Abstract

Low-field bench top $^1$H nuclear magnetic resonance (LF-NMR) relaxometry instruments have been increasingly popular as analytical tools for engineering research. Magnetic resonance imaging, which is a more advanced approach to NMR technology, provides the researcher with images of the internal structure without any disruption to the sample and has been commonly used in medical applications in analysis of soft tissue. The non-invasive and non-destructive nature coupled with the high discriminative power of LF-NMR and MRI, makes them invaluable tools of analysis for a wide range of applications in food science. This review covers the basic concept behind NMR/MRI technology and discusses some of its most commonly used food applications. The review addresses the food scientist with no prior knowledge of NMR/MRI and aims to supply the reader with both the theory of the method and its fundamentals, as well as the practical uses in scientific research and industrial applications.

Keywords NMR relaxometry · MRI · Theory · Food applications · Water distribution

Introduction

Magnetic resonance imaging (MRI) is a technique that has been traditionally used in medical applications to investigate the structure of soft tissue as a tool for clinical diagnosis and has emerged from the utilization of radio frequency range pulses as a means of attaining information on the internal structures of human tissues. Nevertheless, MRI has proven to be a strong analytical tool for engineering research as well, due to its accuracy and versatility. Currently, MRI can be used in characterization of many biological and non-biological systems [24]. Magnetic resonance imaging (MRI) is performed with an NMR instrument equipped with magnetic gradient coils that can spatially gather the data thus creating two-dimensional and three-dimensional images that display areas having different physico-chemical properties (e.g., water content) with different contrasts [24, 43]. In other words, MRI provides spatial distribution of the signal due to presence of gradient in three axes.

NMR relaxometry, on the other hand, does not require gradients (except for diffusion measurements). It features the use of a radio frequency (RF) pulse in order to create a temporary disturbance on a sample placed into another static magnetic field. The relaxation of excited signal is then monitored, and various information on the object can be attained [43]. In contrast to MRI, for an NMR relaxometry experiment, the signal attained comes from the whole sample and spatial information is not obtained. However, it is possible to differentiate signal coming from compartments with varying proton environments (e.g., cellular organelles, water compartments with different mobilities in hydrogels).

The non-invasive, non-destructive nature of both methods and the fact that both qualitative and quantitative data on physical and chemical properties of a wide range of samples can be gathered, have made NMR relaxometry and MRI popular in food-related applications [23].

The basic principle behind the techniques is nuclear magnetism. Nuclear magnetism emerges from the spins of
nucleons (protons or neutrons). In order to obtain a net nuclear magnetization moment, the nucleus should contain an odd number of nucleons. For the experiments, any element with an odd number of nucleons can be used; though, mostly hydrogen is preferred. This owes to hydrogen’s abundance in organic samples (presence in water and oil), and high MR sensitivity (H\textsuperscript{1} gives the highest signal) [58].

To acquire a signal from a sample, it is initially placed into a large static magnetic field (\(B_0\)) (Fig. 1). For this purpose, a variety of magnets (i.e., permanent, superconductive) with a wide range of field strengths (0.2–7.0 T) can be employed [43]. When placed into the magnetic field, the protons within the sample align themselves with this external magnetic field (in \(z\) direction) (Fig. 2).

Every proton possesses a magnetic moment. As seen in Fig. 2, the magnetic moments of protons are aligned either in the same direction or in the opposite direction with the external magnetic field. The former ones possess a lower free energy than the latter. The number of protons that are aligned in the same direction with \(B_0\) are slightly higher than the ones that face the opposite direction. However, this slight difference is enough to create a net magnetic field in the sample in \(+z\) direction. This magnetic field is referred to as longitudinal magnetization.

The protons do not directly face the external magnetic field all the time. Instead, they make a spin top-like movement called precession, shown in Fig. 3. The frequency of this circular motion is identified with the following relation [43];

\[ \omega = \gamma B_0 \]

where \(\omega\) = angular precessional frequency of proton, \(\gamma\) = gyromagnetic ratio and \(B_0\) = strength of the external magnetic field. All the protons have the same frequency owing to the relation above. The magnetization on the \(xy\) plane due to this precession is called transverse magnetization. However, the precessing protons are not in-phase. What this means is that though the protons precess at the same frequency, they are not at the same position at the same time. An illustration is given in Fig. 4. Therefore, the randomly precessing protons cancel each other out, and the net magnetization along the \(xy\) plane (transverse magnetization) becomes zero [6].

To tip away the net magnetization from the \(z\)-axis to the \(xy\) plane, an RF pulse is applied. Owing to this RF pulse, some of the protons align themselves opposite to \(B_0\) which causes a decline in longitudinal magnetization, also precessional movement of protons get in-phase with each other giving rise to a transverse magnetization. When RF pulse is removed, the protons turn back to their previous states. This process is called relaxation. The relaxation of longitudinal and transverse magnetization is measured to attain information on the sample. Figure 5 displays the stages of disturbance and relaxation through changes of net magnetization [6, 58].
Longitudinal relaxation time, $T_1$, (also referred to as spin–lattice relaxation time) refers to the time it takes for the spins to realign themselves along the axis of the external magnetic field, and is computed from the recovery curve (displayed in Fig. 6) of $M_z$ component of the magnetization vector with the relation [43]:

$$M_z(t) = M_0 \left(1 - e^{-\frac{t}{T_1}}\right)$$

where $T_1$ is the time constant of magnetization recovery curve, $M_z(t)$ is the component of magnetization along the z-axis and $M_0$ is the initial magnetization.

Transverse relaxation time, $T_2$, (also referred to as spin–spin relaxation time) refers to the time it takes for the transverse magnetization, to decay to the equilibrium value of zero. $M_{xy}$ component of the magnetization is shown with the relation [43]:

$$M_{xy}(t) = M_0 \left(e^{-\frac{t}{T_2}}\right)$$

where $T_2$ is the time constant of magnetization decay curve in Fig. 7, $M_{xy}(t)$ is the component of magnetization on the xy plane and $M_0$ is the initial magnetization.

The equations above relate the magnetic energy in z direction and the xy plane separately to each relaxation time.

To carry out an NMR experiment, a combination of different RF pulses is applied sequentially and the resulting relaxation in magnetization is measured. Each one of the predetermined combinations is called a sequence. Figure 8 shows an illustration of “spin echo (SE) sequence.” The net signal intensity of SE is expressed in Bernstein et al. [6] by the following relation;

$$S = M_0 \left(1 - 2e^{-\frac{TR}{T_1}} + e^{-\frac{TR}{T_1}}\right)e^{-\frac{TE}{T_2}}$$

where $M_0$ is the initial magnetization, which is directly proportional to the water proton density, TR is the repetition time and TE is the echo time. Repetition time (TR) represents the time between each successive RF pulse, while echo time (TE) refers to the time it takes for the signal to reach a maximum after sending the 90° RF Pulse (Fig. 8). These parameters can be manipulated to increase the effect of $T_1$, $T_2$ or proton density. A higher TR decreases the $T_1$ weighting of the image, and a lower TE decreases the $T_2$ weighting. If these are used in conjunction, it is possible to obtain an image with proton density weighting [6, 43, 58].

Both NMR relaxometry and MRI employ the magnetic signal to output information regarding the sample. As stated before in a simple NMR relaxation experiment, one...
single measurement is taken for the whole sample; whereas for an MRI experiment, these signals are taken for small voxels inside the sample in all three axes, then the signals are encoded for spatial information with the aid of gradient coils and proper processing results in an MR image. Moreover, the minimum TE values used in NMR relaxometry and MRI differ. Short TE’s (around ms) in relaxometry allow the observation of compartments having much shorter $T_2$ than in MRI mode (with minimal TE values around a few ms). In addition, susceptibility and exchange effects can be quite different, depending on TE.

In Fig. 9, MR image of two peaches is given. Some areas of the images are displayed lighter, some are darker. This is the result of changing signal intensities coming from different parts of the peach. Thus, the change in tone is a function of $T_1$, $T_2$ and proton density (as shown by the signal intensity equation above). Variations in chemical content and cellular structure cause changes in $T_1$ and $T_2$ data differentiating local signals received from the material. In medical application, this data can be used for diagnosis of injury and disease within the soft tissue [116], whereas in food systems, these images provide detailed information on the interior structure of food without causing any damage, interfering with the food’s natural structure or interrupting transport processes [94]. However, it should be mentioned that exchange between compartments (e.g., due to changes in membrane permeability) could severely affect the detailed information on the interior structure. Thus, during interpretation, possible exchange between compartments should be taken into consideration. Along with image analysis quantitative analysis regarding the changes in $T_1$ and $T_2$ also provides the researcher with invaluable information on the sample. $T_1$ relaxation time (also known as spin–lattice relaxation time) indicates the effectiveness of the magnetic energy transfer between spinning $^1$H protons and the surrounding lattice. Pure bulk water has a very long $T_1$ time (could be shorter in small confinements such as cell walls though); oil, on the other hand, displays much shorter $T_1$ times.

The changes of the state of oil and water, as well as their interaction with the surrounding macromolecules, can significantly influence $T_1$ times. $T_2$ relaxation time (also known as spin–spin relaxation time) is a measure of the effectiveness of energy transfer between spinning $^1$H protons and the surrounding lattice. Pure bulk water has a very long $T_1$ time (could be shorter in small confinements such as cell walls though); oil, on the other hand, displays much shorter $T_1$ times.

The changes of the state of oil and water, as well as their interaction with the surrounding macromolecules, can significantly influence $T_1$ times. $T_2$ relaxation time (also known as spin–spin relaxation time) is a measure of the effectiveness of energy transfer between spins, and is expected to be shorter for closer proximity between molecules. Thus, $T_2$ is shortest in solids (molecules packed closely resulting in a higher energy transfer efficiency between spins), followed by oil and water. $T_2$ relaxometry measurements, coupled with $T_2$ relaxation spectra, are known to yield information on water content, physical
properties of water and interaction of water with the surrounding macromolecules [6, 43, 55, 136]. For the peaches in Fig. 10, it is roughly possible to say that the darker areas possess shorter $T_1$, $T_2$ relaxation times and/or lower proton densities. Molecular tumbling (the rotation correlation time) is an important phenomenon in relaxation. The change in relaxation times at a low water and fat content could have resulted in slower molecular tumbling due to magnetic interaction between spins not being averaged out. This explains why the thick and rigid outer shell of the seed is darker in color than the flesh of the peach. More explanation of the shorter relaxation times in low-water-content foods could be found in another study [119].

As mentioned, the most significant advantage with NMR relaxometry and MRI is that they are non-invasive or non-destructive on the samples and require no sample pretreatment for analysis [78]. The non-destructive nature and lack of any pretreatment make MRI and NMR relaxometry preferable in analysis of whole foods. In addition, they give equally accurate results for both transparent and opaque samples. This makes the methods ideal for analysis of concentrated emulsions where methods requiring sample transparency (e.g., optical microscopy, static light scattering) cannot be applied [24]. High sensitivity (in terms of contrast differences), multi-planar imaging options (without repositioning the sample) and the relatively short acquisition times further increase the methods’ applicability [58]. Through NMR/MRI, measurements such as local water/oil content, solid fat ratio, oil/moisture migration could be gained, which consequently, provides powerful means of observation of changes in microcellular structure, diffusion of polymers and investigation of heat and mass transfer within the materials [77, 78, 105, 116]. The recent acceptance of NMR/MRI as a technique for food quality determination and the utilization of low-field, affordable, bench-top NMR devices have increased their popularity in the food industry [115]. Despite these advantages, the high running and machinery costs coupled with the complications encountered while interpreting data might limit the methods’ usage [58].

This review discusses applications of $^1$H NMR relaxometry and MRI to food products and processes. There exist multiple comprehensive studies on the subject [45, 75–77, 118]. However, this review differentiates itself by providing a theoretical background on the $^1$H NMR/MRI...
and being addressed to researchers that have no prior knowledge on the subject. The review pursues this manner throughout the whole study by giving comprehensible examples and referring to NMR theory to explain the reasoning behind applications. The aim is to provide the reader, especially food science community, with a general insight on possible applications through illustrations in a range of food products and to show the methods’ potential in food applications.

Applications of MRI and NMR Relaxometry

Postharvest Physiology of Fruits and Vegetables

The abundance of water in fresh fruits and vegetables ensures higher signals in NMR relaxometry/MRI, which makes them ideal samples for the methods. There are quite a number of studies regarding analysis of postharvest physico-chemical changes, detection of certain complications in tissues and even differentiating sensorial quality of various cultivars [25, 63, 87, 103, 122, 131]. While the varying contrasts in MR images indicate differences in tissue structure, the biggest challenge of MRI and NMR relaxation experiments is the interpretation of the data. Changes in relaxation data can be attributed to sample properties such as water/oil content, the physical properties of water, interaction with macromolecules, compartmental structure, membrane permeability [78, 136] as well as non-sample-related influences such as magnetic field strength and inhomogeneities, the sequence used and the effects of the acquisition parameters [43]. The high number of parameters and extrinsic factors that could affect signal intensities necessitates a more advanced approach in interpretation of data. By changing the acquisition parameters, it is possible to gather images that are more T₁, T₂, proton density weighted or a mix of three [58]. In

![Fig. 10](image-url) MR images of the same tomato taken with a 3 T MR instrument with parameters. a TR = 600 ms, TE = 6 ms, b TR = 3500 ms, TE = 55 ms and c TR = 3500 ms, TE = 6 ms

In Fig. 10, three images of the same tomato are given with imaging parameters adjusted such that (a) is T₁ weighted (TR = 600 ms, TE = 6 ms) (b) is T₂ weighted (TR = 3500 ms, TE = 55 ms) and (c) is proton density weighted (TR = 3500 ms, TE = 6 ms). As evident from the figure, the image acquired changes drastically depending on the parameters. Depending on the physical property being examined, the desired contrast could be created with the selection of appropriate parameters. For instance, in investigation of fruits and vegetables, T₂-weighted images when characterized with multi-exponential decay and combined with relaxometry approach could explain differences for different proton compartments in the cells [78, 93].

The physiological changes during development, ripening, storage and processing as well as variations in permanent quality attributes owing to plant variety, location or cultivation season are screened in the form of changes in NMR signal. MRI, on the other hand, can be used to gather spatial information on the crop regarding the changes in relaxation times and proton density [78]. This way, it is possible to detect certain plant diseases, injuries or any kind of quality degrading complications that has no visible sign on the outside (Fig. 9).

One such study, carried out by Zhang and McCarthy [137], investigated the possibility of detecting and characterizing black heart disease in pomegranates through NMR relaxometry and MR imaging. Due to the lack of external symptoms, visible inspection is not viable for detection of black heart disease. T₂ relaxation times are employed as a means of gathering information on compartmental structure of cells. T₂ data, obtained through multi-exponential decay fitting, for healthy and diseased fruits, were significantly different with the former giving three exponential peaks and the latter giving four peaks. In diseased fruits, there was formation of a new fast relaxation component and the three common peaks exhibited lower T₂.
values. This change was correlated to the redistribution of water among cell compartments caused by the infection. Ultimately, MRI exhibited 92% accuracy in detecting the presence of black heart in pomegranates [136].

Change in cell water compartmental structure could be used as an indicator of quality degrading injuries such as chilling and freeze injury. Kotwaliwale et al. [59], in their study on the detection of freeze injury through MR imaging in pickling cucumbers, showed that while there is no significant difference between spin and lattice relaxation times ($T_1$) for healthy and injured pickling cucumbers, the variance in spin–spin relaxation times ($T_2$) could be correlated with freeze damage. The $T_2$ values of damaged samples were found to be higher than control ones. In addition, MR images of freeze-damaged samples displayed a distinctly different subsurface region which was correlated with physically damaged tissues that becomes visible when pickling cucumber is sliced [59]. Other than the distinctive quality affecting diseases, with NMR/MRI, it is also possible to monitor the normal maturity and ripening process of fruits and vegetables. The change in maturity of tomatoes, as identified with the color change from green to red, was monitored with MRI in the study of Zhang and McCarthy [136, 137]. A set of five different MRI sequences was used to take images of tomatoes during various stages of maturity. The sequences were selected to give varying weightings on proton density, $T_1$, $T_2$ and diffusion rate. The varying signal intensities obtained from the pericarp of tomatoes as a function of time were found to be correlated with the maturity of tomatoes. Among the different sequences, diffusion-weighted image and spin echo image with higher $T_2$ weighting had the highest discriminatory power [137].

As previously mentioned, it is highly probable to observe a change in most fundamental NMR parameters during ripening of the crop. However, when carrying out a quantitative research, it might be problematic to isolate the actual reason of the change without further investigations of the tissue. In the study by Clark and MacFall [20] on quantitative magnetic resonance imaging of persimmon fruit during development and ripening, persimmon fruits were investigated with MRI during various stages of development and ripening. During development, both the $T_1$ and $T_2$ relaxation times exhibited an increase; during ripening, $T_2$ values continued to increase smoothly; whereas $T_1$ times exhibited an abrupt decline 2.5 weeks after picking. Though there was an obvious trend in relaxation measurements, Clark and MacFall [20] suggested the use of a more elaborate technique such as scanning electron microscopy or NMR spectroscopy along with MRI, in order to distinctly identify the causal relationships behind the trends. Results acquired through these techniques, when discussed along with the change in MRI parameters, helped to identify the specific variations in cell size and structure that caused the physiological alterations in the crop [20].

Sensorial quality changes in both raw and cooked fruits and vegetables changing with conditions such as harvesting season, cultivar selection and/or processing is another field of application for NMR/MRI. Ciampa et al. [18] investigated the seasonal changes in Pachino cherry tomatoes with MRI and NMR relaxometry. Both images and relaxation times provided useful data in differentiating changes in fruits according to the season (winter, summer and spring). The ability of MRI to give accurate spatial information on water content and its interaction with surrounding macromolecules is found invaluable in highlighting variations in tomatoes depending on seasonal conditions. The molecular movement of water and spatial distribution were distinctly different in summer and winter tomatoes, with the former possessing an increasing water distribution from the outer to inner sections, whereas the latter possessing most of the water in placental cavities of the fruit [18]. Prediction of sensorial acceptance of a crop provides invaluable means of assessing the economic value before cultivation. Thybo et al. [115] demonstrated the possibility of accurately predicting the sensorial quality of potatoes through MR imaging. The comparison of MR imaging data for raw potatoes with subsequent sensorial analysis for five different potato varieties displayed a correlation between sensorial attributes and MR data. It was shown that especially the perception of hardness and adhesiveness could be predicted with a high degree of accuracy, whereas, on the contrary, the attributes of mealiness and graininess as well as specific gravity could not be correlated with relaxation measurements. It was stated that this correlation was enough to demonstrate the potential of MRI/NMR in evaluation of sensorial quality. With better utilization of acquisition parameters and choice of suitable sequences, there exists the possibility of acquiring a higher correlation for all sensorial attributes [115].

The utilization of low-resolution NMR/MRI systems in processing as a means of an in-line analysis method is another important application in food industry. The power of NMR/MRI as a non-destructive analysis method during processing stages is discussed in the study by Milczarek et al. [83]. In the study, processing of peeled canned tomatoes featured steam peeling. However, when bruised tomatoes were subjected to the harsh steam peeling process; bruised tomatoes would disintegrate and led to loss of product. Therefore, a fast on-line analysis that could differentiate bruised tomatoes before they reached the peeling step was necessary. For this purpose, the potential of MR imaging was studied. The difference between sound and bruised tissue was displayed as differences in contrast in tissues. A total of 13 MR pulse sequences (six turbo fast low angle shot, one fast low angle shot, five fast spin echo and one gradient recalled echo) with very low acquisition
times were assessed for their ability to accurately differentiate fruits. Multivariate Image analysis technique was used to classify the images of different sequences. The five MR sequences that exhibited the highest “Variable Importance in Projection” scores were employed. The final imaging time for completion of five successive sequences was measured as 5 s, which is one order of magnitude larger than the time required for an on-line implementation. Nevertheless, Milczarek et al. [83] suggested that the times could be shortened by using fewer sequences or lowering the resolution.

Analysis of Postmortem Muscle

NMR/MRI has been numerously used in analysis of meat, poultry and fish for examination of water and fat distribution, evaluation of overall quality, process induced and postmortem changes in flesh [4, 11, 12, 21, 41, 45]. Both nutritional and sensorial quality of meat is highly correlated with its water-holding capacity [100]. H-NMR and MRI has been shown as an accurate and fast method for determination of water and fat content of meat and investigating its interaction with surrounding macromolecules [104, 111]. In Fig. 11, it is possible to see the spin echo images of a fresh cut meat obtained with a 3T clinical type MR scanner. For the images, spin echo, fat suppression spin echo and water suppression spin echo sequences were employed. In all sequences, TE was set to 12 ms and TR was set to 2000 ms. A fat suppression sequence is based on the principle of neutralizing the signal coming from the fat, which results in an image composed only of the signal from water and the remaining $^1$H containing macromolecules (such as proteins, and starch). This is usually achieved through the use of a pulse gradient spin echo sequence [74]. However, setting the parameters, TE and TR, suitably ensures that the signal comes purely from water. The opposite could be said for a water suppression image (which suppresses signal from water). In other words, the fat suppression image can be acknowledged as a rough representation of water distribution, likewise water suppression image is an indication of fat distribution. The cumulative signal of these two images gives the spin echo image (Fig. 11). The idea of these sequences is using the differences of fat and water self-diffusion. By selecting the gradient duration and strength in accordance with a pulsed gradient echo sequence, it is possible to obtain water/fat-suppressed images. Looking at Fig. 11, it is possible to observe that the fat tissue is brighter than the rest of the meat in water suppression image and darker in the fat suppression one. On the contrary, muscle tissue, which is composed of approximately 75 % water, appear brighter in fat suppression image and darker in water suppression one [3]. Similarly in Fig. 12, spin echo, fat and water suppression MR images of peanut and raisin cakes are shown. Roasted peanuts contain very low amounts of water (of around 2 %) and high amounts of fat (around 75 % by weight) [80, 90]. The moisture content of peanuts was measured to be around 15 % by weight, and raisins unlike peanuts possess very low fat (<1 % by weight) [91]. As evident from Fig. 12, in SE and water suppression images, peanuts are brighter than the rest of the cake, and in fat suppression images, peanuts are observed as dark spots. The opposite is valid for raisins. In other words, using a fat suppression sequence, the signal from peanut is almost completely neutralized, whereas same could be said for raisins in water suppression images. Spin echo images, as expected, look like a sum of the water and fat suppression ones. Examples such as these support the conclusion that employment of MR makes it possible to obtain images depicting a rough water and fat distribution in samples.

The physical and chemical changes in protein within the muscle tissue affect its interaction with water, which results

Fig. 11 MR images of fresh meat taken with the sequences. a Spin echo, b fat suppression spin echo and c water suppression spin echo

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in changes in texture. The deterioration in texture during storage is known to affect the functional, nutritional and sensorial quality [100]. Renou et al. [100] investigated the effects of freezing on meat with MRI. It was possible to differentiate the extracellular water, muscle tissue and fat with fat-suppressed spin echo sequences. Fresh and five distinct freeze-thawed samples kept at \(-20\)°C for 1–41 days were thawed at 4°C immediately before analysis. The radial diffusion coefficient and \(T_2\) values increased from 0.85 to 1.15 mm\(^2\)/s and 42 to 48 ms, respectively. The increase in \(T_2\) values was attributed to the redistribution of water within muscle due to the change in protein structure over storage. The results are supported with the accumulation of free water inside the extracellular space during rigor mortis onset, owing to the ability of free water to diffuse more freely and isotropically [100].

Koizumi et al. [57] studied the distribution of fat and muscle tissue in frozen meat and during thawing. Started with frozen meat initially, images were acquired every 5 min during thawing for 75 min. Two-dimensional gradient echo images of thawed meats, with echo time (TE) set to 7 ms and repetition time (TR) set to 1 s, distinctly portrayed water and fat. The signal from the fat tissue of pork meat sample was relatively weak at beginning of thawing, and the oil signal in the fat tissue started to intensify. During thawing, signal of water from the muscle tissue that was localized at the bottom of the test tube spread along the whole sample within 45 min. In the last stages of thawing, the signals from the fat tissue intensified again. The results were indicative of thawing in meats [57].

Being able to identify the distribution of water in skeletal tissues provides food scientists with a higher understanding of changes in meat quality. Other than the extrinsic parameters such as storage time/temperature and processing conditions, intrinsic parameters affecting meat quality, such as muscle type and developmental stage of the animal, have been investigated with the aid of NMR relaxation parameters. Bertram et al. [7] measured the relaxation times for four different types of muscle cut from animals with varying developmental stages. Researchers were able to identify three different water populations, with each of them corresponding to a distinct spin–spin \((T_2)\) relaxation time. The study revealed a dependence of \(T_2\) data on both developmental stage and muscle type. The changes in relaxation times with varying stages of growth were correlated with protein content, the resulting data thus pointing to the relation between muscle microstructure and NMR relaxation data [7]. It is possible to observe the effect of cooking on meat and demonstrate the changes with NMR relaxation data. The decrease in water content and changes in molecular interactions during cooking can be monitored as changes in \(T_2\) values [127]. Shaarani et al. [110] found three distinct water compartmental structures corresponding to three \(T_2\) values: a long \(T_2\) component associated with water between fiber bundles, the intermediate \(T_{22}\) was associated with myofibrillar protein densities and the short \(T_{23}\) that were claimed to be associated with other macromolecules. \(T_{21}\) obtained from the major constituent of muscle exhibited an increase owing to the changes caused by protein denaturation. The decrease in


\[ M_0, \text{ protein density, values were accepted as an indicator of moisture loss} \ [110]. \]

The ability to analyze diffusion coefficient with MRI makes it a powerful tool in studying mass transfer operations that take place during industrial processing of meat. Ruiz-Cabrera et al. [104] utilized MRI to monitor change in water distribution with time during drying of pork meat. The signal amplitude from images was converted into moisture content using \( T_2 \) values calibrated according to samples with known moistures. The diffusion coefficient data were acquired using the moisture content data with the utilization of Boltzmann transformation. The 1D mass transfer model was sufficiently accurate which accounts for MRI’s accuracy in determination of water content [104].

Both NMR relaxometry and MRI have also been used in characterization of poultry. In a study by Hall et al. [41], MRI's effectiveness as a means of authentication of fresh meat, poultry and fish has been evaluated. The prices of fresh carcass are susceptible to seasonal changes, and it is more profitable for retailers to buy carcass during a low-cost season and freeze-thaw it, later to sell for a higher price labeled profitable for retailers to buy carcass during a low-cost season. This was explained by the partial denaturation of some myofibrillar muscle proteins, followed by protein aggregation taking place during freeze thawing. Though MR images of two samples were hardly distinguishable, the drop in \( T_1 \) times were consistent in all types of meat which led the researcher to the conclusion that MRI was a promising method as a means of validation for fresh meat [41].

Yuan-Hui et al. [133] carried out a similar study where the effect of the freeze-thaw cycles on the physiochemical quality of chicken carcass was investigated using a low-field NMR instrument. In frozen-thawed samples, with increasing freeze-thaw cycle and thawing length, the researchers have observed an increase in purge loss. The increase in purge loss was negatively correlated with the \( T_{22} \) relaxation times, which was associated to loosely bound water. \( T_{22} \) also gave a significant correlation with sensory characteristics, thawing time and freeze-thaw cycle with the correlation coefficients being 0.731, 0.722 and -0.731, respectively. Additionally, MR images of fresh and frozen-thawed samples were significantly different. Freeze-thaw cycles negatively affected water-holding property of the meat triggering drip loss. It was possible to quantify drip loss as it was accompanied by a darker MR image (a decrease in signal intensity). MR was also successful in displaying localized areas of water loss. Frozen-thawed chicken images displayed higher signal intensities (lighter pixels) close to the surface of the meat and lower signal intensities (darker) on the inside. This was related with the movement of water from inside to the outside [133].

In another study by Li et al. [62], MRI was used to investigate the state and distribution of water in frozen chicken breasts thawed with high pressure. For this purpose, \( T_2 \) relaxation time data for conventional water bath and pressure-induced thawing (with three different pressures; 100, 150 and 200 MPa) were compared. Relaxation of transverse magnetization fit to a biexponential curve, thus giving two distinct relaxation times, one owing to the loosely bound water (\( T_{21} \)) and the other to more tightly bound water (\( T_{22} \)). Thawing loss was significantly reduced with high-pressure thawing compared to the conventional method, and with higher pressures, thawing loss was further prevented. MR results suggested an increase in \( T_{21} \) time with a simultaneous decrease in \( T_{22} \) with increasing pressure. This finding, together with the decrease in thawing loss, was interpreted as the influence of increasing pressure on transforming the water from a loosely bound water fraction (\( T_{22} \)) to a more tightly bound one (\( T_{21} \)) [62].

Freezing storage is one of the most common methods of preservation for fish. Actually, if the fishery product will not be consumed raw, it is an obligation in the EU to either treat light preservation methods such as salting, drying, smoking and marinating, or freeze it at a core temperature of \(-20 \text{ °C}\) or lower for at least 24 h (CD 91/493/EU of 22 July 1991). Out of these, frozen storage is the most efficient and popular way of hindering microbial spoilage in fish [107]. NMR/MRI has proven useful in characterizing freezing induced quality deteriorations, since most of these changes are accompanied by changes in mobilization, state and compartmentalization of water. Sánchez-Alonso et al. [107] investigated the potential of low-field NMR in evaluating the quality changes in hake during a frozen storage at \(-10 \text{ °C}\) for 6 months. Out of the three water populations—strongly bound water (\( T_{2b} \)), water immobilized inside compartments (\( T_{21} \)) and free water (\( T_{22} \))—with increasing storage time, \( T_{22} \) displayed an increase that is accompanied by a similar decrease in \( T_{21} \). This hints at an increase in free water in the fish due to release of water out of cellular compartments. The decrease in water-holding capacity, apparent viscosity along with a loss of juiciness supported this conclusion. A linear regression-based mathematical model relating the two relaxation times, \( T_{21} \) and \( T_{22} \), to storage time was highly indicative of the experimental results (\( R^2 = 0.98 \)) [107]. Another study by the same researchers (2014) demonstrated the potential of NMR in differentiating the influence of different freezing methods (liquid nitrogen flushing, air blast freezer or walk-in freezer) and temperatures (\(-10\) and \(-20 \text{ °C}\)) on quality attributes. In terms of NMR relaxation times, there were no changes between samples frozen at \(-20 \text{ °C}\) and unfrozen samples.
At $-10$ °C, the $T_{21}$ (associated with free water) increased, and the formation of a new peak was observed. The absence of this peak at $-20$ °C freezing was explained with morphological alterations and protein denaturation, which were favored by a slower freezing procedure. Different freezing procedures did not display any significant changes in relaxation times as well as quality of the fish. However, the formation of a new water population could be used to estimate the quality-deteriorating effect of frozen storage on fish [108]. With postmortem changes in fish, NMR/MRI also could prove useful in studying the effect of antemortem handling stress on quality. Aursand et al. [4] examined the potential of low-field $^1$H NMR and $^{23}$Na/$^1$H MRI in estimating the effect of antemortem handling, fillet location and brine salting. It was seen that rested fish with respect to exhausted fish seemed to exhibit higher reduction in $T_2$ with brine salting. This was to be expected as salt penetration rate, and final salt concentration was found to be higher in exhausted fish. This was explained to be caused by the change in muscle microstructure (accompanied by a lower pH and higher water content compared to rested fish) due to the effect of stronger rigor contractions during exhaustion [4]. Another study by Collewe et al. [22] featured the utilization of MRI as a fast and easy method to quantify the amount of fat in fish flesh. To maximize the feasibility of the process for industry, the potential of a fast sequence (short sequence length) is studied. The experiment length varied between 55 s to 2 min for each fish cutlet. A correlation of 0.77 and 0.87 between fat content and signal intensities of $T_1$-weighted images of ventral and dorsal part of the fish, respectively, was found. The findings were promising considering the applicability of the procedure for the industry as an on-line analysis method [22].

Dairy Applications

In characterization of milk, cheese and ice cream, NMR/MRI has been performed in a number of studies. $^1$H NMR’s ability to differentiate signals coming from different fat populations, makes it ideal for characterization of high-fat foods such as milk cream. In a study by Bertram et al. [8], low-field $^1$H NMR’s sensitivity to fat content was utilized to estimate the liquid fat population in milk. A milk cream consisting of short-chain fatty acids and another with long-chain fatty acids only were separately cooled (from 31 to 4 °C), and the change in $T_2$ relaxation data was monitored. Both creams showed $T_2$’s coming from a number of fat populations (varying between 10 and 100 ms). This $T_2$ distribution was attributed to size differences between fat globules. Additionally, during cooling, clear shifts were monitored in NMR relaxation behavior at 17 and 22 °C for creams containing short- and long-chain fatty acids, respectively. This shift was associated with a phase change and was confirmed with DSC results [8].

Ice cream with its high fat content is also ideal for NMR analysis. One such study covered the use of NMR in characterization of various ice cream formulations containing different types of fat, proteins and emulsifiers. NMR relaxation times were found to be sensitive to formulation and differences in stages of manufacturing; most importantly, NMR could be used to acquire a good estimation of solid fat ratio. The sensitivity of NMR on crystallization behavior of ice cream was stated to be an ideal way of monitoring post production changes in ice cream crystal structure and maximizing product quality [69]. A few studies featured the utilization of $^1$H NMR relaxation to monitor the changes during acidification of milk [42, 106]. In the study by Harbourne et al. [42], $T_2$ times were used as a measure of water ability, thus were regarded as an indicator for the degree of gelation. A lower $T_2$ was accompanied by a higher storage modulus ($G'$) and a thicker gel [42]. Similarly in another study by Salomonsen et al. [106], the stability and texture of pectin-added acidified milk drinks were monitored with the help of a low-field $^1$H NMR. The number of different water populations and the changes in $T_2$ times were found to be associated with water mobility, water-holding capacity, and emulsion stability and pectin concentration. The method was recommended as an industry friendly, low-cost and easy method to identify the textural and stability problems in acidified milk drinks [106].

There are a number of studies using NMR/MRI to examine changes in milk during cheese production, brining or ripening of cheese [2, 13, 27, 28]. Using a low-field NMR instrument, El-Bakry et al. studied changes induced by changing process length, salt type and concentration, addition of emulsifying salts in a model (imitation) cheese both during production and at the final product [27–29]. The imitation cheese was manufactured in a farinograph. At varying stages of cheese manufacture, samples were taken and analyzed. NMR relaxometry was used to predict the amount, state and mobility of fat and water. The three components with distinct $T_2$ relaxation times, $T_{21}$, $T_{22}$ and $T_{23}$, were associated with bound water, fat and free water, respectively. The changing water and fat content with varying processing times were highly correlated ($R^2 = 0.95$) with the area of the peaks (area of $T_{21}$ + $T_{23}$ correlated with water, area of $T_{22}$ correlated with fat content). The relative changes in peak area of NMR relaxation spectra as well as $T_2$ relaxation times were explained with
the changes in water and fat mobility during rennet-induced casein coagulation and the resulting phase separation [28]. In another study by the same researchers, NMR relaxometry measurements were carried out to measure the effect that replacement of NaCl with KCl would have on water and fat mobility in imitation cheese. Results indicated that salt substitution did not cause a significant change in $T_2$ times, which was interpreted as the absence of an observable effect on molecular mobility in the state of water or fat [29]. The ability of ions to decrease NMR relaxation times along with the increase in signal intensities with water content could be exploited to quantify the water and salt uptake during brining. Altan et al. [2] studied the changes in $T_1$, $T_2$ relaxation times and signal intensities with respect to time in a brining procedure of 169 h, using both MR images and NMR relaxometry data. The amount of water penetrated into the cheese was strongly correlated with mean signal intensities ($R^2 = 0.984$). Two distinct components were obtained by analysis of $T_2$ relaxation spectrum. The component having a short $T_2$ was highly correlated with salt content at that particular time [2]. Such studies demonstrate the potential of NMR for time-dependent mass transfer studies, where it is crucial to have a fast and accurate method for quantification of the diffusate. Castell-Palou et al. used a time-domain NMR method to acquire moisture profiles of cheese during drying. Employing a mass transfer model based on Fick’s first and second law, it was possible to estimate the external mass transfer coefficient and effective moisture diffusivity. The proposed model was validated with NMR moisture profiles and mean moisture content, and was found to be closely representative of the real system (with a mean relative error of 4.4 %) [13].

Analysis of Cereals, Dough and Baking Processes

NMR/MRI has found application for a variety of analysis purposes in cereal and baking research. MRI’s capability to closely estimate moisture distribution was utilized to monitor moisture migration into cereals [30, 48, 70, 81, 128], transfer of water during boiling of pasta [33, 60, 109] and moisture loss accompanied by crust formation during baking [44, 65, 124, 125]. $T_1$ and $T_2$ relaxation times and ability to distinguish water populations in samples were employed to explain changes in water–starch interactions and the state of water during gelatization [19, 31, 36, 85, 102, 113] as well as in quality assessment of cereals and baked products [14, 50, 72]. However, the most common application of MR imaging in this field owes to the non-invasive imaging potential of the method. High-field MR scanners can accurately picture the interior of dough and baking products, with a well enough resolution that allows assessment of porosity and monitoring the expansion of dough during baking. As such, quite a number of studies have used MRI as a non-destructive imaging tool [10, 37, 67, 68, 99, 120, 123, 129, 135].

Extruded cereals are widely preferred by consumers from all around the world as a quick substitute for a palatable and highly nutritional breakfast [81]. However, the palatability is shaped by the rehydration and water/fat diffusion processes taking place when these foods are soaked into milk. So, investigation of the rehydration process is of utmost importance in order to control the loss of crispness and optimize the processing conditions to yield the more preferable results. To evaluate the effect of different kinds of milk (with varying fat content) on moisture penetration, Melado et al. [81] used three different commercial cereals, each composed of varying concentrations of whole-wheat flour, oat bran, wheat bran, wheat flour and corn. Additionally, some of the samples were coated with syrup. Depending on the sample, MR measurements were carried out either each 30 s for 60 min or each 60 s for 120 min with a 2D proton density-weighted, Rapid Acquisition with Relaxation Enhancement (RARE) sequence using a high-field MR instrument operating at 200 MHz. The penetration of milk resulted in an increasing "gray level" in the images with increasing time. Penetration was significantly slower for coated samples. Additionally, low-fat milk displayed higher penetration rates [81]. Using a similar high-field MR instrument, Horigane et al. [48] studied water penetration into rice grains. 3D gradient echo images made it possible to differentiate how water distributed inside the milled and brown rice grains of two japonica cultivars during water soaking. In Koshikari variety milled grains, water first penetrated onto the ventral side surface later to follow a route through cracks and finally diffused to the whole endosperm. In Yamadanishiki varieties, water directly filled the cracks and diffused into the endosperm from the inside. The route of water penetration is a valuable information in deciding the appropriate cultivar for a specific purpose or selecting the most suitable processing conditions for a grain [48]. Besides direct soaking into water, high-field MR imaging renders it possible to observe water transfer between two components with highly contrasting water activities such as apple filling inside low-water-activity biscuits. Weglarz et al. [128] investigated water transfer from apple fillings to biscuits by a combination of 3D MR images and high-resolution X-ray images. Water penetration was found to be positively correlated with signal intensity. Referring to the MR images, capillary action was suggested as the dominant mechanism of mass transfer early on which was later further accelerated by formation of additional swelling-induced pathways [128].

Low-field NMR instruments, while not capable of providing images, still prove useful in quantification of overall water absorption and estimating its distribution. During
water uptake into rice crispies, mean $T_2$ relaxation times increased with increasing moisture absorption. A multi-exponential relaxation model yielded three different $T_2$ times, one of which ($T_{23}$) was attributed to water trapped inside small pores, which is in strong interaction with surrounding macromolecules. $T_{23}$, unlike the other two components, displayed a decrease with increasing time. This was explained with the higher diffusion rates between water trapped in pores and the solid matrix which induces increased concentrations of the leaching solutes inside the smaller pores. Hence, with $^1$H NMR relaxometry, along with water, solute exchange could be monitored as well [70].

Boiling, which is the most common method of cooking dry pasta products, is another treatment where moisture penetration is prominent. To observe the change of moisture distribution inside dry spaghetti during boiling, Sekiyama et al. [109] gathered MR $T_2$ maps for different holding times (varying between 10 and 120 min) with the aid of a multi-slice multi-echo (MSME) sequence. At earlier stages of boiling, the $T_2$ times gradually decreased from the surface to the center of the spaghetti. After 120 min holding time, this trend in $T_2$ distribution with position was replaced by a more uniform distribution. The final $T_2$ maps displayed 4 distinct regions, which was explained by the varying degrees of gelatinization of each region [109]. In another study by Lai and Hwang [60], white salted noodles boiled for 5–25 min, similarly exhibited a gradually decreasing $T_2$ distribution, moving from the surface to the center of the spaghetti. After holding times (varying between 10 and 120 min) with the aid of a multi-slice multi-echo (MSME) sequence. At earlier stages of boiling, the $T_2$ times gradually decreased from the surface to the center of the spaghetti. After 120 min holding time, this trend in $T_2$ distribution with position was replaced by a more uniform distribution. The final $T_2$ maps displayed 4 distinct regions, which was explained by the varying degrees of gelatinization of each region [109].

For a similar purpose, Zhang et al. [135] designed a gas permeable lid to stop oven rise at different heights and analyzed local expansion with MRI. Spin echo images were taken every 30 s for 45 min of baking with a 0.2 T open MR instrument. Upon analysis of MR images, the researchers have come up to the conclusion that the earlier the dough meets the lid, the closer the densification is to the top surface of the bread. Additionally, with the development of a baking model, the occurrence of compression was related with the overall expansion and crust formation [135]. Similarly, Whitworth and Alava [130], coupled MRI with X-ray images to analyze dough expansion during baking and have suggested that rupture of the crust caused prolonged local expansion, which results in a higher heterogeneity in pore size and densification within the crumb [130]. A recent study, by Lucas et al. [65], complimented the studies of Wagner et al. [123] and Zhang et al. [135] by implementing numerical models and measurement of total CO$_2$ release as well as various macroscopic measurements such as total water loss, overall expansion with the aim of fully comprehending the mechanisms of expansion and compression in the dough. The mathematical models for local expansion for four different portions of bread (top surface, bottom surface, top middle, bottom middle regions) agreed well with the MRI data. Simulated profiles of gas fraction accompanied by the MR images gave a more detailed insight on the mechanism of heterogeneity in crumb structure [65]. Besides real-time baking analysis, there are a variety of studies employing the non-destructive imaging power of the method to
examine dough during other steps of processing or analyze the final baked products, some of them being: quantification of pore size distribution [99], assessment of local porosity during various dough treatments [37, 68], quantification of ice fraction in dough during freezing [67], use of magnetic resonance microscopy to monitor dough fermentation [5, 10], analysis of porous network in extruded cereals [117].

In baking besides volumetric changes, the loss and redistribution of water is another important incident affecting the quality of the final product. Amount and distribution of water directly influence textural properties such as softness of crumb and crispness of the crust, as well as shelf life. It is also a necessary component for some essential chemical changes that occur during baking (e.g., Maillard browning, starch gelatinization) [125]. Thus, knowing moisture distribution would help explain how parameters like temperature, and dough formulation alters final product quality. The ability of MRI to image the distribution of water in samples was previously mentioned a couple of times. However, in baking products, it is hard to relate signal intensities directly with moisture content since a change in temperature, presence of oil, the amount of porosity and densification of the dough greatly alter the signal intensities. Despite the challenges, there are a variety of studies in literature employing MR for this purpose. Bajd and Sersa [5] used MRI to measure the thickness of bread crust. The images were acquired in an oven placed into an MR imaging device, and measurements were taken each 7 min for the total baking time of 49 min. Owing to the low moisture content, the signal from crust was much smaller than the signal from crumb. The high contrast in the signal of the two components ensured eased distinction of the two phases. MR images made it possible to see the formation and thickening of crust, also compare crust thickness of breads from four different dough formulations [5]. In a similar manner, with the aid of MRI, Hong et al. [47] monitored the baking of a chocolate chip cookie to observe that the initially uniform moisture distribution was replaced by a moisture gradient from the surface to the center as the cookie was baked [47]. Heil et al. [44], on the other hand, in addition to visually analyzing baking-induced moisture gradient, also correlated overall MR signal intensities with overall moisture content. The correlation coefficient was found as $R^2 = 0.849$ [44]. The absence of an extra shimming procedure before each experiment and the non-uniform response of the receiver coil were suggested as the reasons for scattering in data. Pores appear as void dark spots in MR images, with no signal. When the whole cross section of sample was chosen for image analysis, the average signal intensity was greatly influenced by the changes in porosity. This could be another possible reason for the low correlation coefficient.

Apart from the physical phenomena, there are numerous chemical changes taking place during baking, out of which gelatinization constitutes a widely popular research area. Differential scanning calorimeter (DSC) has been frequently used in this regard. X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), optical microscopy, Fourier transform infrared spectroscopy (FT-IR) and rheology measurements are some of the other methods commonly employed in analysis of starch gelatinization [31]. Nevertheless, the aforementioned methods all give limited information on the dynamic state of water, and its interaction with the starch granules. $^1$H NMR is one of the most effective techniques in analysis of the state of water and the degree of diffusive and chemical exchange between water and surrounding macromolecules [46]. A variety of studies employed $^1$H NMR in investigation of starch gelatinization. Fan et al. [31] investigated the effect of microwave heating on starch gelatinization by comparing $^1$H NMR results of microwave-heated and conventionally heated starch suspensions. In all samples, $T_1$ times displayed two distinct peaks over the temperature range of 40–60 °C. The short $T_1$ was suggested to belong to water that is more rigidly bound to and restricted with starch granules, whereas the long $T_1$ belonged to a water fraction that was less restricted by starch. After 60 °C where granule swelling starts, the peaks started to merge and at around 80 °C no clear distinction could be seen, which was indicative of a completed starch dissolution and generation of a continuous gel network. Additionally, plotting the changes in $T_2$ times with respect to temperature made it possible to identify the glass transition temperatures ($T_{g}$) as the middle point of a major step change in $T_2$ values [31]. In another starch gelatinization study carried out by Tananuwong and Reid [113], the interactions between water and starch were investigated for varying water contents, maximum heating temperatures and starch types. All samples displayed two distinct water populations in $T_2$ relaxation spectra, attributed to extra and intra-granular water. During gelatinization, the mass transfer barriers between the two populations got weaker, which allowed rapid exchange between the two water compartments. This behavior was observed as a gradual merging of the two peaks above gelatinization temperature. A completed gelatinization was recognized by formation of a homogenous gel, which resulted in a single water fraction in $T_2$ relaxation spectra [113]. Gonera and Cornillon [36] investigated the changes in water mobility during gelatinization in the presence of sugar and various gums. The researchers observed two distinct water populations with respect to each relaxation time ($T_1$ and $T_2$). An NMR instrument with a temperature control unit was used to increase the temperature from 45 to 95 °C with 1 °C increments. When samples were at
around their respective gelatinization temperatures (identified by a modulated DSC-MDSC), they displayed a sharp step increase in short relaxation times accompanied by a step decrease in long relaxation components. NMR was shown to be almost as accurate as MDSC in determination of gelatinization temperature. Besides gelatinization, addition of sugar and gums also seemed to restrict the extent of gelatinization temperature. Besides gelatinization, another method could be arranged as T2a, T2b, T2c and T2d in descending order. T2a was assigned to bulk water that remained external to starch granules. T2b and T2c were assigned to parts of bulk water that was in diffusive exchange with amylase and amyllopectin of starch. The fastest relaxing component, T2d, was assigned to water trapped within the crystalline layers of starch composed of closely packed amylase and amyllopectin helices. The samples were then heated from 20 up to 77 °C. At 54 °C, T2a, peak area, that was the percentage of extra granular water, started to decrease up until it completely disappeared at 58 °C. This decrease was accompanied by an increase in T2b and T2c peak areas, referring to an increase in diffusion between water and starch molecules. Meanwhile, T2d exhibited a large decrease in relative percentage (from 15 to 3 %). During gelatinization, granules swell until they absorb most of the external water. The swelling destabilizes the crystalline regions, and crystal structure progressively diminished finally to be completely disrupted. All of which was in agreement with the relaxation time findings [102].

Mathematical Modeling of Heat and Mass Transfer

In mathematical modeling of food engineering processes involving heat and mass transfer, fundamentals of transport phenomena constitute the basis of the theoretical models that provide an estimation of the temperature or concentration changes within the system. To validate the accuracy of the suggested model, experimental procedures are necessary. Macroscopic measurements (e.g., moisture content) are widely used for the purpose. However, positional measurements that involve the use of probes pose a variety of challenges as they might interfere with the natural transport mechanisms, and introduce a bias in measurements. The number of non-invasive techniques to visualize and quantify temperature or concentration gradients is limited. Temperature and oil and water contents are some of the key parameters affecting MRI signal. Hence, by the correct choice of sequence and acquisition parameters, it is possible to gather signal gradients highly correlated with temperature, moisture or oil distributions. This feature of MRI has been employed in determination of heat and mass transfer coefficients [49] as well as for evaluation of the heat and mass transfer models describing various unit operations (i.e., drying) or changes in foods during storage as a tool for temperature mapping [49, 56, 71, 88, 89, 98, 132] and quantification of oil/moisture distribution [26, 32, 51, 61, 73, 84, 105, 112] (Ref: Unit operations).

Apparent diffusion coefficient, T1 relaxation time and proton chemical shift (PCS) (a.k.a. phase mapping) are the most sensitive MR parameters [101]. Thus, for temperature mapping, the sequence should measure one of these parameters. Nevertheless, PCS is seen as the method of choice for temperature mapping of water-based systems with MR, since it yields promising results even at low magnetic field strengths and it is not influenced by physical and chemical changes in structure [9, 38]. Nott et al. [89] assessed the accuracy of the four MR-sensitive parameters for temperature mapping for microwave heating of both model and real food systems. Chemical shift imaging rendered the most accurate temperature estimations, followed closely by T1-weighted gradient echo (GE) MR images. However, for porous media, air inside the samples could generate local susceptibility artifacts, which could induce phase variations and limit the use of PCS-based methods for porous samples [71]. Hence, T1-weighted MR sequences are more suitable for temperature mapping of porous media. Lucas et al. [71] compared the accuracy of temperature mapping by three different T1-weighted sequences: Two-dimensional (2D) spin echo (SE), 2D gradient echo (GE) and tri-dimensional (3D) gradient echo (GE) sequences. The acquisition times ranged between 1.5 and 5 min. Comparison of temperature measurements by optical fibers (measured 2 cm from surface) revealed that all three sequences gave comparably close estimations of temperature. Yet due to its lower sensitivity to susceptibility differences in porous systems, T1-weighted 2D SE sequence was suggested [71]. However, the long acquisition times make this type of MR protocols infeasible as an online temperature-monitoring method. Another study aiming to validate MR temperature mapping against fiber optic thermometry featured temperature measurement of a 5 % starch gel using a T1-weighted GE sequence that yielded faster measurements by setting low TE and TR times (50 ms TR, 10 ms TE, 30° flip angle). The fast scan times (ranging between 1.6 and 51 s) allowed real-time measurement of the sample. Results were in good agreement with fiber optic measurements [88].

The accurate and non-invasive temperature prediction led researchers to employ MRI as the sole method of real-time temperature measurement in evaluation of simulated heat transfer models of cooking in food systems.
et al. [98] carried out a comprehensive study on mathematical modeling of microwave, radiation and convection combination heating. Comparing with real-time MR temperature maps of a model food system acquired with a GE fast low angle shot (FLASH) sequence, they have assessed the prediction accuracy of four different simulation models for the four combination heating modes (varying in heating mechanisms and convection temperature). The 3D MR temperature profiles were in agreement with the simulated results. Additionally by changing the model parameters, the researchers could investigate the effect of different factors that shape the heating patterns such as heating modes, placement of the sample inside the oven and microwave cycling. The model was optimized in comparison with MR temperature maps [98]. For the similar purpose of validating a heat transfer model, Knoerzer et al. [56] utilized a GE pulse sequence aimed at acquiring temperature maps with the changes in phase distributions (PCS method). Displaying a novel approach, the computer-simulated model employed two equation solvers in conjunction (one for electromagnetism and the other for thermal analysis). The models were tuned and optimized with regard to MR temperature maps, and the final simulated results were in good agreement with MR temperature profiles of the model food [56]. Ye et al. [132] monitored temperature changes during ohmic heating where temperature mapping was especially important. The temperature dependence of electrical conductivity caused heterogeneity in cooking rate that resulted in localized undercooked or overcooked spots. MR results confirmed this critical effect temperature had on heating rate. The simulated model predictions yielded good agreement with the MR temperature maps acquired with a FLASH sequence using a chemical shift imaging method [132]. In another study by Hulbert et al. [49], a finite element model was developed to define heat transfer inside a slice of carrot being heated with water at 80 °C flowing with approximately 4.4 cm/s. Assuming the model was adequate for the system, the researchers applied a trial and error approach to compute heat transfer coefficients that matched the temperature contours of the model with MR profiles. The reported heat transfer coefficients (117–389 Wm2 K) were in the range of literature results [49].

To track the changes in moisture profile during food processes like soaking, boiling and drying, MRI and NMR was used multiple times. Steglich et al. [112] related the moisture profile with signal intensity and $T_2$ maps and acquired 3D moisture maps of pasta during boiling. The images coupled with bright field and polarized light microscopy allowed not only to observe local water content, also made it possible to investigate the state of water and microstructure of samples [112]. Mikac et al. [82] used a macroscopic model to estimate the water uptake during boiling into beans. They used a $T_2$-weighted 3D RARE (rapid acquisition with relaxation enhancement) and a 3D SPI (single point imaging) sequence both to evaluate the prediction power of the model and to visualize changes in water profile and mobility inside beans [82]. Mohoric et al. [84] also used 3D RARE imaging sequence to examine the cooking of rice kernels with a relatively high spatial resolution. A number of trials were carried out to maximize resolution while keeping the scan time reasonably short to allow real-time monitoring. The resulting images yielded minimal differences when compared to gravimetric measurements and model estimates [84]. Maeda et al. [73] investigated the diffusion of water into buckwheat and wheat noodles during cooking and compared the results with simulated data of Fick’s second law. Contour plots of moisture content gathered from MR data and 1D signal intensity profiles fitted well with the model results [73].

Internal water migration is the rate-defining mechanism in drying of foodstuff. Thus, a correct estimation of water diffusivity ($D$) is the key to an accurate model. Experimental determination of $D$, however, is quite challenging, as it is a function of water and temperature. This causes $D$ to vary with time and position during drying. Frı´as et al. [32] used MR to develop a model for $D$ (of paddy rice kernels) from the fitting of the moisture profiles. The proposed model was capable of accurately simulating the moisture transport during drying of paddy rice [32]. Ishida et al. [51] by monitoring the drying of rice seeds, observed the water transfer pathways. The generation of cracks owing to a high drying rate was clearly observed. The declining signal intensity curves with time correlated well with the overall moisture content [51]. Likewise, Jin et al. [53] employed MR imaging to validate the simulated results of a proposed drying model for air-dried broccoli florets [53], and Castell-Palou et al. [13] utilized a TD-NMR device to quickly measure overall moisture content of cheese samples (after calibrating signal intensities with respect to samples with known moisture contents), later to compare it to the simulated model [13].

Being able to see spatial water distribution could also shed light to the multiple underlying mechanisms of moisture transport during drying. The effectiveness of the Fickian diffusion model by Derossi et al. [26], in defining the osmotic dehydration kinetics of apples inside a sucrose solution, was validated by moisture content measurements and MR images. The images displayed the presence of a dehydration front that was displaced during drying from the edges to the core of the apples. An analysis of different slices of apple cylinders led the researchers to the conclusion that all layers of apple tissue were responsible for the drying process. An analysis of the MR images revealed that the drying mechanism could
be identified with some of the previously proposed mechanisms such as capillarity, hydrodynamic mechanism (HDM) and Darcy flows [26].

The 3D imaging feature of MRI has also been utilized for modeling purposes in literature [34, 52]. To come up with 3D simultaneous heat and moisture transport model on a single wheat kernel, Ghosh et al. [35] extracted the 3D model of kernel from images acquired with a 3D multi-slice Hahn-spin echo sequence. After development of the theoretical model, the extracted geometry was imported into a commercial finite element software package (COMSOL Multiphysics™), and simulated results were compared with MR images of kernel dried under similar conditions to model parameters. Models were quite satisfactory in predicting the actual moisture transport, and MR observations revealed that germ that contained higher moisture than the endosperm released the moisture in a slower rate compared with the endosperm [34].

Along with water, oil is another material whose presence greatly influences MR signal intensity. This renders it possible to observe migration of oil using MRI. Oil migration is an important phenomenon that contributes to quality loss in confectionary products especially chocolates. During storage, migration of liquid oil and the subsequent deformation in crystal structure in chocolates could introduce an undesirable texture and a popular quality defect characterized by a gray coating on the surface of the product called fat bloom [17, 61]. The rate and extent of migration is dependent on storage conditions. This emphasizes the importance of mathematical modeling of migration kinetics [17]. The non-intrusive ability of MRI to visualize water and fat distribution of samples has been previously mentioned. The fact that these systems contain next to no water, ensures that the signal acquired is mostly coming from the fat. As such, there exists a variety of studies in literature that utilize MRI to monitor oil migration into chocolates from popular high-fat fillings (e.g., peanut better, hazelnut butter) [1, 17, 61, 79, 105].

Figure 13 shows results of an MR experiment investigating the migration of oil from peanut butter into chocolate. The peanut and chocolate is placed such that peanut was spread along to top surface of the chocolate and mass transfer took place only in one direction. The images were acquired with a 3T MR Scanner (Siemens, Germany) using a Spin Echo sequence; with TR = 1000 ms and TE = 13 ms. The samples were imaged everyday over the course of 7 days. Day 0 image (Fig. 13a) displayed a clear distinction between the signal coming from the peanut butter (top) and chocolate (bottom). As oil migrated from the peanut butter to the chocolate, signal of chocolate increased and the gap between the signals of the two components gradually diminished, finally (after day 5) reaching an equilibrium oil partition between the two phases (Fig. 13d, e).

Conclusion

The applications discussed above are some of the most widely used methods of utilizing magnetic resonance technology in food science. Apart from these, low-field NMR relaxometry and MRI have been used in the following:

- Analysis of water content, mobility and distribution [16, 92, 95] as well as measurement of fat content and solid fat ratio [86, 111, 121] and protein content [96].
- Analysis of structural changes in various foods and macromolecules [94, 126].
- Examination of physical, chemical and microbiological quality of foods [40, 41, 95, 97, 134].
- On-line monitoring and process control [15, 39, 54].
- Inspection of rheology in wheat doughs [64].
Low-field bench-top $^1$H NMR systems have proven useful and will most likely continue to find various applications in food science. Despite the high cost of equipment, MR imaging instruments have increasingly been popular in food-related applications and are particularly effective in imaging the internal structures of foods, especially when it is of utmost concern not to damage the sample (as in time-dependent studies). Nevertheless, NMR techniques are still applied purely in food science research and are yet to be popular in industrial processes as a standard procedure of quality control. Thus, more studies in this growing field are still necessary to prove the methods’ potential and make it more applicable to the industry as well as food engineering research.

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**References**


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