

spin-spin relaxation behaviors are not yet well understood. In a heterogeneous system, spins exist in a wide variety of environments, giving rise to a spectrum of relaxation times. In addition, chemical and diffusive exchange, an important factor affecting spin-spin relaxation, would also give rise to a variety of T_2 values, assuming there is a wide range of exchange rates within the heterogeneous system (Zimmerman and Brittin 1957, Lillford et al 1980, Belton and Hills 1987). Therefore, the measured relaxation decay is a sum of the contributions from all spins, which may have sampled many different environments or exchanged with other spins at different rates during the course of the NMR experiment (Kroeker and Henkelman 1986). It is thus reasonable to assume that a continuum of relaxation times would arise from a continuum of different environments in which spins exist and different exchange rates. Some researchers have used continuum models to follow the relaxation behavior in various systems, although they focused on the state of water instead of on that of biopolymers that interacted with water (Lillford et al 1980, Kroeker and Henkelman 1986, Whittall and MacKay 1989, Newcomb et al 1990, Menon and Allen 1991, Araujo et al 1992, Tellier et al 1993). Lillford et al (1980) claimed that the continuous distribution of relaxation times is a better representation of the information content in relaxation experiments.

The continuum approach seeks a continuous distribution of relaxation times and effectively adjusts a continuous variable number of degrees of freedom to the minimum value necessary for a given data set. The CONTIN computer program of Provencher (1982a,b) has been used by researchers to process noisy data including NMR relaxation decay data (Lee 1993, Labadie et al 1994). It can produce relaxation time (e.g., T_2) spectra that can be regarded as a probability distribution of spins at various relaxation times. One of the advantages of the continuum approach is that it is consistent with the continuum nature of food systems. Furthermore, additional information may be obtained from continuum models. There are often several peaks on a T_2 spectrum. A larger number of peaks or broader peaks would be expected for heterogeneous samples than for more homogeneous samples. Therefore, the number and degree of variation of the peaks could be used to indicate the homogeneity of the sample under analysis.

The objectives of this study were to compare the continuum method with the discrete method in the analysis of NMR spin-spin relaxation measurements of flour dough systems of different moisture contents and to corroborate the occurrence and magnitudes of such measurements with existing theories of water-flour and water-dough molecular behavior.

METHODS AND MATERIALS

Mathematical Model

Proton relaxation is normally in exponential form, and the relaxation time constants can be determined from the decay curves. For a 90-degree pulse, the resultant free induction decay curve can be expressed as:

$$A(t) = A_0 \exp\left(-\frac{t}{T_2}\right) \quad (1)$$

where A is the amplitude at delay time t , and A_0 is the amplitude at equilibrium.

Usually, for heterogeneous systems like dough, a multicomponent model is used (Ruan and Chen 1998):

$$A(t) = \sum A_{0i} \exp\left(-\frac{t}{T_{2i}}\right) \quad (2)$$

Equations 1 and 2 work well with simple systems. Both models must make several assumptions, such as some predetermined number of discrete components in the decay curve (Schmidt and Lai 1990).

Whittall and MacKay (1989) proposed a method called "non-negative least squares" (NNLS), which uses a continuum approach

to analyze this type of data. The general integral equation describing multiexponential relaxation is:

$$y(t_i) = y_i = \int_a^b S(T) e^{-\frac{t_i}{T}} dT, \quad i = 1, 2, 3, \dots, N \quad (3)$$

where $y(t_i)$ or y_i is the observed amplitude measured at time t_i , $S(T)$ is the unknown amplitude of the spectral component at relaxation time T , which could be T_1 or T_2 . The limits a and b are chosen to contain the values of T expected for the physical system being analyzed.

A linear inverse method has been developed to solve this equation. Assuming a large number of known relaxation times T_j solved from the corresponding amplitudes S_j , it is assumed that the spectrum is a sum of M δ functions with unknown areas S_j at known relaxation times T_j :

$$S(T) = \sum_{j=1}^M S_j \delta(T - T_j) \quad (4)$$

Substitution of equation 4 into equation 3 results in:

$$y_i = \sum_{j=1}^M S_j \exp\left(-\frac{t_i}{T_j}\right) \quad i = 1, 2, \dots, N \quad (5)$$

This is an equation of linear systems whose general form is:

$$y_i = \sum_{j=1}^M A_{ij} S(T_j), \quad i = 1, 2, 3, \dots, N \quad (6)$$

where A_{ij} is a matrix with elements $\exp(t_i/T_j)$, and M is set large enough so as not to bias the solution into a small number of relaxation times. Because of the noise contamination, equation 6 cannot be solved exactly.

A non-negative least-squares algorithm has been developed for this kind of relaxation time analysis, in which extra constraints are incorporated into the matrix \mathbf{A} of equation 6 to alter the discrete character of the basic least-squares solution. A general form is to minimize

$$\sum_{i=1}^N \sum_{j=1}^M (A_{ij} S(T_j) - y_i)^2 + \mu \sum_{k=1}^K \sum_{j=1}^M (H_{kj} S(T_j) - f_k)^2 \quad (7)$$

for fixed $\mu > 0$, a trade-off parameter. \mathbf{H} is a matrix representing K additional constraints, and f_k is the corresponding vector of right-hand side values. The least square solution is obtained when $\mu = 0$ (Whittall and MacKay 1989).

The computer program CONTIN, developed by Provencher (1982a,b) was used to analyze the data collected in the NMR experiments. CONTIN is a Fortran program for inverting noisy linear operator equations. This program uses the NNLS method, but even more, it is a general-purpose constrained regularization method, which finds the simplest solution that is consistent with prior knowledge and the experimental data. CONTIN has been proven as a favorable approach compared with conventional NNLS and linear programming approaches (Overloop and Van Gerven 1992), or the Pade-LaPlace method (Labadie et al 1994). The degree of successfulness of this program is dependent on the number of temporal data points, the time range of the measured data, and the signal-to-noise ratio (Lee 1993, Labadie et al 1994). These issues had been considered when this program was run on a UNIX workstation.

Preparation of Dough Samples

The general-purpose flour provided by a local milling company contained $\approx 12.5\%$ protein and 0.45% ash. The moisture level of this flour was 12% , determined using Approved Method 44-15A (AACC 1995).

A set of dough samples with different moisture contents (12, 18, 23, 28, 35, 40, and 45%) was prepared for the study. At the low moisture contents of 18, 23, and 28%, it was very difficult to form

a homogenous mixture of flour and water. Therefore a method from Davis et al (1969) was used to prepare the low-moisture samples. In preparation of these low-moisture samples, dry flour of known weight was well mixed with ice powder whose weight was also known, in the presence of liquid nitrogen. After the nitrogen vaporized, the mixtures were sealed in a glass container and equilibrated at 5°C for 24 hr before use. The samples of 35, 40, and 45% moisture contents were prepared by using a bread maker (Chefmate bakery oven, model cm725, MK Seiko Co. Ltd., Korea).

NMR Measurements

A 20-MHz PCT NMR analyzer (Process Control Technology Corp., Ft. Collins, CO) with a vertical bore of 16-mm diameter was used to measure the proton spin-spin relaxation time (T_2). All the samples were measured in duplicate at room temperature. Samples, each ≈ 15 g, were weighed and placed in NMR test tubes of 12-mm diameter. The total dry weight of all samples was kept the same so that the data were comparable. A 90-degree pulse (Onepulse) and the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences were used to acquire relaxation curves. The pulse width and sequence repetition time for both pulses were 20 μ sec and 1 sec, respectively; the dwell time between data was 0.7 μ sec for the Onepulse and 100 μ sec for the CPMG; the number of data points acquired was 120 for the Onepulse and 60 for the CPMG. Sixteen scans were accumulated to increase the signal-to-noise ratio. The data were analyzed using both the discrete multiexponential curve-fitting model (equations 1 and 2) and the continuous distribution model (CONTIN). From the multiexponential model, the T_2 values and corresponding amplitudes of three discrete components were determined for each sample. From the CONTIN program, spectra illustrating T_2 amplitude were determined for each sample.

RESULTS AND DISCUSSION

Discrete Model

The NMR relaxation data, fitted into the discrete model (equations 1 and 2), were resolved into three exponential components representing three fractions of protons having distinct spin-spin relaxation times in the dough samples. The spin-spin relaxation times and amplitudes of the three components are labeled T_{21} , T_{22} , T_{23} , A_1 , A_2 , and A_3 , respectively. For all samples, the T_{21} value was ≈ 11 μ sec, T_{22} was 1 ± 0.5 msec, and T_{23} was 7.5 ± 2.5 msec.

The changes in amplitudes of the samples as a function of overall moisture content are shown in Fig. 1. The curves can be divided into three distinct regions (I–III) based on the moisture

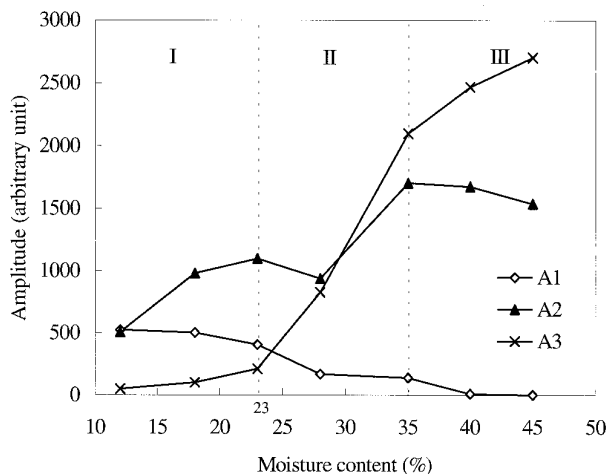


Fig. 1. Changes in proton amplitudes for three flour fractions (A_1 – A_3), determined with the discrete model as a function of moisture contents. Region I is $<23\%$ moisture content; II is >23 and $<35\%$; III is $>35\%$.

content. The experiment began with the dry flour, which had a moisture content of 12% and approximately two monolayers of water molecules (Lee 1970). Figure 1 shows that region I is dominated by the relatively immobile fractions (A_1 and A_2) with few “free” protons (A_3). When the moisture content increased to 23%, the solidlike fraction (A_1) decreased slightly, while the second fraction (A_2) increased. As the overall moisture content was further increased, fraction A_1 gradually decreased to a very low level. This indicates that when more moisture was added to the system, some of the proton fraction that originally had a spin-spin relaxation time of ≈ 11 μ sec relaxed more slowly, with much longer spin-spin relaxation times, causing it to fall into the A_2 fraction. The effect of added moisture on the relaxation rate of protons close to the flour solids may be due to some morphological changes caused by the added water and to interactions between the water protons close to the flour solids and protons of added water that were two or more layers away from the flour solids, which may weaken the exchange between the exchangeable flour solid protons and water protons close to the solids. The continuous increase in the second fraction of water (A_2) in region II suggests that the flour was further hydrated by one or two additional monolayers (Lee 1970), probably because of the increase in the number of available water-binding sites uncovered by the additional water (Bushuk and Mehrotra 1977b). This fraction of water (A_2) was then saturated with a further increase in moisture content $>35\%$, as indicated by the plateau in region III. At a moisture content of 35%, the flour had sufficient water to mobilize the flour constituents and allow rapid development of gluten, distribution of lipids, and consequently formation of a dough of minimum extensibility (Daniels 1975). The liquid phase or “free” water (A_3) began to appear when the moisture content exceeded 23% and rose rapidly until the moisture content reached 35%. Sorption isotherm studies (Lee 1970, Daniels 1975) showed several distinguished regions of water molecules in dough in the moisture content range of 0–40%. They are first monolayer (0–6.5% or 0.2 a_w), second monolayer (up to 14% or 0.7 a_w), capillary condensation (up to 23% or 0.95 a_w), and free water ($>23\%$). A “free” water phase was attained at a moisture level of 35% or 1.0 a_w . The latter three regions appeared in a moisture range similar to that used in the present study, indicating good agreement between our NMR study and the sorption isotherm study.

Continuum Model

Analysis of the data obtained from the Onepulse and CPMG experiments using the CONTIN package resulted in spectra

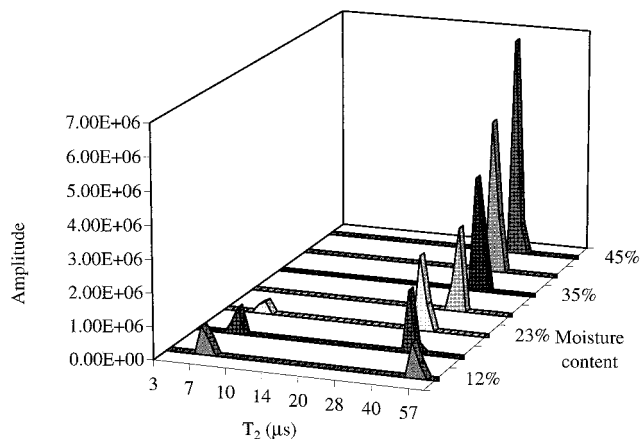


Fig. 2. Continuous distribution of spin-spin relaxation times (T_2) determined by the Onepulse experiment as a function of moisture content. Peaks on each curve at moisture contents of 12, 18 and 23% are labeled P1 and P2 from left to right. Above a moisture content of 23%, the single peak on the curve is labeled P2.

(continuous distribution) of T_2 (Figs. 2 and 3). The x , y , and z axes are moisture content, T_2 value, and amplitude, respectively. Figure 2 shows the T_2 spectra computed from data obtained from the Onepulse experiment. At moisture contents of 12–28%, two peaks appear on each spectrum. Water molecules covered by these two peaks can be regarded as two groups having distinctly different mobility. Because the T_2 values of these two groups range from 1 to 66 μsec , proton signals falling into these two groups can be regarded as from the solids (proteins and carbohydrates) or water molecules very close to the solids. Below 23% moisture content, the increase in the area of the second peak ($T_2 > 20 \mu\text{sec}$) and decrease in average T_2 values of individual peaks could be attributed to the increased available binding sites of the swollen flour substrates as a result of addition of water (Bushuk and Mehrotra 1977b). The disappearance of the first peak at moisture $>23\%$ may be due to the same reasons explained earlier. The increase in both peak area and T_2 a moisture content of $>23\%$ suggests that, at the 23% moisture level, all the water-binding sites on the flour solids have been hydrated. Any additional water would be two or three layers away from the flour binding sites and would therefore exchange and relax more slowly than the water molecules in the inner sites.

The CPMG experiment was intended to detect proton signals having relatively longer spin-spin relaxation times than the Onepulse experiment. The analysis of the data obtained from the CPMG experiments indicated that, at moisture contents below 18%, no signal was detected, suggesting that the dry flour had little mobile water. At $\geq 18\%$ level, there were one to three peaks in the spectra (Fig. 3). T_2 values shown in Fig. 3 range from 10^2 to $10^5 \mu\text{sec}$, suggesting that the detected signals were from water molecules with relatively high mobility. The number and size of peaks increased and the mean T_2 values shifted to the right (increasing T_2 value) with moisture contents increasing up to 28%. The appearance of new peaks suggests that new physical and chemical environments were formed within the system as a result of addition of water to the system. This coincides with the beginning of dough formation at the moisture levels $>23\%$.

It is apparent that the moisture content of the dough samples affects the shape of the spectra. A broader distribution could indicate greater variation in the chemical and physical properties of the

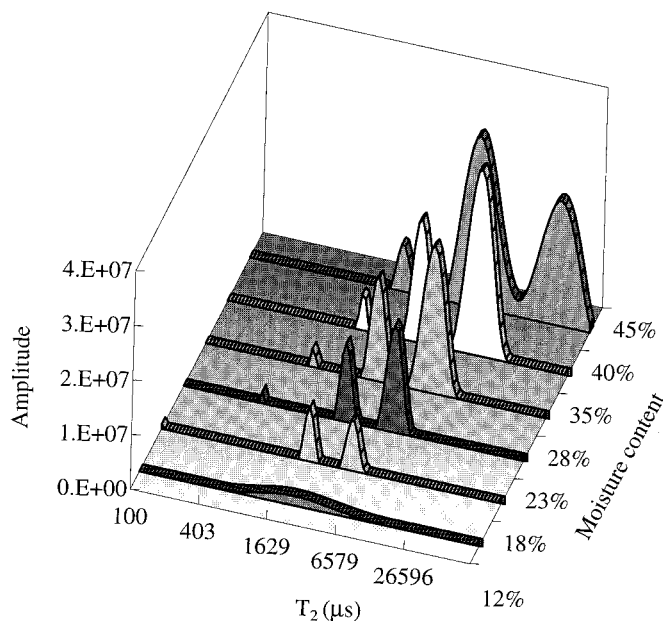


Fig. 3. Continuous distribution of spin-spin relaxation time (T_2) determined by the Carr-Purcell-Meiboom-Gill experiment as a function of moisture content. At and above moisture content of 23%, peaks on each curve are labeled P3–P5, respectively, from left to right.

system. Calculation of the coefficient of variation (cv) of individual peaks would thus provide information about the homogeneity of the systems under analysis. The following equations were used to compute the coefficients of variation of spin-spin relaxation times (Devore 1982):

$$SD = \sqrt{\frac{\sum S_i (T_{2i} - \bar{T}_2)^2}{\sum S_i - 1}} \quad (8)$$

$$c.v.\% = \frac{SD}{\bar{T}_2} \times 100 \quad (9)$$

where T_2 and S are spin-spin relaxation time and amplitude, respectively; SD is the standard deviation of T_2 ; and $\bar{T}_2 = \sum T_2 S_i / \sum S_i$ is the weighted average of T_2 . The results are shown in Fig. 4.

Figure 4 shows that the coefficient of variation of T_2 values in the range of 5–60 μsec (the two peaks shown in Fig. 2) remained almost constant as the moisture content was increased, suggesting that the environments with which the solidlike and tightly “bound” water protons were associated did not change very much while the moisture content increased substantially.

The coefficients of variation of those longer T_2 values (the three peaks shown in Fig. 3) show a gradual and slow increase up to a moisture content of 40%, which may be a result of the gradual formation of the bicontinuous network structure of dough and uneven distribution of water among the flour constituents, as discussed earlier. Upon reaching a moisture content of 40%, which is more than the normal dough moisture level, the coefficients of variation rose sharply, suggesting that the excess water may have created a very unhomogeneous dough morphology.

CONCLUSIONS

The spin-spin relaxation times (T_2) of flour dough samples with different moisture contents were determined using pulsed NMR and analyzed using two different models, a discrete model and a continuum model. With the discrete model, three fractions of protons relaxing at three different rates were identified. The fraction with $T_2 \approx 10 \text{ msec}$ was considered to contain the exchangeable protons of flour constituents and water protons close to the flour constituents. T_2 of this fraction did not change much as moisture content was increased. However, the slight decrease in the amplitude of this fraction may be caused by the “shifting” of the T_2 value of some of the protons in the fraction due to morphological change and interactions between water protons. The intermediate fraction with spin-spin relaxation times of 1 ± 0.5

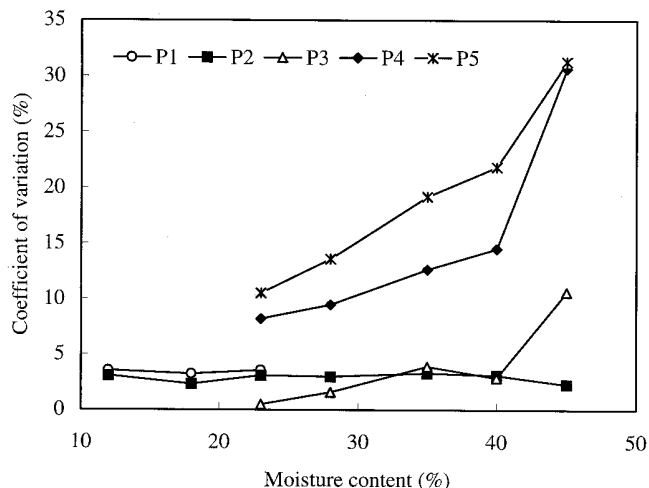


Fig. 4. Coefficient of variation of spin-spin relaxation times determined using the continuum model. See Figs. 2 and 3 for labels of P1–P5.

msec and the slow-relaxing fraction with a time constant of 7.5 ± 2.5 msec changed markedly as moisture content was increased. This was especially evident at 23 and 35%, two critical moisture levels related to dough rheology.

The continuum model presented five proton groups when moisture content was at or over 23%. Significant change in the position, height, and area of peaks on the spectra was observed at a moisture level of 35%. It seems that the continuum model followed the reactions of dough systems to addition of water in a way similar to that of the discrete model. However, the fact that the continuum model does not require an assumption about the number of discrete components should be regarded as an advantage over the discrete model. In addition to depicting the state of water, the continuum model allows the calculation of coefficients of variation of spin-spin relaxation times within certain time domains and therefore may provide information about the homogeneity of the morphology and physical state of dough systems.

LITERATURE CITED

- American Association of Cereal Chemists. 1995. *Approved Methods of the AACC*, 9th ed. approved October 1975, revised October 1981 and October 1994. ;The Association: St. Paul, MN.
- Araujo, C. D., MacKay, A. L., Hailey, J. R. T., Whittall, K. P., and Le, H. 1992. Proton magnetic resonance techniques for characterization of water in wood: Application to white spruce. *Wood Sci. Technol.* 26:101-113.
- Belton, P. S., and Hills, B. P. 1987. The effect of diffusive exchange in heterogeneous systems on NMR line shapes and relaxation processes. *Molec. Phys.* 61:999-1018.
- Belton, P. S., Colquhoun, I. J., Grant, A., Wellner, N., Field, J. M., Shewry, P. R., and Tatham, A. S. 1995. FTIR and NMR studies on the hydration of a high-Mr subunit of glutenin. *Int. J. Biol. Macromol.* 17:74-80.
- Bushuk, W. 1966. Distribution of water in dough and bread. *Baker's Dig.* 40:38-40.
- Bushuk, W., and Mehrotra, V. K. 1977a. Studies of water binding by differential thermal analysis. I. Dough studies using the boiling mode. *Cereal Chem.* 54:311-320.
- Bushuk, W., and Mehrotra, V. K. 1977b. Studies of water binding by differential thermal analysis. II. Dough studies using the melting mode. *Cereal Chem.* 54:320-325.
- Daniels, N. W. 1975. Some effects of water in wheat flour dough. Pages 573-586 in: *Water Relations of Foods*. R. B. Duckworth, ed. Academic Press: Glasgow.
- Davis, R. J., Daniels, N. W. R., and Greenshields, R. N. 1969. An improved method of adjusting flour moisture in studies on lipid binding. *J. Food Technol.* 4:117-123.
- Devore, J. L. 1982. *Probability and Statistics for Engineering*. Brooks/Cole: Monterey, CA.
- Dexter, J. E., and Matsuo, R. R. 1979. Effect of water content on changes in semolina proteins during dough-mixing. *Cereal Chem.* 56:15-19.
- Hills, B. P., Takacs, S. F., and Belton, P. S. 1990. A new interpretation of proton NMR relaxation time measurement of water in food. *Food Chem.* 37:95-111.
- Kroeker, R. M., and Henkelman, R. M. 1986. Analysis of biological NMR relaxation data with continuous distribution of relaxation times. *J. Magn. Reson.* 69:218-235.
- Labadie, C., Lee, J. H., Betek, G., and Springer, C. S. J. 1994. Relaxograph imaging. *J. Magn. Reson., Ser. B.* 105:99-112.
- Lee, F. A. 1970. The effects of bound and available water on enzymic processes in wheat flour doughs. *Food Technol. Aust.* 22:516-520.
- Lee, J. H. 1993. Magnetic resonance studies of tissue ^{23}Na and $^1\text{H}_2\text{O}$ signals. PhD thesis, State University of New York: Stony Brook.
- Leung, H. K., Magnuson, J. A., and Bruinsma, B. L. 1979. Pulsed nuclear magnetic resonance study of water mobility in flour doughs. *J. Food Sci.* 44:1408-1411.
- Leung, H. K., Magnuson, J. A., and Bruinsma, B. L. 1983. Water binding of wheat flour doughs and breads as studied by deuteron relaxation. *J. Food Sci.* 48:95-99.
- Lillford, P. J., Clark, A. H., and Jones, D. V. 1980. Distribution of water in heterogeneous foods and model systems. Pages 177-195 in: *Water in Polymers*. S. P. Rowland, ed. Am. Chem. Soc.: Washington, DC.
- Menon, R. S., and Allen, P. S. 1991. Application of continuous relaxation time distribution to the fitting of data from model systems and excised tissue. *J. Magn. Reson.* 86:214-227.
- Newcomb, C. H., Graham, S. J., and Bronskill, M. J. 1990. Effects of nonlinear signal detection on NMR relaxation time analysis. *J. Magn. Reson.* 90:279-289.
- Overloop, K., and Van Gerven, L. 1992. NMR relaxation in adsorbed water. *J. Magn. Reson.* 100:303-315.
- Provencher, S. W. 1982a. A constrained regularization method for inverting data represented by linear algebraic or integral equations. *Compu. Phys. Comm.* 27:213-227.
- Provencher, S. W. 1982b. CONTIN: A general purpose constrained regularization program for inverting noisy linear algebraic and integral equations. *Comput. Phys. Commun.* 27:229-242.
- Richardson, S. J., Baianu, I. C., and Steinberg, M. P. 1986. Mobility of water in wheat flour suspensions as studied by proton and oxygen-17 nuclear magnetic resonance. *J. Agric. Food Chem.* 34:17-23.
- Ruan, R., and Chen, P. L. 1998. *Water in Food and Biological Materials: A Nuclear Magnetic Resonance Approach*. Technomic: Lancaster, PA.
- Sahi, S. S. 1994. Interfacial properties of the aqueous phases of wheat flour doughs. *J. Cereal Sci.* 20:119-127.
- Schmidt, S. J., and Lai, H. 1990. Use of NMR and MRI to study water relations in foods. Pages 405-452 in: *Water Relationships in Foods*. H. Lavine and L. Slade, eds.; Plenum Press: New York.
- Sharma, N., and Hanna, M. 1992. Assessing handling properties from flow parameters as influenced by dough water content. *Cereal Foods World* 37:27-29.
- Sharma, N., Hanna, M. A., and Chen, Y. R. 1993a. Flow behavior of wheat flour-water dough using a capillary rheometer. I. Effect of capillary geometry. *Cereal Chem.* 70:59-63.
- Sharma, N., Hanna, M. A., and Marx, D. B. 1993b. Flow behavior of wheat flour-water dough using a capillary rheometer. II. Effects of water, protein, mix, and rest time. *Cereal Chem.* 70:63-67.
- Sidwell, V. D., and Hammerle, O. A. 1970. Changes in physical and sensory characteristics of dough and of bread containing various amounts of fish protein concentrate and lysine. *Cereal Chem.* 47:739-745.
- Tellier, C., Mariette, F., Guillemet, J., and Marchal, P. 1993. Evolution of water proton nuclear magnetic relaxation during milk coagulation and syneresis: Structural implications. *J. Agric. Food Chem.* 41:2259-2266.
- Toledo, R., Steinberg, M. P., and Nelson, A. I. 1968. Quantitative determination of bound water by NMR. *J. Food Sci.* 33:315-317.
- Tschoegl, N. W., Rinde, J. A., and Smith, T. L. 1970. Rheological properties of wheat flour doughs. I. Method for determining the large deformation and rupture properties in simple tension. *J. Sci. Food Agric.* 21:65-70.
- Webb, T., Heaps, P. W., Russell Eggitt, P. W., and Coppock, J. B. M. 1970. A rheological investigation of the role of water in wheat flour doughs. *J. Food Technol.* 5:65-76.
- Whittall, K. P., and MacKay, A. L. 1989. Quantitative interpretation of NMR relaxation data. *J. Magn. Reson.* 84:134-152.
- Zimmerman, J. R., and Brittin, W. E. 1957. Nuclear magnetic resonance studies in multiple phase systems: Lifetime of a water molecule in an adsorbing phase on silica gel. *J. Phys. Chem.* 61:1328-1333.

[Received September 11, 1997. Accepted November 25, 1998.]