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Fast Field Cycling ^{1}H-NMR relaxation properties during convective dehydration of mango fruits

Giuseppina Adiletta[a], Donatella Albanese[a,*], Marisa Di Matteo[a], Luciano Cinquanta[b], Onofrio Corona[b], Pellegrino Conte[b]

[a]Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II, 84084 Fisciano (SA), Italy.
[b]Department of Agricultural, Food and Forest Sciences, University of Palermo, Viale delle Scienze 4, 90128 Palermo, Italy
*dalbanese@unisa.it

The cultivation of mango fruits is increasing in the Mediterranean areas, including Italy, where a niche production has developed in the Tyrrhenian coast of Sicily. These fruits are rich in antioxidant substances, presenting a pleasant taste and aroma, fundamental qualities for the sensory acceptance of consumers. However, being climacteric fruits, mangoes are highly perishable, due to their rapid ripening after harvesting. As a result, large amounts of mangoes are lost annually in many areas of the world. In order to prevent this, the drying technique is widely used. It allows to lengthen the shelf-life of the fruits. In order to optimize this process, it is necessary to deepen the knowledge on the drying effects on the structure and mobility of the residual water in the fruit. The objective of this paper is to describe the effects of convective drying at different temperatures on the Fast Field Cycling Proton Nuclear Magnetic Resonance (FFC ^{1}H-NMR) relaxation properties, water activity and shrinkage in Keitt mango fruits.
The FFC ^{1}H-NMR relaxometry investigations on mango fruits revealed that the convective drying lead not only to a reduction in the overall water content within the mango tissues, but also to a progressive immobilization of the same water, depending on the temperature. From a qualitative and microbiological point of view, the results may indicate that the measure of more immobilised water in the dried fruits can be useful to predict their shelf-life.

1. Introduction

Mango fruits (*Mangifera indica* L.) have a high palatability, due to their sweetness and richness of taste, besides having a high nutritional value, which explain the great quantity of production (Farina et al., 2020). In terms of total fruit production on a global basis, mango is the second largest after banana (Ram et al., 2020), covering in the world an area of 5,588,716 ha with a world's production of 55.8 million tons (FAOSTAT, 2019). Asia accounts for approximately 77% of global mango production, the Americas and Africa account for approximately 13% and 9%, respectively. Mango has a long history of cultivation, which has recently expanded to countries in temperate zones with protected crops (Matheyambath et al., 2016). For the favourable climatic conditions of the areas of the Mediterranean basin, especially Sicily, mango harvesting has been extended to six months (from June to November) (Liguori et al., 2020). However, a significant amount of mango crops is lost each season due to its short shelf life caused by rapid ripening after harvest and inadequate storage systems. Facing this problem, drying can constitute an efficient solution of preservation (Russo et al., 2019). However, as drying can affect the physicochemical and nutritional properties of mango, it is suitable to deepen the knowledge about its effects on the structure and mobility of residual water in the fruit.
During drying process, the heating can influence the mobility of residual water, which can be evaluated using nuclear magnetic resonance (NMR) relaxometry. Fast Field Cycling Proton Nuclear Magnetic Resonance (FFC ^{1}H-NMR) relaxometry is a non-destructive low-field magnetic resonance technique measuring longitudinal spin relaxation rate, $R_1=1/T_1$, as a function of the magnetic field strength over a wide range of frequencies using only one instrument. Particularly, the spin magnetisation relaxation highlights the state of mobility of the water (low

or high) based on relaxation properties. The aim of this work is to investigate water mobility by FFC ^{1}H-NMR relaxometry analysis after convective hot air drying of mango fruits at 50 and 70°C, water activity and shrinkage in slices of Keitt mango, cultivated in Sicily.

2. Materials and methods

2.1 Raw materials preparation

Keitt mango fruits (*Mangifera indica* L.) were picked at the Cupitur Company in Acquedolci (Me), Sicily, Italy. Fifteen fruits (five per tree) were harvested by hand at commercial ripeness and used for drying process.

2.2 Convective drying tests

The uniformity of dimension and colour, the freshness, no mechanical damage and defects, were the parameters evaluated to choose mango fruits for drying experiments. After the washing, several mangoes were peeled and sliced (30.0 ± 0.2 mm of diameter and 5.0 ± 0.1 mm of thickness). Sample randomization was performed to avoid undesirable differences in the structure of mangoes that could negatively affect the analysis. Drying experiments of Keitt slices were conducted in a convective dryer (FCV/E6L3, Zanussi, Pordenone, Italy) operating at a constant temperature. The slices were placed on a plastic grid in the dryer and dried at 50 and 70°C with an airflow rate of 2.3 m s^{-1}, until an average moisture content of 0.30 ± 0.02 kg water kg^{-1} dry weight was reached.

2.3 Water activity measurement and shrinkage evaluation during drying

At time 0, in the middle and at the end of drying the water activity (a_w) and shrinkage were calculated.
To measure a_w, a water activity meter (Testo 650, Testo Inc., West Chester, PA, USA) was used at 25 °C. For the evaluation of shrinkage during drying, the initial volume (V_0) and volume at a given time (Vt) of the mango were calculated by measuring in 10 slices of fruit the diameter and thickness using a Vernier digital caliper (0.01 mm accuracy).

2.4 Fast Field Cycling (FFC) ^{1}H-NMR relaxation experiments and data elaboration

The theory about fast field cycling NMR relaxometry has been discussed in detail elsewhere (Conte, 2019; Conte and Lo Meo, 2020). FFC NMR experiments were done by using a Stelar Spinmaster FFC 2000 relaxometer (Stelar s.r.l., Mede, PV- Italy) at the constant temperature of 25 °C. When pre-polarization was needed, the proton spins were polarized at a polarization field (B_{POL}) corresponding to a proton Larmor frequency (ν_L) of 10 MHz for a period of polarization corresponding to around four times the T_1 estimated at this frequency. After each B_{POL} application, the magnetic field intensity (indicated as B_{RLX}) was systematically changed through the proton Larmor frequency range 9–0.015 MHz. When the pre-polarization was not needed, B_{POL} was null, while B_{RLX} was varied in the ν_L range 20–9 MHz. The period τ, during which B_{RLX} was applied, was varied on 32 logarithmic spaced time sets, each of them adjusted at every relaxation field in order to optimize the sampling of the decay/recovery curves. FIDs were recorded following a single ^{1}H 90° pulse of 5.5 μs applied at an acquisition field corresponding to the proton Larmor frequency of 7.20 MHz. A time domain of 100 μs sampled with 1000 points was applied. Field-switching time was 3 ms, while spectrometer dead time was 15 μs. For all the experiments, a recycle delay of 1 s was used.
All the decay/recovery curves acquired by applying the aforementioned experimental runs were exported to OriginPro 7.5 SR6 (Version 7.5885, OriginLab Corporation, Northampton, MA, USA) in order to apply equation (1), for the decay curve, and (2), for the recovery curve, respectively (Conte, 2019):

$$M(\tau) = a + b \cdot exp\left[-\left(\frac{\tau}{T_1}\right)^k\right] \quad (1)$$

$$M(\tau) = a + b \cdot \left\{1 - exp\left[-\left(\frac{\tau}{T_1}\right)^k\right]\right\} \quad (2)$$

Here, M(τ) is the magnetization intensity at the selected τ value; *a* is the offset; *b* is the magnetization intensity at the Boltzmann equilibrium; τ is the period of time during which B_{RLX} is applied; T_1 is the longitudinal relaxation time. Finally, *k* is a constant accounting for the heterogeneity of the complex system where a multitude of different components of the motion can be recognized. Its values are 1 when the system is mono-component. The advantage of equations (1) and (2) lies in the possibility of handling a wide variety of behaviors within a single model. For this reason, assumptions about the number of exponentials to be applied in modelling relaxometry data are no longer needed.

The data points obtained from equations (1) and (2) have been used to draw the nuclear magnetic relaxation dispersion (NMRD) profiles, that is longitudinal relaxation rates ($R_1=1/T_1$) vs ν_L.
The NMRD curves have been elaborated by applying the free model analysis provided by Halle et al. (1998) depicted in equation (3):

$$R_1 = \sum_{i=1}^{n} c_i \frac{\tau_{c_i}}{1+\left(\nu_L \tau_{c_i}\right)^2} \quad (3)$$

In equation (3), the subscript *i* refers to the different components of the motion in the complex system; R_1 is the longitudinal relaxation rate; τ_{ci} is the i-th correlation time, a typical parameter for spectral density which, in turn, describes random molecular motions (Kimmich and Anoardo, 2004); and c_i is a constant. The sum of the c_i values is the mean square fluctuation containing the information about the equilibrium structure of the system, and it is independent of the molecular dynamics. Finally, it is noteworthy that the set of $\{c_i, \tau_{ci}\}$ parameters from Equation (3) have no physical meaning, unless independent information suggests that the investigated system can be modelled by a fixed number of Lorentzians. In the latter case, a direct physical interpretation of the parameters can be attempted (Halle et al., 1998). However, according to Halle et al. (1998), the aforementioned parameters can be used to calculate a weight-averaged correlation time as in relation (4):

$$\tau_c = \frac{\sum_{i=1}^{n} c_i \tau_{c_i}}{\sum_{i=1}^{n} c_i} \quad (4)$$

3. Results and Discussion

All the experimental results obtained by using FFC ^{1}H-NMR relaxometry and the details retrieved by the application of the free model analysis by Halle et al. (1998) are reported in Figure 1.

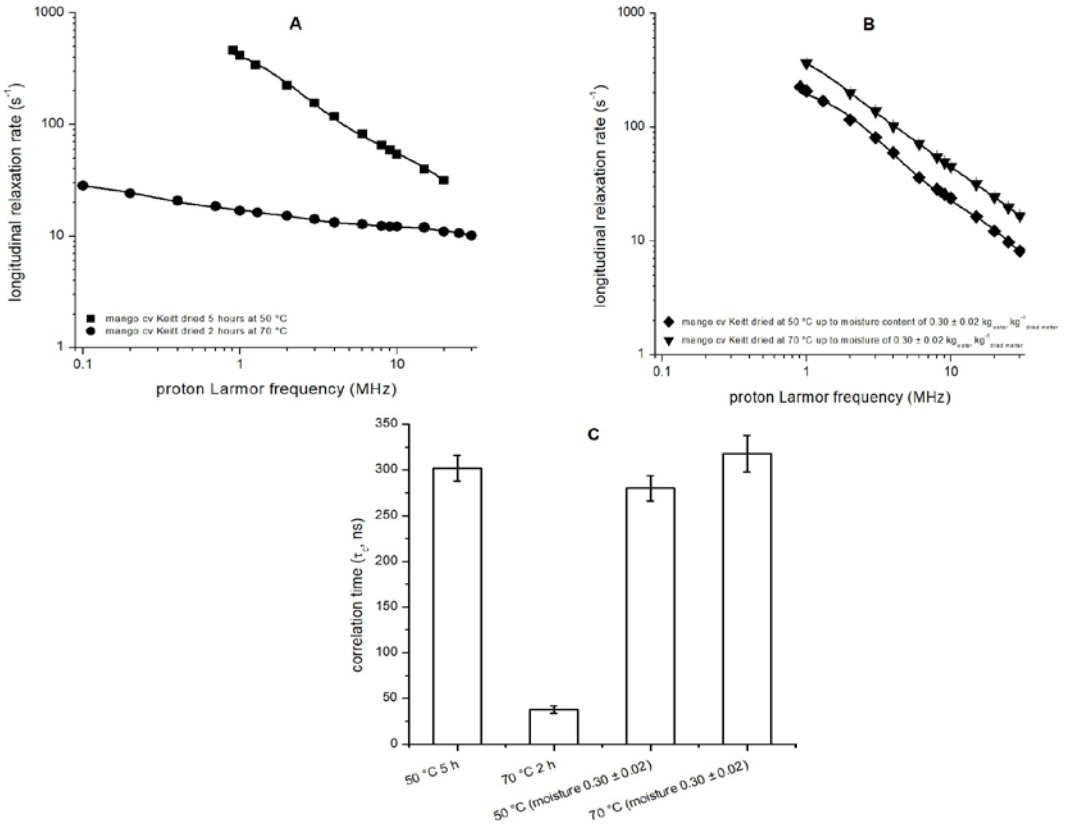

Figure 1. A. NMRD profiles for the mango fruit dried 5 hours at 50°C ( ) and 2 hours at 70 °C (Ï); **B.** NMRD profiles of the mango fruit dried at 50 °C (

Figure 1A shows the NMRD profiles acquired for the mango tissues dried at 50 °C for a period of 5 hours (50°C-5h) and at 70 °C for a period of 2 hours (70°C-2h). According to the theory (Conte, 2019; Conte and Lo Meo, 2020), the slower the longitudinal relaxation rate (R_1), the faster the molecular motion of the water molecules is, as a consequence of weaker interactions with the plant tissues. Therefore, we can state that drying mango fruit at the largest temperature for a shorter period of time produced a system containing more mobile water molecules. This result can be explained by the different amount of time during which the drying procedures were applied. In fact, the longer the heating time, the larger is the amount of water that can be removed from a plant tissue. This is also true when a plant tissue is heated at two different temperatures, with the lowest one applied for longer than the highest one (Akoy, 2014). In order to support the data reported in Figure 1A, measurement of water activity (a_w) was done. Results revealed values of a_w = 0.752 ± 0.001 and 0.788 ± 0.001 (Table 1) for the 50°C-5h and 70°C-2h samples, respectively, thereby corroborating the hypothesis about the larger amount of mobile water still available for hydration of mango tissues in the 70°C-2h sample as compared to the 50°C-5h one.

Table 1. Water activity and shrinkage values in fresh mango fruits, at the middle, and at the end of drying at 50 and 70 °C.

	Fresh samples	Dried at 50°C for 5h	Dried at 70°C for 2h	End drying at 50°C	End drying at 70°C
Water activity	0.941 ± 0.001	0.752 ± 0.001	0.788 ± 0.001	0.454 ± 0.001	0.463 ± 0.001
V/V0	0	0.291 ± 0.001	0.322 ± 0.001	0.272 ± 0.001	0.250 ± 0.001

Figure 1B reports the NMRD profile of the mango samples heated at 50 °C and 70 °C till the amount of water was the same (0.30 ± 0.02 $kg_{water}\ kg^{-1}_{dried\ matter}$) at the end of drying process. Based on the discussion above, we can rely that the water molecules present in the sample after having heated it at 70 °C behave as pseudo-ice, being more rigid than those in the sample treated at 50 °C. This appears to accord with the study from Conte et al. (2019), where the effect of temperature on the water mobility in apple slices was investigated. When a plant tissue is heated, water molecules move towards the gas phase at a rate depending on the applied temperature. In particular, at the largest temperature water moves away from the mango surface more rapidly than at the lowest one. As a consequence, the residual water is hooked to the plant tissue with a strength which is dependent upon the evaporation rate (Conte et al., 2019). Therefore, as expected, the longitudinal relaxation rates in the proton Larmor frequency interval used for the present study, are faster for the sample heated at 70 °C till water content of 0.30 ± 0.02 $kg_{water}\ kg^{-1}_{dried\ matter}$, as compared to the sample heated at 50°C till the same amount of water content.

The quantitative evaluation of the NMRD profiles by the application of the free model analysis given in equations (3) and (4) confirmed the aforementioned qualitative evaluation (Figure 1C). In fact, Figure 1C reports the correlation times for the water molecules occurring in the mango tissues treated as reported in Materials and Methods section.

The correlation time describes the average dynamics of the complex system under investigation. It measures the time needed for a molecule to rotate one radian or to move by a distance equal to its gyration radius. The longer the correlation time, the more restrained is the molecular motion of the water molecules which are the observed target in the present study. Conversely, as water molecules are subjected to a more rapid motion, correlation time decreases.

As expected from the qualitative evaluation of the NMRD profiles given above, the correlation time of the water in the tissue heated at 50 °C for 5 hours is longer than that obtained at 70 °C for 2 hours, thereby revealing that the molecular motion of the water molecules is more restrained in the former than in the latter sample (Figure 1C). Moreover, the correlation time of the water system heated at 70 °C till moisture content of 0.30 ± 0.02 $kg_{water}\ kg^{-1}_{dried\ matter}$, resulted longer than that in the tissue treated at 50 °C (Figure 1C), thus confirming the expectations about the effects of the temperature on water mobility in mango fruit tissues after heating treatments.

4. Conclusions

As evidenced in Conte et al. (2019), the more restrained the water molecular motion is, the longer is the shelf-life of the food products. In fact, water motion restrictions make the residual water less available for microorganism, thereby preventing a fast decomposition rate of the food systems. In the present study, a comparison between different heating temperatures of mango fruit have been evaluated. According to the results from FFC ^{1}H-NMR relaxometry, we can argue that the best conditions to obtain a longer shelf-life for the

mango fruit slices are to heat them 5 hours at 50 °C, instead of 70 °C applied for a shorter period of time. Particularly, we observed that drying mango fruit at the largest temperature for a shorter period of time produced a system containing more mobile water molecules, still available for hydration of mango tissues and growth of microorganisms. Therefore, FFC ^{1}H-NMR analyses could effectively complement information on water mobility in foods during convective hot air drying process, usually described by the sole determination of the water activity. These results may indicate that measuring the most immobilized water in fruits dried by FFC ^{1}H-NMR may be an additional index to predict their shelf-life. Further research to validate the data already reported and optimise the choice of drying temperatures will have to concern with the studies on shelf-life, rehydration and texture of dried fruit.

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