The life of cereal food begins when the grains are harvested in the field. At this point, the cereal grains need to be assessed for quality, especially in terms of composition, in order to determine whether they will contribute to the required food value of the final product and the required shelf life. After harvesting, cereal grains are transported to the production facilities for intermediate or final product manufacturing, where they go through several processing steps. Various unit operations are applied to the cereal grains in order to achieve final product characteristics. During these processing steps, changes occur in the cereal food materials at the molecular level, resulting in desirable, macroscopically observed physicochemical properties. Therefore, a rapid tool to quantitatively monitor the composition of cereal grains and products becomes very useful. A technique that could rapidly and noninvasively quantify the molecular level changes occurring to the cereal products during the processing steps could also become a powerful tool for process control and product development. Time-domain nuclear magnetic resonance (TD-NMR) is a technology that meets these requirements. TD-NMR can very rapidly (in most cases, in seconds) look at material properties at a molecular level. The measurement is noninvasive and does not need any solvent or other chemicals for sample preparation. Thus, this technology is being widely used for various process control, quality control, and R&D applications in many industries, including but not limited to food, pharmaceutical, petrochemical, polymer, biotechnology, and consumer goods (18, 19).

TD-NMR Technology: A Noninvasive Tool for High-Throughput QC and Rapid Cereal Product Improvement

Time-domain nuclear magnetic resonance (TD-NMR) is widely used for various process control, quality control, and R&D applications in many industries, including but not limited to food, pharmaceutical, petrochemical, polymer, biotechnology, and consumer goods.

Total oil, moisture, and protein content of bulk cereal grain samples can be measured very quickly using a TD-NMR benchtop instrument to assess the quality of the grains at the harvest point. The same technique can be used to implement rapid quality control of incoming cereal grains at the food processing plant.

TD-NMR technology can be a powerful tool for rapid analysis of physicochemical properties of cereal food materials and thus can contribute significantly toward their quality improvement.

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TD-NMR: How It Works

The Instrument

When we hear “NMR,” the picture that may come to mind is of a large, high-field, high-resolution NMR instrument that definitely needs NMR experts to conduct the experiments and interpret the data. Another instrument that may come to mind is the magnetic resonance imaging (MRI) scanner that can be seen at healthcare centers. However, TD-NMR technology can be implemented successfully without using large, complicated instruments (Fig. 1). The instruments used for these types of measurements are usually benchtop with a small footprint. The sample to be analyzed is placed inside the probe, as is, and the measurement happens with a push of a button on software run on a PC. The quantitative information about the physicochemical properties of the samples is printed on the software after only a few seconds of measurement. Some variations of this instrument also have a hand-held probe; the probe can be taken to a large sample for in situ measurements (4). A TD-NMR instrument is comprised of magnet poles, usually permanent magnet, radio frequency coils (the probe), and necessary electronics (i.e., transmitter, receiver, analog-to-digital converter, amplifier, microprocessor, etc.), and is controlled by a PC through a software graphical user interface (GUI) (Fig. 2). The magnetic field strengths that are most commonly used in TD-NMR instruments are very low, ranging from 0.047 to 1.4 tesla (2 to 60 MHz hydrogen frequency). TD-NMR instruments have also been developed to work at the Earth’s natural magnetic field, but the limitations in sensitivity make it impractical for rapid analysis. Since this NMR instrument does not use a super conducting magnet—unlike...
nuclear spin. Since these atomic nuclei have a charge (a positive charge because of their constituent protons), as well as spin, they have a magnetic moment, i.e., behave like tiny magnets. When a sample is outside of the NMR instrument, these magnetic moments point randomly in all possible directions and, therefore, the net magnetization—the ensemble average—of all of these spins remains at zero. As the sample is placed inside the NMR probe, these nuclei align themselves parallel to the direction of the magnetic field (created by the permanent magnet poles in the case of TD-NMR), along or against the field. The spins along the magnetic field direction are energetically favored. There are always more spins “along” the magnetic field than “against” it. This excess of spin provides the NMR signal (12) (Fig. 3). The ensemble average of these spins (net magnetization vector) precesses around the direction of the magnetic field. The spin frequency is characteristic to a specific nucleus (e.g., $^1$H) and directly proportional to the strength of the magnetic field (within the range of the magnetic field dealt with in TD-NMR instruments).

During an NMR measurement, one or more radio frequency pulses are sent to the sample matching or “in resonance” with the precession frequency of the spins and the nuclei in the entire sample, which have the matching frequency, get excited. As a result, the net magnetization vector is flipped by a specific angle. As this magnetization vector rotates inside the coil/probe, it induces voltage (cf. electric generators), which is the NMR signal. This analog signal is then amplified, digitized, and sent to the PC (Fig. 4). The software then does the necessary signal processing to provide the final quantification of material property. In the case of high-resolution NMR, this data is Fourier transformed to obtain the frequency domain spectra. In the case of MRI scanners, this data translates into spatial domain data or an image. But in low-field TD-NMR measurements, mathematical calculations are done on the time-domain data itself. Many powerful experiments can be done in time domain through intelligent design of pulse sequences and data processing techniques, e.g., free induction decay (FID), spin echo, transverse relaxation, longitudinal relaxation, self-diffusion, restricted diffusion, one-dimensional imaging, exchange and correlation spectroscopy, and combinations thereof (Fig. 5).

What Can TD-NMR Do?

TD-NMR technology can perform various quantitative analyses at different stages of cereal food production with the...
Biotechnology Toward Better Cereal Grains

Many research projects are ongoing in industry and academia to improve the quality of grains in terms of its constituents, e.g., oil or protein content. When a new strain with a higher yield is detected, the researchers would like to propagate that specific strain to improve the yield even more. If a chemical analysis is used to quantify the oil/protein content to detect which seeds were better, the seeds are already destroyed in the detection process. TD-NMR allows these researchers to non-invasively measure oil and protein content in single seeds in a few seconds (Fig. 6). Therefore, they are able to go through the selection process quickly and propagate those same seeds that are detected to be higher yielding strains.

Grain Analysis While on the Plant

In situ measurement of grains that are on live plants can be done using a hand-held, one-sided TD-NMR probe. Therefore, the oil content in the corn cob can be determined while it is on the plant in the field. This can help to determine harvesting time or estimate the oil yields.

Grain Quality Assessment

Total oil, moisture, and protein content of bulk cereal grain samples can be measured very quickly using a TD-NMR benchtop instrument to assess the quality of the grains at the harvest point (Fig. 7). The same technique can be used to implement rapid quality control of incoming cereal grains at the food processing plant. The TD-NMR technology, by virtue of not being an optical technique, is not affected by the color or texture of the grains and the NMR signal is obtained from the entire bulk of the sample, not just the surface or near-surface elements. This allows the user to avoid recalibration and issues related to sample heterogeneity. The calibration development is also very simple, involving only a small set of samples. The moisture content (1) value can also provide a quick quantitative estimation regarding the shelf life of the grains.

Process Control in Cereal Food Production

The interaction between water and large molecules, such as starches, plays a significant role in product characteristics as the cereal grains go through many unit operations during the manufacturing process (Fig. 8). Operational parameters influence how changes occur in cereal intermediate products and TD-NMR looks at this dynamic system at a molecular level through a fast measurement sequence. TD-NMR is a powerful way to look at molecular mobility (3). A few seconds of measurement, followed by automated data processing, can provide quantitative estimation of water-polymer interaction (6). This allows real-time process control based on fundamental quantitative measurement. Hence, it can be used as a decision-making tool, ensuring consistency in final product characteristics. The same
TD-NMR technology can be used to monitor extraction processes, e.g., the extraction of oil to make ingredients for low-calorie cereal-based food products (11). Many enrobing materials are used in cereal-based products, e.g., chocolate coating on cookies. In order to have consistent coating thickness within specifications and proper melting characteristics during end use, the formulations for these coating materials need to meet a certain melting profile. The quantitative quality control of these raw materials can very easily be done using TD-NMR (5) (Fig. 9). It can also provide information on the extent of crystallization in sugars (8) present in cereal products—the close monitoring of which can help achieve desired mouth-feel in complex food products.

**Product Stability and Shelf-Life Study**

Once the cereal food is manufactured to the desired characteristic specifications, the next challenge is to maintain the same physicochemical attributes during its distribution and storage. The degradation of cereal food products’ quality can, in most cases, be linked to molecular level phenomena, e.g., retrograding starches leading to the staling of bread, sogginess in crunchy baked products, etc. TD-NMR has been used to quantify these molecular-level transformations during long-term or accelerated shelf-life studies, providing a useful tool to model the kinetics of these processes, which in turn help design better cereal food products, packaging materials, and shipment or storage conditions.

**In-Package Analysis**

Cereal food products, even after packaging, can be noninvasively monitored for physical and chemical properties using a TD-NMR instrument with large-bore probes (Fig. 10). Since TD-NMR is a nonoptical technique, the opacity or color of the packaging material does not affect measurement results. The total mass, oil content, etc., has successfully been measured very rapidly in packaged cereal-based food products. The degradation or shelf-life monitoring of final products (as mentioned in the last paragraph) can also be done without opening the package.

**Cereal Food Product and Process R&D**

Rheological and sensory properties are one of the main attributes of a successful food product. The macroscopic properties (those we observe in the food products) originate from molecular-level interactions. A control over these interactions provides the key to successful product development. TD-NMR provides a rapid and easily executable technique to measure these processes (15). Many times, the starch molecules in cereal grains are partially hydrolyzed through thermal or chemical treatment(s) to achieve certain product characteristics (7). The extent of this hydrolysis process and how that affects the interaction with small molecules, such as water present in the food system, helps

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**Fig. 7.** Accuracy of bulk grain analysis by time-domain nuclear magnetic resonance (TD-NMR) (oil content).

**Fig. 8.** Starch-water interaction during cooking of rice studied by time-domain nuclear magnetic resonance (TD-NMR).

**Fig. 9.** Melting profile quantification using time-domain nuclear magnetic resonance (TD-NMR).
us to better understand the process and thus process optimizations or product formulations become faster and more economical. Most of these unit operations can be simulated inside the TD-NMR probe and the dynamics of the molecular interactions can be recorded in quantitative terms (17). Some designed cereal food products have a multilayered structure, e.g., a baked cereal product may have hydrogel at the center and a crunchy layer around it. It may be assumed that if these two components have the same percentage of moisture content then there will be no moisture migration from one layer to the other during storage; therefore, the gel will not become stiff and the outer layer will not become soggy. But this mass transfer is not solely dependent on the absolute water concentration gradient; rather, it is controlled by the differences in the mobility of the water in the two layers, i.e., how much water is available for diffusion. TD-NMR can quantify the distribution of water mobility in these systems and thus provide faster product development (Fig. 11). Another example can be the interaction of products, such as corn flakes and milk. The porous microstructure developed in this type of product can be controlled by the proper choice of ingredients and process parameters. The porous microstructure, in turn, dictates how the milk will penetrate the flakes and what kind of sensory properties will result. Again, this sensory property will originate from the interaction of milk with the polymer molecules present in the cereal flakes. TD-NMR has been used in R&D to monitor this milk-cereal flake interaction, leading to process optimization for improved microstructure (13). The mouth-feel of some processed cereal foods can be due to the dissolution of their carbohydrates as we chew them. Research has also measured the kinetics of this dissolution process, leading to better product formulation. Often, the flavor dispersion in cereal-based food products is done in the form of encapsulates or emulsions. The flavor release significantly depends on the surface area around these droplets or encapsulates. Hence, the size distribution information on these droplets or encapsulates will provide a predictive tool for the control of the flavor release process. TD-NMR can directly look at the restricted diffusion of the molecules inside these droplets or encapsulates and compute the size distribution (22). By virtue of the noninvasiveness of the technique, the effect of temperature, or any other condition, on the change in size distribution can also be monitored. Another challenge in cereal-based food products is to understand how the thermal history of the dough affects the quality of the baked end product. Frozen storage of the dough can often produce baked products with undesirable properties. TD-NMR can be used to look at the diffusion of water and ice crystal formation during frozen storage. In situ baking has also been done inside the NMR probe, providing detailed information on the interaction of water with macromolecules as baking progresses (10) (Fig. 12). This provides the tool to investigate the effect of the thermal history of the dough on baking and helps optimize the baking process parameters to achieve the attributes similar to products made out of fresh dough. The one-dimensional imaging capability of a benchtop TD-NMR instrument can also be utilized for cereal food research, e.g., drying kinetics, diffusion coefficient as a function of saturation, water or oil migration, etc. All of this quantitative information from fast TD-NMR imaging/profiling can serve as extremely useful input parameters for mathematical modeling or simulations of cereal food manufacturing processes. The information on the mobility of water, and the evolution thereof, during product storage through TD-NMR measurements, provide important information regarding degradation of large molecules, as well as the change in the amount of water available for microbial metabolism and growth. This has been shown to provide an estimate as to the extent of food spoilage (16).

Future Research Directions

One of the many efforts visible in academic, as well as industrial research, is connecting the microstructure of food materials with functional attributes in macroscopic scale. TD-NMR can prove to be a powerful tool in these investigations through relaxation and restricted diffusion measurements, because the molecular phenomena taking place in the microstructures will have a signature on the TD-NMR signal. The implementation of more complex pulse sequences for two-dimensional experiments (e.g., exchange or correlation spectroscopy) using low-field TD-NMR instruments (20) is also opening doors for the more sophisticated study of dynamic systems, e.g., the exchange of molecules between dispersed and continuous phases in emulsions. The use of the intelligent

**Fig. 10.** In-package product analysis.

**Fig. 11.** Mobility of water from time-domain nuclear magnetic resonance (TD-NMR) measurement.

**Fig. 12.** Water-macromolecule interaction during in situ nuclear magnetic resonance (NMR) baking.
combination of pulse sequences to produce data with more information content followed by chemometric operations allows TD-NMR measurements to simultaneously quantify multicomponents within the same sample (21).

Conclusion

TD-NMR is a technology that can be implemented using a benchtop or handheld instrument. The measurements do not need any sample preparation, other than placing the sample inside the probe. In the case of large samples or in situ measurement, a handheld probe can be used. TD-NMR is completely noninvasive—no physical or chemical changes occur to the sample during the data acquisition. Most of the measurements take only a few seconds. The product property information is obtained from the NMR-active atomic nuclei present in the entire sample; it is a true bulk measurement. The color or texture of the material does not affect the NMR measurement because it is not an optical technique (14). Unsupervised, automated measurement sequence can easily be implemented using this technology. The TD-NMR measurements are widely used for analysis inside the laboratory or at-line process monitoring. It is also being used for online process control for some applications. The development of a stable calibration for TD-NMR is a very simple and short procedure. TD-NMR technology can be a powerful tool for rapid analysis of physicochemical properties of cereal food materials and thus can contribute significantly toward their quality improvement.

References

15. Tombo, X., and Ghosh, S. Extrac-