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Magnetic resonance imaging of single rice kernels during cooking

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Abstract

The RARE imaging method was used to monitor the cooking of single rice kernels in real time and with high spatial resolution in three dimensions. The imaging sequence is optimized for rapid acquisition of signals with short relaxation times using centered out RARE. Short scan time and high spatial resolution are critical factors in the investigation of the cooking behavior of rice kernels since time and spatial averaging may lead to erroneous results. The results are confirming the general pattern of moisture ingress that has been suspected from previous (more limited) studies. Water uptake as determined by analysis of the MRI time series recorded during cooking compares well with gravimetric studies. This allows using these real-time MRI data for developing and validating models that describe the effect of kernel microstructure on its cooking behavior.

Keywords: Hydration; Gelatinization; Rice; Cooking; RARE; Magnetic resonance imaging

1. Introduction

Cooking is one of the most important processing steps in the preparation of foods. It involves transport of heat and mass (water) and commonly several ingredients in the cooked food material undergo phase transitions, such as gelatinization of starch. To a large extent the rates of these processes are governed by the initial phase-composition and microstructure of the material. MRI has been deployed successfully to study the interaction between structure of a food material, and the dynamic transport (heat, mass) and phase transition events that occur during cooking [1]. MRI is ideally suited for such studies since it can detect both molecular mobility and localization in a dynamic and non-invasive manner. Typically, the deployed MRI techniques were based on conventional spin-echo methods. For many materials, however, conventional spin-echo techniques do not provide sufficient spatial and temporal resolution. An important example where the conventional MRI approaches fall short in resolving power is cereals like rice. Rice kernels typically have spatial dimensions of millimeters, cooking times in the tens of minutes during which glassy and crystalline starch becomes gelatinized. To be able to make useful observations with spin-echo MRI, investigators either emphasized spatial or time-resolution, sacrificing one feature in favor of the other.

An example is given by Takeuchi et al. [2] who acquired structural information in only one spatial dimension in order to obtain sufficient time-resolution to monitor moisture distribution in a rice kernel in real time during cooking. This approach is valid if one can assume that the object under study is structurally

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homogeneous [3], which is in general not the case. Stapley et al. [4] employed 2D single slice imaging during the cooking of whole wheat grains, but in these grains the cooking process is much slower than in rice.

In another approach, 3D information on the internal structure of rice kernels could be obtained [5] visualizing internal structures (cracks, pores, and creases) that can facilitate water transport. However, this approach inevitably involved long acquisition times (4.6 h), and hence was not suitable for real-time observation of water transport in such complex microstructures.

Here we present an optimized 3D imaging strategy based on a RARE or Turbo-Spin-Echo sequence to get both high temporal and spatial resolution in order to establish relations between moisture content profiles, rice kernel microstructures, and extent of gelatinization [6–8]. The experimental results delivered by such real-time observation at this high spatial resolution can be employed to establish and validate different hydration mechanisms [9,16,17]. Current models of water uptake are often limited to a single dimension and the swelling of the substrate is not taken into account. A more sophisticated model for water uptake in a three-dimensional substrate structure for different types of water diffusion (ordinary (concentration-driven) Fickian diffusion and high water demand-driven diffusion) as well as the swelling of the substrate during water uptake has recently been developed [10], and can be used to simulate and interpret moisture 3D ingress patterns as observed by the presented MRI method, e.g., to reveal the effect of preprocessing steps on cooking time.

2. Experimental

The experiments were conducted on a 0.7 T Bruker Avance MRI system employing a 10 mm i.d. microimaging detection coil. The filling factor with this detection coil is not optimal but the large diameter is needed because rice is cooked inside the probe. In the imaging experiment it is necessary to prevent grain motion during cooking. Embedding the grain in glass wool stabilizes the position; the embedded grain rests on a bed of glass beads inside a 5 mm o.d. glass tube. The tube is inserted in a glass Dewar tube that holds an electric heater; air is flowing in from the bottom (see Fig. 1). The temperature is controlled by an Eurotherm controller. Since the temperature measurement near the grain disturbs the magnetic field, the temperature was measured in a test experiment using the same parameters as in the actual measurement. The temperature raised approximately linearly to the cooking temperature, set at 90 °C, within a minute after the heater was turned on. After a few degrees of overshoot, the temperature stabilized in some 30 s and remained constant to within a few degrees during the cooking period. The stability of

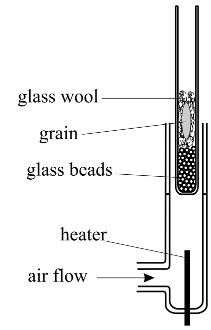

Fig. 1. The test tube with a grain. The grain is embedded in glass wool to prevent motion and lies on a glass-bead bed. The tube is then filled with excess water. Air is heated in a Dewar glass tube and led pass the glass tube containing the grain.

the temperature is not important, as long as it is above the temperature of gelatinization (81 °C) since the relative change in gelatinization rate per temperature unit is around 0.1 [8] and the gelatinization is much faster (the characteristic time on the order of seconds) than the water penetration rate (on the order of minutes), so the moisture profile is mainly determined by the water diffusion process. The insensitivity of the process on small changes in the cooking temperature is also observed experimentally. The detection coil is cooled down with a stream of cold air to prevent overheating which would decrease S/N.

The 3D RARE imaging sequence [11] was used to record images with resolution of $128 \times 32 \times 16$ voxels with the volume of $117 \times 156 \times 313\ \mu m^3$. The RARE sequence is used because it enables rapid acquisition and adequate resolution. The importance of spatial and temporal resolution, as stressed in Section 1, is demonstrated in Section 3.

An image is scanned in 64 s and the images in time series span 30 min of the cooking process. The 3D imaging technique is used because the slice that can be excited with a soft pulse in a faster 2D experiment is too thick to enable accurate assessment. The image is oriented in such a way that the scan time and field of view are optimal: read-out gradient points in the longitudinal direction of the grain; 128 points are sampled in this direction. One phase direction is scanned in 32 steps and the other in 16 giving 16 slices of thickness 300 μm with a resolution of 128×32 pixels with a field of view of $15 \times 5\ mm^2$ representing the 3D volume. Four scans are averaged in a single image. The slices of a typical image are shown in Fig. 2. Turbo factor 16 and repetition time of 500 ms were used in the scans. The receiver bandwidth was set to 50 kHz. The first echo was observed at 6.6 ms after excitation and subsequent echoes were 4.2 ms apart. All RF pulses used were block pulses of 40 μs duration. A $\pi/2$ excitation pulse was used. Transverse phase encoding started at the origin of k-space and was stepped symmetrically to the

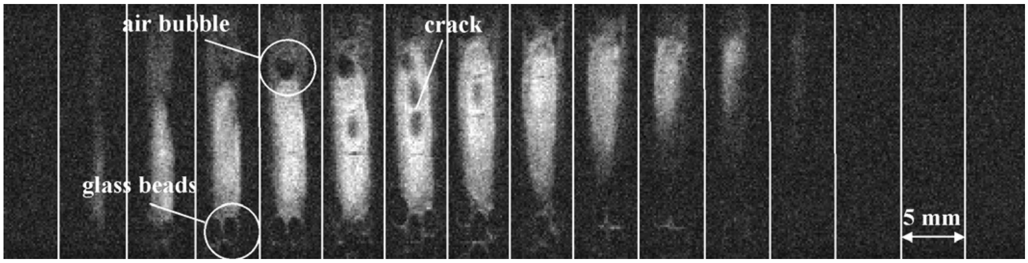

Fig. 2. A set of 16 slices representing 3D volume. Each slice shows an axial cross-section of the grain (dimension: 5 × 15 mm; slice thickness around 300 μm). An example at time 22.5 min from a time series represented in Fig. 4 is shown. Several features are distinguishable: an air bubble trapped at the top of the grain, glass beads at the bottom of the grain, cracks in the grain, and the grain itself. The core of the grain is not cooked yet. Free water around the grain is hardly visible at the cooking temperature and at the actual imaging parameters.

maximum and minimum phase [12]. The phase in the slice direction was stepped linearly from minimum to maximum. The effective echo time for the RARE images was equal to the first echo time of 6.6 ms. Phase encoding, turbo factor, number of slices, and resolution in the phase gradient direction were set in a way to cover the zero of k-space in the first echo after excitation thus minimizing the relaxation effect on the amplitude of the image.

3. Results and discussion

In this study we investigated the cooking process of de-husked dry rice of the IR64 variety (Indonesia).

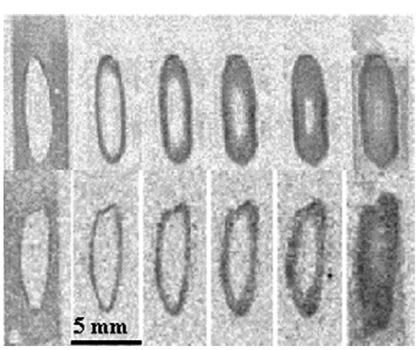

Fig. 3. Single slice images out of a 3D series during cooking of a rice kernel. Each of the images in the top series ('slow scan') was scanned in 4.5 min and the images follow each other in time. The images in the bottom row ('fast scan') were scanned in 64 s and there is a 3.5 min time gap between the subsequent images. The top and bottom row are averages of 16 and four scans, respectively.

The importance of an as short as possible imaging time is stressed by the results presented in Fig. 3. In the 'slow scan' series (image time 4.5 min per image), the transition from non-hydrated to hydrated starch appears gradual whereas in the 'fast scan' (image time of 64 s per image) it is sharp. The smooth front in the 'slow scan' image series is a result of averaging: during acquisition the moisture front moves substantially (more than the dimension of a pixel). From these results we conclude that imaging time is important to avoid artifacts caused by moisture front ingress during data acquisition (smoothing of the front—leading to a false diffusion model).

In Fig. 4 we present a series of images of the central slice out of a 3D data set (obtained in 64 s per image) as a function of cooking time. This series also highlight some consequences of the experimental procedure. The preparation of the probe with a sample takes about 5 min. During this time some cold hydration of the surface layer is possible. Then the first scan is made at room temperature. In this image the grain signal is barely above the noise level; signal of free water around the grain emphasizes glass beads and tube walls. Glass wool embedding the grain is not as compact to restrict the motion of water molecules and water can be considered as free. Stronger signal is observed on the peripheral layer of the grain. A possible reason can be water interacting with the grain surface, leading to shorter T_1, and thus less T_1 saturation. This layer is possibly equivalent to the layer of gelatinized starch reported in [13].

The heater was turned on after the first scan was completed at room temperature, and then images were scanned in succession as fast as possible. Images follow approximately 75 s apart and each image takes 64 s to

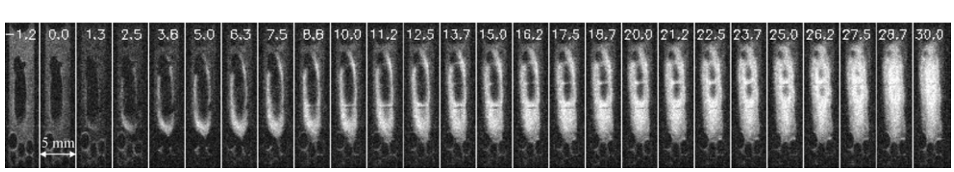

Fig. 4. Time series of the central slice in cooking process. Numbers at the top of the scans indicate the time in minutes from the beginning of cooking.

complete. The signal of free water around the kernel decreases because the temperature and thus diffusional and convectional motion increases.

The grain structure is not uniform (see Figs. 2 and 4). Fissures on the surface and inside of the grain may stimulate water ingress or sometimes hinder it (trapped air bubbles). Artifactual front smearing due to spatial averaging over adjacent parts with different moisture contents and/or porosity may cause false interpretations of cooking behavior. This is an important reason to use 3D images with the highest resolution possible in the study of the process. Fig. 5 shows images rendered in 3D, showing that the cooking process proceeds faster along cracks. They reveal, e.g., a slightly faster ingress of water from the bottom, due to a small temperature gradient over the kernel. This emphasizes the need for good spatial resolution in three dimensions.

The signal observed in the MRI images contains contribution of water molecules that have penetrated into the kernel microstructure, and water that is taken up by gelatinized starch. The contribution of starch signal itself is very small because of the short transverse relaxation time (shorter than 1 ms). The only signal observable in imaging, which does not result from water protons penetrating from the exterior, originates from water molecules already present inside the starch granular structure. Some crystalline water molecules are released when starch gelatinizes. Crystalline water itself is not detected. Isotherm data [14] suggest that in starch with a moisture content below 0.1, water is very strongly associated with the starch molecules, which explains the very

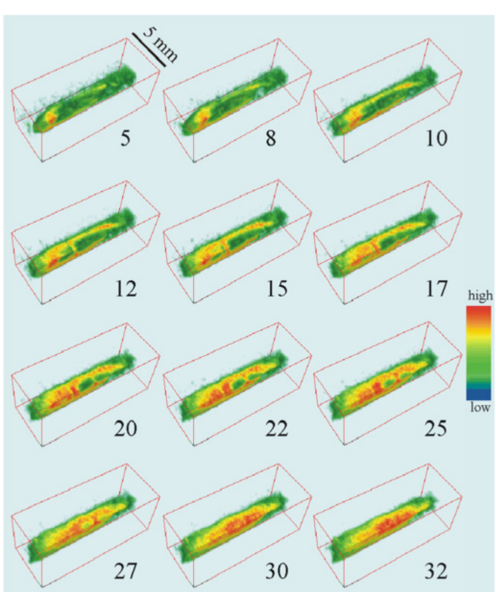

Fig. 5. The water uptake of a rice kernel as a function of time during cooking as visualized in 3D space. The 3D model is clipped by a horizontal and vertical plane through the center of the kernel. The color ranging from blue to red corresponds to the intensity scale (amount of water).

short relaxation times. Water embedded in starch can be in small pores in and around starch substrate, trapped inside the amylopectin molecules because of molecular topology or bound through hydrogen bonds, and in a form of amylose solution. Water content of dried kernels is typically well below 0.3 and in our measurement no signal from native starch is detected (see first images in Fig. 4).

The effect of relaxation on the pixel intensity in RARE imaging is intricate (see [11]), but is roughly given by

$$A = A_0[1 - \exp(-TR/T_1)]\exp(-TE_{\mathrm{eff}}/T_2), \quad (1)$$

where TR is the repetition time and TE_{eff} is the effective echo time of the RARE sequence.

The free water signal is saturated because the repetition time of 500 ms is short compared to the longitudinal relaxation time. Water inside gelatinized starch with shorter T_1 (less than 0.5 s [4]) exhibits stronger signal even if proton density is lower. The variation of T_1 over the sample is small and is neglected in further analysis. However, the signal is influenced by T_2, which depends on moisture content and temperature. T_2 increases with moisture content as is shown in previous studies [3,4,15]. It is impossible to determine true moisture content from a single image and any attempt to do so prolongs the measurement time thus reducing temporal resolution, which, however, is important, since the process progress is rapid. Nevertheless, a one on one relation of the signal intensity and moisture content exists: higher signal indicates higher moisture content. In literature roughly linear relations between T_2 and moisture content m (wet basis) are reported. This is shown in Fig. 6A, which is based on the data presented in [3], measured at 100 MHz. Results obtained at 200 MHz are similar [4], whereas those measured at 10 MHz show a bit steeper relation [15]. If one assumes that the amplitude A_0 is proportional to m, then the NMR signal is a monotonically increasing function of the moisture content as well. Defining $S = A/[1 - \exp(-TR/T_1)]$ and $A_0 = S_0 m$, we obtain the dependence of the NMR signal $S/S_0 = m\exp(-TE_{\mathrm{eff}}/T_2)$. This relation between S/S_0 and the moisture content m is shown in Fig. 6B, using the relation presented in Fig. 6A and the actual TE_{eff}.

The process analysis is based on the NMR signal alone and we cannot measure the true moisture content but rather the relative moisture content, based on the signal above the detection threshold. This detection threshold, representing baseline moisture content, is the limit moisture content that can still be observed in the NMR signal at the actual experimental parameters (around 0.2 in our case). Stronger deviation from linear behavior is apparent at low moisture content and hence care should be exerted in transforming low NMR signals to moisture content. The NMR signal from the moisture front thus underestimates the moisture content because

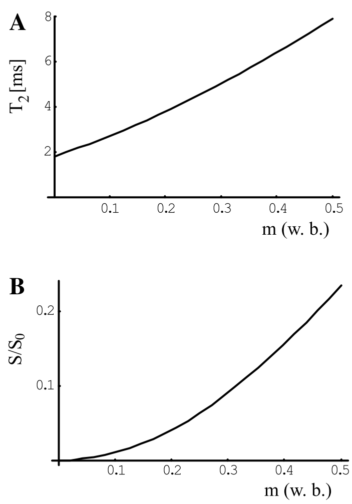

Fig. 6. (A) Relation between T_2 and moisture content m as presented in [3], (B) calculated relation between NMR signal S/S_0 and moisture content (for details see text). NMR signal is linearly related to moisture content (B) in the range relevant to the experiment. Relaxation time is in the first approximation a linear function of moisture content as well, as shown in (A).

the signal is weaker not only because spin density is smaller, but also because the relaxation time is shorter.

The results of water uptake rate as observed by analysis of our MRI data correspond well with the results of other techniques. The method can be used on grains of different variety and treatment to compare the processes of cooking rate, water ingress rate, or relative moisture uptake. For a comparison, the normalized integrated MRI signal is compared to the gravimetric results (Fig. 7). The integrated MRI signal has been normalized by relating the MRI signal of a fully cooked grain to the gravimetric moisture content of equilibrated cooked grains.

A more detailed interpretation of the measurements can be obtained by considering 1D plots across the grain, perpendicular to the longitudinal axis (Fig. 8). The ingress pattern of water in this grain is characterized by a relative sharp front. Such fronts results from diffusion behavior as described by a so-called Water Demand model [9,10], where diffusion is driven by the ceiling moisture content related to the extent of gelatinization of the rice substrate network.

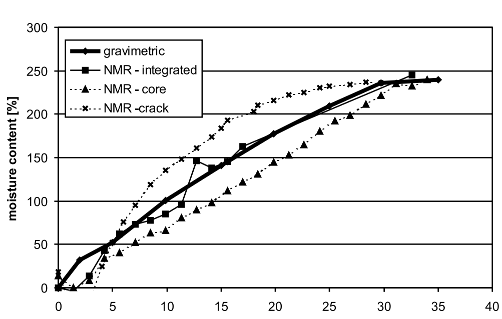

Fig. 7. Plot showing integrated NMR signal as a function of cooking time. The signal was baseline subtracted and normalized to match the gravimetric results. The increase in the value indicates water uptake and is a measure of cooking rate, the amount of total water uptake and indicates the end of the cooking process. The dashed lines correspond to the NMR signal integrated over partial volumes, indicated as 1 and 2 in the inset of Fig. 8. A faster hydrating part corresponds to the crack in the grain (volume marked with 2 in the inset of Fig. 8).

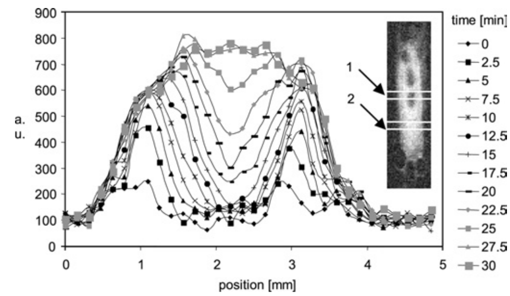

Fig. 8. One-dimensional plots of relative moisture content across a kernel (approximately at the center), as it changes with cooking time. In the inset the position of the cross plot is indicated with 1. A plot across the position indicated by 2 has the same shape, only the rate of ingress is higher. The gravimetric plots corresponding to these partial volumes are represented by dashed lines in Fig. 7.

One can also analyze the diffusion process by following the increase of the total of this 1D plot as a function of time. This gives us equivalent information as gravimetry. The importance of good spatial resolution is again demonstrated by comparing the totals from different positions: the dashed line with triangles in Fig. 7 shows the increase in moisture content for the line going through the center of the grain and the dashed line with crosses shows the same for the position 3 mm below, where a fissure in the grain enables much faster hydration (starch is fully hydrated in half the time).

4. Conclusion

Other imaging techniques than MRI, such as X-ray tomography or confocal laser scanning microscopy, have a better spatial resolution, but MRI is superior in the real-time assessment of the rice cooking process. With proper data evaluation it also offers quantitative information notwithstanding the fact that the measured signal is hard to interpret since a lot of factors influence its strength. Relaxation changes with moisture content, temperature, and the degree of gelatinization and it is necessary to combine the information with the results of other measurements such as relaxometric measurements. These measurements, however, are time consuming and cannot be performed in a 3D map during cooking.

In previous applications of MRI to cooking rice kernels, T_2 maps were used to measure absolute moisture content. However, difficulties in determining the relation between T_2 and m, speak against this approach whenever fast measurements are asked for, and relative result suffices. Freezing the process by temperature quenching does not necessarily work especially on a short time scale. Also using the relation of T_2 and m determined at room temperatures for the rapid 1D measurements at cooking temperature is questionable. An additional problem of fast 1D analysis is the poor resolution, which is problematic considering the heterogeneous structure of a single grain.

With the presented analysis it is possible to assess the ingress of water in rice kernels during cooking in real-time mode, and with good spatial resolution in three dimensions. The results obtained on the rice variety studied confirm the general pattern of moisture ingress (i.e., the shape of moisture profiles and the fact that it enters reasonably evenly from all exposed surfaces) that has long been suspected from previous (more limited) studies. Now we can extent such studies to develop and validate models that relate kernel microstructures (porous structure as well as state of starch on molecular level) with their cooking behavior, e.g., in rice grains that are preprocessed in various manners in order to accelerate the water uptake, i.e., to reduce the cooking time. These preprocessing steps alter the internal structure of the rice grains. Such an approach is clearly not limited to rice, but can be applied in the broad field of food technology.

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