Low field, time domain NMR in the agriculture and agrifood sectors: An overview of applications in plants, foods and biofuels

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Journal of Magnetic Resonance 323 (2021) 106899

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

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ARTICLE INFO

Article history:
Received 29 July 2020
Revised 19 December 2020
Accepted 20 December 2020

Keywords:
TD-NMR
Relaxation
Agriculture
Food
Biofuels
Vegetables
Fruits
Oil
Starch

ABSTRACT

In this contribution, a selective overview of low field, time-domain NMR (TD-NMR) applications in the agriculture and agrifood sectors is presented. The first applications of commercial TD-NMR instruments were in food and agriculture domains. Many of these earlier methods have now been recognized as standard methods by several international agencies. Since 2000, several new applications have been developed, using state of the art instruments, new pulse sequences and new signal processing methods. TD-NMR is expected, in the coming years, to become even more important in quality control of fresh food and agricultural products, as well as for a wide range of food-processed products. TD-NMR systems provide excellent means to collect data relevant for use in the agricultural environment and the bioenergy industry. Data and information collected by TD-NMR systems thus may support decision makers in business and public organizations.

1. Introduction

Agriculture has been one of the most important means by which mankind has maintained and improved the human existence on earth, providing food, fiber, fuels and by-products. In this perspective paper, we will present a selection of applications of low-field, time-domain NMR to study agriculture and agri-food products and processes. We limit our selective review to applications of NMR instruments with a magnetic strength (B_0) $\leq$ 2 T and a magnetic field homogeneity (ΔB_0) $\gg$ 10 ppm. This class of NMR instruments is known as low-field, low resolution or time-domain NMR. To avoid misunderstanding with other low field NMR applications such as the one used in middle resolution NMR [1], we will preferentially use the expression time-domain NMR (TD-NMR).

The first applications of commercial TD-NMR instruments were in food quality control and the determination of oil content in intact oilseeds [2]. Modern day applications of TD-NMR started around the year 2000 when versatile pulse programs and more user friendly computational interfaces were introduced [1]. These applications have been growing in popularity due to the development of cheaper, lighter and portable instruments, based on unilateral and Halbach magnets, miniaturized electronics and advanced signal processing procedures based on inverse Laplace transform, multivariate statistic and machine learning [1].

Most of the new TD-NMR applications are based on the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence that yields an exponential or multiexponential decay, governed by transverse relaxation times, T_2 [1,3]. The CPMG is the workhorse sequence of TD-NMR because it has minimal dependence on magnetic field inhomogeneity and pulse imperfections. Moreover, the full T_2 decay curve can be rapidly measured in single scan [1,3]. TD-NMR analyses of agri-food products have also been studied with

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https://doi.org/10.1016/j.jmr.2020.106899
1090-7807/

fast continuous wave free precession (CWFP) sequence that can be used to measure T_1 or both T_1 and T_2 in a single shot experiment [4–6].

An important advancement in TD-NMR, in the last decades, has taken place in the signal processing. The Levenberg-Marquardt algorithm remains the easiest way to fit NMR data. It combines two minimization methods: the gradient descent method and the Gauss-Newton method [7]. Laplace inversion is another approach, in which the NMR signal decay should be treated as an integral response of a continuous distribution function, rather than a limited number of discrete components [8]. However, the inverse Laplace transform is an ill-conditioned and ill-posed problem, making the number of solutions very sensitive to the signal to noise ratio. To remedy this problem various numerical improvements have been proposed. Lawson and Hanson developed an algorithm, called nonnegative least squares (NNLS) that greatly increased the stability of the solution by imposing positivity constraints on the solution amplitudes [9]. Later, a smoothing parameter called α regularizer was incorporated to further increase the stability of the solution and produce continuous distributions of relaxation times [10,11]. Until the recent decade, the most common numerical method implemented for dealing with this kind of ill-posed inverse Laplace transform problem was based on L2-norm regularization. Two main methods were used to handle this and other types of inversion, i.e., Tikhonov regularization [12] and Maximum Entropy Method [13,14].

The explicit regularization algorithms replace the original ill posed problem (least-squares fitting problem) by a neighboring well-posed one. A fitting residual term added by a penalty term is commonly used to form a well-posed problem. The penalty term can take on different forms. Song et al. [15] involved Frobenius norm of the spectrum as the penalty term, called L2 regularization. The L2 regularization gives preference to solutions with smaller norms and can be solved easily by Butler–Reeds–Dawson (BRD) algorithm [16]. Adoption of a more complex penalty term which operates the solution with a low-pass filter yielded the common constrained regularization (CONTIN) computer program [17]. However, unequal penalization is introduced by the low-pass filter; this algorithm tends to under-smooth strong peaks and over-smooth weak ones [18]. Unlike traditional algorithms implementing L2 regularization, recently the L1 penalty term has been involved to constrain the sparsity of resultant spectra, imposing two penalty terms simultaneously [18,19]. The problem was subsequently solved by a Primal Dual interior method for Convex Objectives (PDCO) solver.

An integrated approach, which includes validation of analyses by simulations, testing repeatability of experiments and validation of the model and its statistical assumptions, was found to provide better resolved and more accurate solutions when compared with those suggested by previous L2 based tools [18–20]. Multivariate statistic [21] and machine learning [22] have been also largely used in TD-NMR for pattern recognition, clustering, classification and quantification.

When 1D relaxometry analysis is used for complex mixtures, the peaks of different components are prone to overlap, resulting in the misinterpretation of the spectra. This is the major limitation of 1D relaxometry. It has been shown that 2D relaxometry experiments, T_1-T_2, T_2-T_2, D-T_2, D-T_1, can overcome these obstacles [3,15,20,23–28]. The most popular bi-dimensional (2D) experiment is T_1-T_2 correlation mapping, as has been applied to various food systems and biofuels [3,24,25,29–31]. Since then, several versions of these multidimensional experiments were proposed enabling then study of chemical exchanges and complex diffusion dynamics [3,25]. Illustrations of these recent innovations are presented below in a selection of applications in agri-food products, plant sciences and in the analysis of raw and processed food and biofuels.

2. Applications in the plant sciences

2.1. Classical TD-NMR approaches: homogeneous, unilateral, and mobile laboratories

Due to its ability to non-destructively access information relating to water status, water mobility and the associated structural changes at cell, tissue and whole plant levels, TD-NMR represents a valuable method to characterize living plants [32–48]. Indeed, from measurements of NMR relaxation times and diffusion coefficients, it is possible to evaluate water status and distribution at subcellular level, cell/vacuole dimensions and membrane permeabilities determining water transfers inside the cells and, at larger scales, water transport across several cell layers and flow in water transport tissues. Information about changes in the absolute and relative water and dry matter contents in tissues can be extracted from the NMR signal of liquid and solid proton fractions. These parameters, which generally are inaccessible by means of classical methods, are of great interest for plant physiologists. They make it possible to assess water and nutrient fluxes associated with adaptive responses, either through experimental approaches or potentially by using NMR data as input for mechanistic models at the organ or whole plant level.

In plant cells, water molecules in the various cell compartments and organelles experience particular physical and chemical environments and therefore exhibit distinct T_2 values. In fleshy fruits and tubers, long, intermediate and short T_2 components have been assigned to the vacuole, the cytoplasm and the cell wall and/or to extracellular water, respectively [32]. More recently, Musse et al. [34] demonstrated that in leaves, the transverse relaxation signal can be used to distinguish chloroplast water from the other water pools. In some cases, two-dimensional diffusion-relaxation measurements have been demonstrated effective to improve the accurate assignment of the signal components to water pools [49], as they are less impacted by the diffusional exchange between compartments that governs relaxation behavior.

Several studies have demonstrated TD-NMR methods to be an efficient tool to characterize the effects of the abiotic environment on organ development. Van As et al. [33] demonstrated variations between day and night in water flux and T_2 in plant stems. Transverse relaxation experiments have, in an original way, revealed differences in the hydraulic functions of spongy and palisade leaf tissues, associated with structural changes and with early events of leaf senescence [37]. It has also been shown that N depletion [36] and water deficit impact the water distribution in leaves, thus opening the possibility to consider NMR as a phenotyping tool, in laboratory or field conditions using a mobile NMR lab (Fig. 1- left) [38] or non-invasive portable unilateral NMR instruments [39]. Relaxation measurements have also been used to investigate cell expansion in fruit tissues [40]. The potential of TD-NMR to measure exchange of water at the cell scale as well as to probe the membrane permeabilities that regulate this transport have been demonstrated by Van Der Weerd et al. [41]. Combining NMR and microscopy, they measured changes in membrane permeability in response to osmotic stress in millet and maize plants. The membrane permeability over longer cell to cell distances, together with cell dimensions, can be accessed from restricted diffusion measurements, by varying the diffusion labeling time [35]. The impact of human activity on plant biodiversity is also a major issue about which NMR can provide valuable information. It may be used to study how ecological stressors (chemical, biological, and physical) affect different species and ecosystems. By sampling genotypes collected all over the word, gene banks are available for studies on the ecophysiological role of plant tissues and their adaptive trait as a function of environmental changes [42].

Fig. 1. Left -mobile TD-NMR lab with conventional spectrometer next to a field of oilseed rape. Adapted from Publication [38], Copyright (2017), with permission from Springer Nature; Right - small scale C-shaped magnet measuring water dynamics of growing bean pod in a greenhouse [53].

2.2. Sensor-like applications of TD-NMR to monitor living plants

While TD-NMR is extensively used to characterize harvested agricultural products, it is not yet routinely used to measure intact growing plants. Although in vivo applications have been demonstrated as early as 1994 [33], they remain challenging for two reasons. The first is that living plants tend to be highly heterogeneous on all levels of organization (organelles, cells and tissues). This gives rise to complex and poorly defined relaxation spectra [50]. As outlined before, it is possible to deal with this complexity, but it requires expert operators, careful experimental design, and samples with well-known properties. For examples of such applications, the reader is referred to the reviews by Van As (2007) [50] and Van As and van Duynhoven (2013) [51].

A second reason is hardware. To measure relevant processes in living plants, they need realistic environmental conditions. Most commercial systems, however, are neither mobile nor built to be run in dusty or moist environments or under variable climatic conditions. Changing temperatures are likely to upset the climatization of the sample, the magnet and the spectrometer, affecting the finely tuned experiment. Another hardware related problem is that the plant part of interest needs to fit inside the probe head. Most commercially available machines are built to accept test tubes, but not plants with long stems and pots. To address the problem of accessibility, the use of custom made magnets and probe heads has been explored. Examples are conventional or Halbach magnets with especially wide bores, open C-shaped magnets (Fig. 1 – right), or openable Halbachs [33,43–45]. Unilateral magnets have been used as well [39,52]. The problem of varying temperatures has been addressed by climatizing the magnet [46]. Such magnets may be paired with other custom built hardware, such as affordable, small scale spectrometers. Utilizing these it may be possible to construct mobile TD-NMR devices for plants that are mobile and affordable, as well as commercially viable.

A way to address the problem of complex relaxation spectra in plants may be to simplify the measurement and accept some loss of information contained in the NMR signal. One of the most straightforward parameters to measure, and the most interesting one for plant physiology, is water content (WC). Almost any (FID or CPMPG based) means to measure proton density can directly and quantitatively be correlated with it. Such approaches have been used to measure the diurnal dynamics of WC in trees and to characterize the expansion growth of fruit [46]. The fact that plant WC reflects water potential has been used to investigate how mangroves deal with changing salinity [47]. The TD-NMR methods used in these examples are basic as well as effective. They are robust against external influences and RF noise, require only the simplest of magnets and spectrometers, and lend themselves for automated, sensor like use. Hardware requirements for such applications are few, but it may be helpful if the NMR magnet is homogeneous. Given that condition, the entire sample can be excited and the sample volume can readily be estimated. The field strength, however, can be limited. In the examples above, field strengths between 0.25 to 0.5 T (10 and 20 MHz) were used, but the use of resistive magnets of very low field strength of 860 μT - 36.6 kHz has been demonstrated as well [48].

3. Food analysis and processing

The most frequent application of TD-NMR, in the last decades, has been the analysis of food products and processes [3,27,54–58]. As pointed out by Hills [3] most of these new applications are based on relaxation and diffusion measurements, which have provided an unique window to study food microstructure and the dynamics behavior of molecules in complex food matrix. He has shown the potential of TD-NMR in quality control in the food sector, using novel NMR devices for *ex situ* and online measurements, new ultrafast methods and the use of multidimensional relaxometry and diffusometry [3,54–57].

TD-NMR has been used as a rapid and non-invasive technology to assess the quality (food composition, adulterations) of intact and processed products, as well as the effect of processing (drying, cooking, freezing, curing, salting) and storage in food and ingredient quality [3,22,24,54–60]. Some of these experiments have been performed dynamically, i.e. the product is transformed while inside the spectrometer and acquisitions performed during the transformations [58,61].

In the last two decades TD-NMR relaxometry and diffusometry have been widely used to characterize fat content and water compartmentalization in animal tissues and food derived from pork, beef, eggs, broilers and aquatic food products [3,54,58,60]. It also has been widely used to study vegetables, grains and cereals [3,54,59].

Animal and plant products have also been studied using 2D experiments. Fig. 2 shows the T_1-T_2 maps of lean beef (A) [29] and intact banana (B) [59]. In this figure, there is a direct correlation between the T_2 and T_1 signals, which shows that the T_1 of the stronger peak in beef is much longer than T_2, while both relaxation times are similar in banana.

Coupled with chemometric methods, TD-NMR has been used to classify foodstuffs according to physical properties, chemical composition and adulteration [3,62]. Fig. 3 shows the soft independent modeling of class analogy (SIMCA) 3D class projection of CPMG (a) and CWFP (b) decays of 99 beef samples from steers (◆) and heifers (◇) from three races (Angus, Bonsmanra and Canchim) [62]. This figure shows that both signals can be used to classify beef samples from the three races, according to animal sex. However,

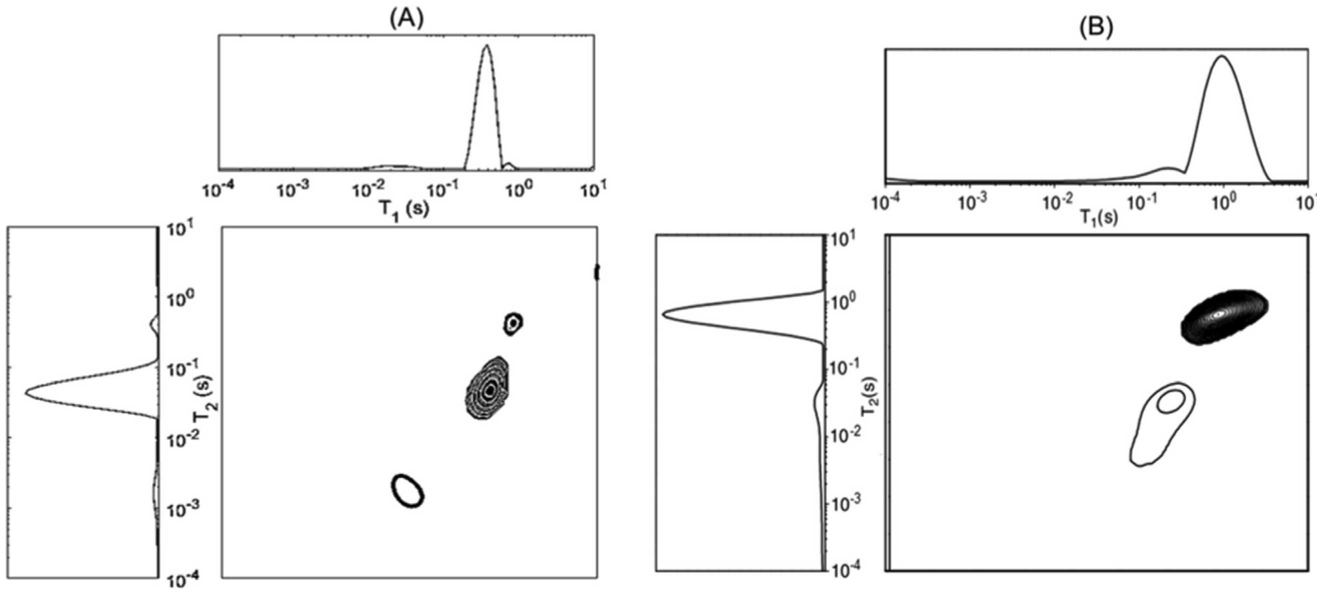

Fig. 2. A) T_1-T_2 map acquired by CWFP-T_1-CPMG method for a lean beef sample. Adapted from Publication [29], Copyright (2010), with permission from Elsevier; B) T_1-T_2 map acquired by IR-CPMG method for a banana sample. Adapted from Publication [59], Copyright (2010), with permission from John Wiley and Sons.

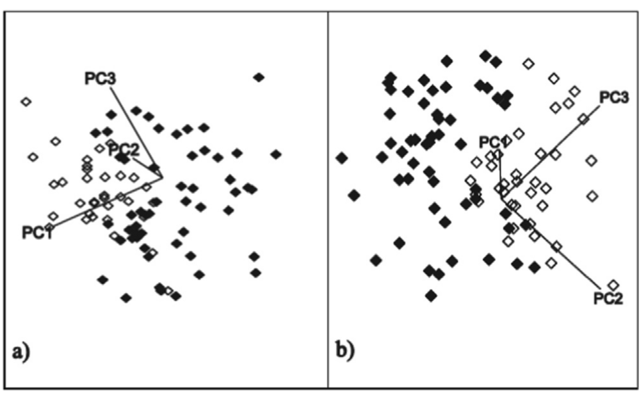

Fig. 3. SIMCA 3D class projections obtained with the CPMG (a) and CWFP (b) decays of 99 beef samples from three animal races (Angus Bonsmanra and Canchim) separated by the animal sex, steers (◆) and heifers (◇). Reprinted from Publication [62], Copyright (2014), with permission from Elsevier.

the CWFP signals show a better separation between the two classes than CPMG.

In addition to the capacity to quantify molecules, TD-NMR was shown to be most efficient for characterization of chemical and structural assembly of lipid (Fig. 4) [31,63]. Knowledge of the basic triacylglycerol molecular packing organization opened the way to follow after chemical and structural changes occur during the biochemical processes, such as triacylglycerol/oil oxidation in various vegetable oils and food products and to apply it to monitor PUFA-rich lipid oxidation (Fig. 5) [31,64].

Self-diffusion measurements by TD-NMR, using pulsed field gradient (PFG) sequences have also been used for quantitative, qualitative and structural studies of food products. PFG has been widely applied to access microstructural information of droplets in emulsions and porous matrices [66]. The water mobility in different protein and polysaccharide systems has been investigated with the aim of describing the structure of dairy [25] or starchy products [57]. Recently, the GAUSS-SR sequence was developed for measurements using unilateral NMR systems where diffusion phenomena strongly affect the acquired data. This sequence was shown of particular relevance for studying water in heated samples or for measuring restricted diffusion in porous media [67].

The solid-state components of food, characterized by very short relaxation times, have been studied using NMR probes with short dead-times. 1D and 2D TD-NMR relaxometry (T_1, T_2 and T_2*) has been used to study mobile molecules such as water and lipids, as well as the solid components (carbohydrates, proteins) in grains, flours and processed foodstuffs [57,58,68,69]. Depending on the transformation process and plant botanical origin, cross-relaxation phenomena due to magnetization transfers could be highlighted in 2D experiments (Fig. 6) [69].

4. Biofuels applications

The capacity of proton TD-NMR to monitor quality aspects of materials has also found application in the field of biofuels, in the following related sub fields:

4.1. Monitoring of biomass resources suitable for biofuel production

Quantitative and qualitative studies were reported for determination of fat content in wide range of oilseeds and various bio-waste characterized by high fat levels [70,71]. Furthermore, due to different chemical and physical morphologies, the utility of 2D T_1-T_2 to differentiate between different fatty acid profiles of different oilseeds was demonstrated [65]. Using multidimensional T_1-T_2 mapping, degradable cellulosic components from organic plant and animal waste materials could be estimated for later application in biofuel plants (Fig. 7) [31,71].

4.2. Monitoring of biofuel production processes

TD-NMR was shown to be suitable for monitoring transesterification reaction products, fatty acid methyl esters, used as biodiesel. It was demonstrated to be applicable for monitoring of free sugars release from degraded lignocellulose in the process of bioethanol production. Furthermore, TD-NMR was also shown to be efficient in monitoring organic waste degradation in anaerobic conditions used for production of biogas [31].

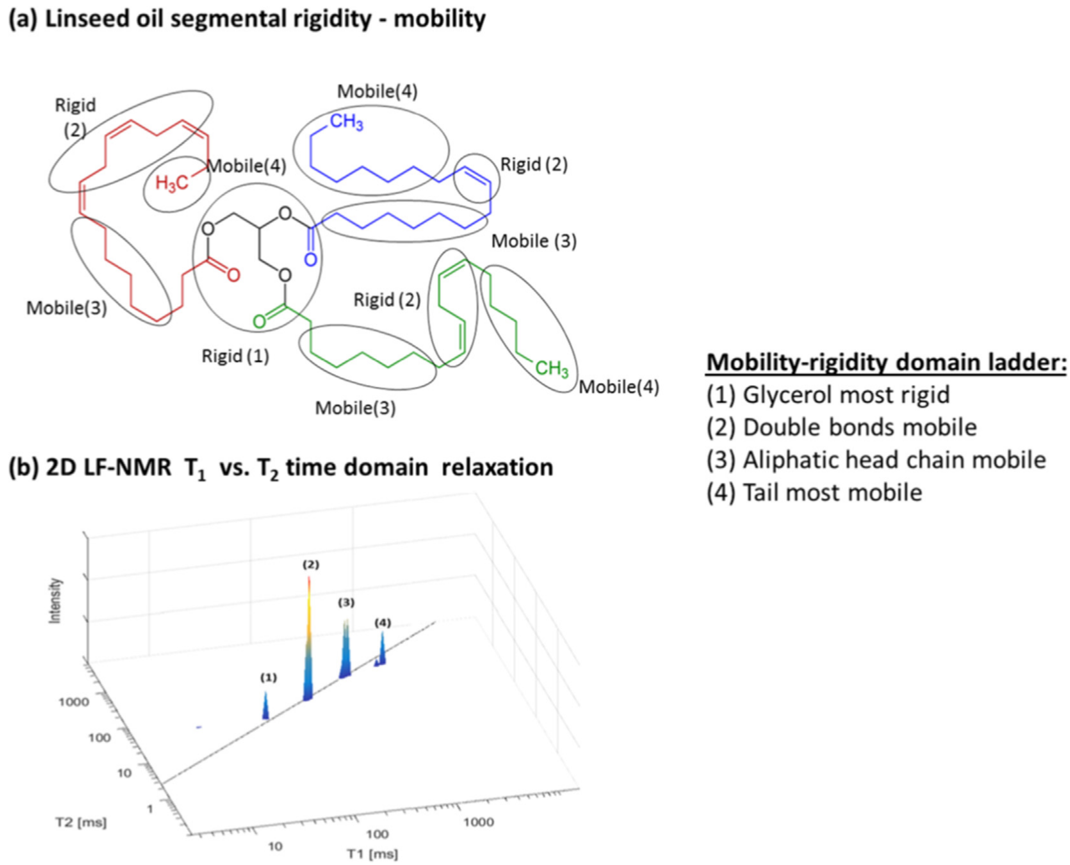

Fig. 4. Linseed oil morphological and chemical structure organization. (a) Linseed oil molecular structure and functional group segmental rigidity-mobility; (b) 2D T_1 vs. T_2 relaxation time map of linseed oil. Segmental ladder sequence of most rigid to most mobile: 1- glycerol; 2- double bonds; 3- aliphatic chain; 4- tail aliphatic chain. Adapted from publication [65], Copyright (2019), with permission from John Wiley and Sons.

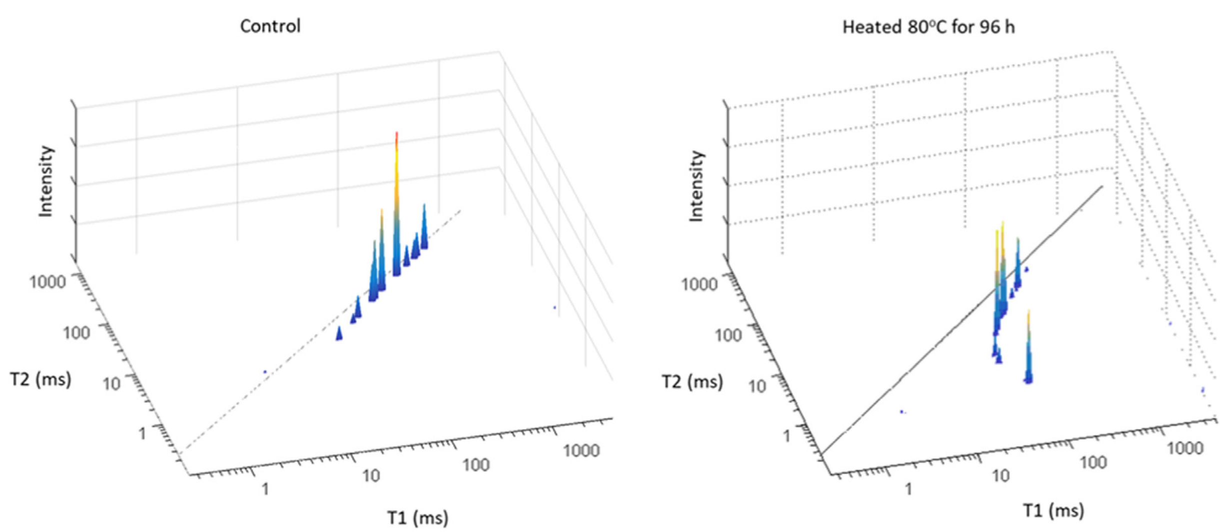

Fig. 5. ^{1}H TD-NMR 2D T_1-T_2 relaxation time of control fresh liquid PUFA-rich pomegranate seed oil spectrum (left) and thermal autoxidized viscous pomegranate seed oil (heated 80 °C for 96 h). Clear pattern of peaks shifts to lower T_2 values and bending effect is observed.

4.3. Monitoring of final biodiesel product quality

The oxidation stability of biodiesel composed of fatty acid esters derived from vegetable oils, is one of the major issues challenging its widespread use as an alternative fuel. The poor oxidative stability of biodiesel, compared to petrodiesel, is caused by its high content of unsaturated fatty acid methyl esters that negatively affects fuel properties such as storage lifetime. The relationship between new molecules formed by oxidation and their new solution morphologies is a complex subject that affects the physico-chemical properties of fuel. It is highly important to understand how the oxidized unsaturated fatty acid methyl esters and the non-oxidized components of the biodiesel interact and affect the final properties of multi component biodiesel mixtures. TD-NMR relaxometry was proven to be an advantageous tool to study autoxidation of biodiesel.

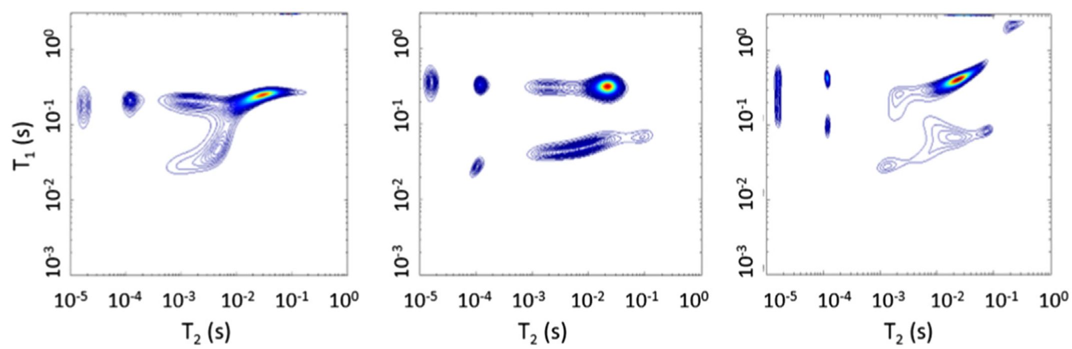

Fig. 6. T_1-T_2 correlation map acquired with IR-FID-CPMG sequence at 90 °C for starch–water mixtures: wheat (column 1), waxy corn (column 2) and potato (column 3). Different water pools are observed depending on the starch botanical origin. Adapted from Publication [69], Copyright (2020), with permission from Elsevier.

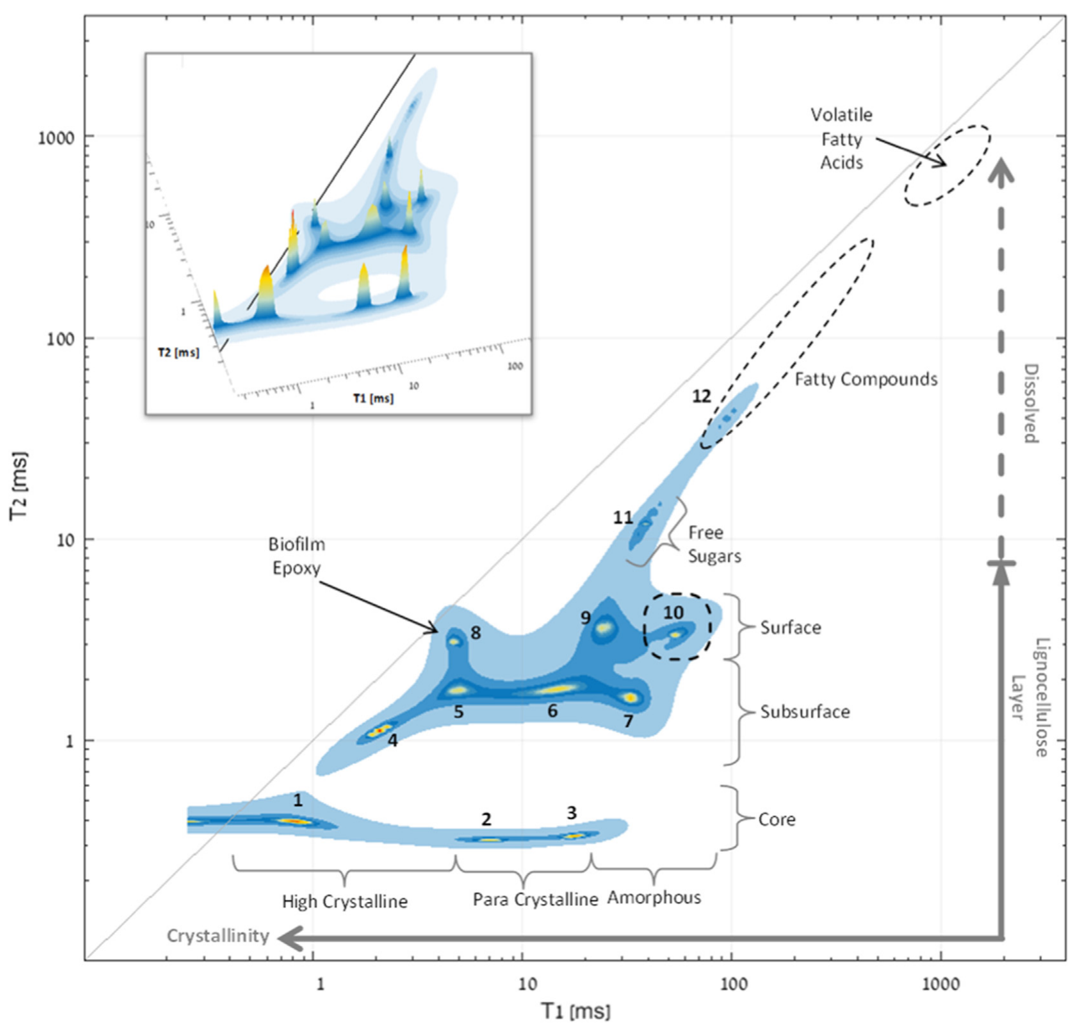

Fig. 7. – Morphological spectrum of T_1-T_2 relaxation times of cattle manure before anaerobic digestion (A). Two-dimensional map and 3D map are presented within. T_1 relaxation time indicates the crystallinity and T_2 indicates the layer of lignocellulose. Over all, there are 12 domains with different properties of porosity and crystallinity divided into three layers of lignocellulose and a diagonal of dissolved compounds. Peak 10 represent the most amorphous cellulosic population released from the other crystalline core lignocellulose fibers and easily degraded in the anaerobic process to produce biogas. Adapted with permission from [31]. Copyright (2018) American Chemical Society.

Fig. 8 demonstrates the interactive effect of new oxidative products and stable non-oxidized components upon each others molecular movement and morphology during the process of autoxidation of linseed biodiesel [63,70,71]. The results show that the oxidized products of fatty acid methyl esters have secondary interactions with biodiesel components, which were not oxidized but were mutually affected by each other. TD-NMR relaxometry was proven to be an advantageous tool to study this process of autoxidation. It is a direct, rapid, non-destructive method that can be used to study the underlying structural and compositional mechanisms, which contribute to changes in the fuels physico-chemical properties.

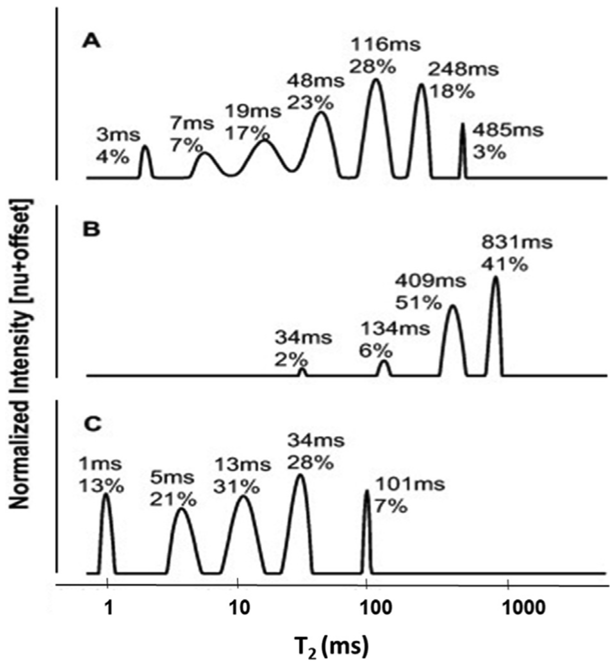

Fig. 8. Combined TD-NMR T_2 distributions of (A) linseed biodiesel at 96 h of heating (shown as reference), (B) supernatant, pure linseed biodiesel remaining fraction dissolved in heptane, and (C) polymerized viscous precipitation, oxidation end product fraction not dissolved in heptane. The relative contributions of each peak in relation to the other peaks and intrinsic T_2 values are shown on each plot. Adapted from Publication [70], Copyright (2016), with permission from Elsevier.

The characterization of changes in molecular interactions and their effect on biodiesel properties is one of the major contributions of TD-NMR relaxometry. Additionally, the possibility of TD-NMR to analyze heterogeneous and at times heterophasic, whole samples directly, significantly supports to the characterization of fuel's physico-chemical state.

5. Future of TD-NMR in agri-food products and processes

In the coming years, TD-NMR is expected to find even more applications in quality control of fresh and processed agricultural products. It may also be used more extensively for the collection of data relevant for environment and bioenergy industrial fields. To make this possible, several improvements may be implemented in order to open up TD-NMR to non-experts.

First, TD-NMR involves the analysis of multi-exponential decays, which often is a difficult task for non-experts. In this process, user-dependent hypotheses are at the basis of the analysis and processing of data (the choice of regularization type and initial relaxation values, for example). Implementing user-friendly algorithms with suggestions for initial guesses and more widespread training in the correct application of such algorithms would be real progress in this domain.

Second, efforts should focus on establishing a systematic relationship between NMR parameters and the physico-chemical characteristics of the sample before deploying the analytical procedure, i.e. to assign the number of water relaxation populations. This could be done at the initial project stage by using multi-dimensional NMR, quantifying other parameters, e.g. dry matter deposition, water content, cell identification (in the case of living tissues) or using chemometrics. Once this stage is performed by specialists, the application will become feasible even for non-experts, allowing it to be deployed at a larger scale.

Third, hardware development might be needed to extend the use of TD-NMR outside the lab, i.e. to enable applications in greenhouses, fields or factories. Two generic parallel approaches can be used. The first one would be to design relatively generic hardware, which could be used for several applications. The other would be to tailor hardware specifically to particular applications. Obviously, this would involve the magnet (e.g., C-shaped, Halbach or unilateral magnets) but also the RF and gradient coils. During the conception, the portability of such systems should be considered, as well as the magnetic-field dependence of permanent magnet with temperature.

Finally, developing 'push-button' applications could be key to achieve a truly widespread use of LF TD-NMR by non-expert users. Such applications must deal with both data acquisition and processing, to provide a fully automated pipeline. Data and information collected by TD-NMR systems may then become even more freely available to support decision makers in businesses and public organizations. These advances would also provide new opportunities for phenotyping of plant and animals of agronomic interest.

CRediT authorship contribution statement

Luiz Alberto Colnago: . **Zeev Wiesman:** Writing - review & editing. **Guilhem Pages:** Writing - review & editing. **Maja Musse:** Writing - review & editing. **Tatiana Monaretto:** Writing - review & editing. **Carel W. Windt:** Writing - review & editing. **Corinne Rondeau-Mouro:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This study was partially supported by FAPESP–Brazil, grants # 2019/13656-8 and 2020/07017-0, by the french ANR-program (grant number ANR-08-BLAN-0061) and by the Regional Council of Brittany (France). We are most grateful to the AgroScans core facility (PRISM, Rennes-Angers, France) for its technical support and to the Israeli Ministry of Science, Technology and Space.

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