Impact of grinding processes on the microstructure and porosity of wheat bran

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Abstract. Plant matrices such as wheat bran exhibit complex structures and compositions, where interactions between polymers, water, and solvents strongly influence fractionation and extraction efficiency. This study proposes analytical approaches (ATR-FTIR, Time-Domain NMR, and solid-state NMR) to characterize these interactions and support the optimization of grinding and extraction processes. The main objective was to test whether FTIR data describing water binding states in powdered wheat bran can be correlated with water mobility measurements obtained by NMR under two relative humidity conditions. The influence of grinding modes (shear versus impact) and particle sizes (300 and 500 µm) on hydration properties was investigated. Results support combining FTIR and NMR to characterize molecular interactions and structural changes within plant matrices. Overall, this integrated approach provides insights into relationships between grinding processes and fragmentation mechanisms. Mechanical stress leads to matrix breakdown, producing different water affinities. Despite similar grid sizes, significant differences in particle size distribution and functional properties were observed, reflecting distinct stresses applied. Experiments at two humidity levels show that comminution conditions strongly influence hygroscopic sensitivity, confirming the decisive role of milling. Thus, technological functionality cannot rely solely on composition and microstructure but must include mechanical deconstruction governing water interactions and resulting properties overall.

1. Introduction and context of the study

Wheat bran is a by-product of conventional wheat milling which is currently undervalued as only 10% is currently used for food applications [1]. To incorporate bran into food products and other materials, wheat bran is often reduced into a fine powder involving a milling step. During the milling, the bran is subjected to mechanical stresses generated by the grinder such as compression, impact, friction, shear and extension, [2] that can influence its functional properties and so the quality of the final products [3]. A better understanding of the influence of the milling step notably the effect of different mechanical loading modes on the hydration water properties could bring new insights for a better processing and valorization of this by-product.

Molecular-level understanding relies on ATR-FTIR, which revealed that milling alters particle size and molecular structure, modifying water interactions in wheat bran [4]. Complementary studies using DVS, NMR relaxometry, and solid-state NMR linked relaxation and molecular interactions parameters to water retention, structure, and porosity [5-8]. These methods are well-suited to describe lignocellulose–solvent interactions and predict their impact on system porosity. Previous work [4] applied a direct subtraction method adapted from [9] to isolate, in FTIR, the spectral contribution of interfacial hydration water. Subtracting the lyophilized spectrum from the native spectrum highlights absorption bands associated with different water types in the plant matrix. Corrected, normalized, and smoothed spectra were used to interpret the effects of milling on water bonding states. The ATR-FTIR and NMR methods were combined to evaluate the binding strengths between water and the bran matrix.

2. Materials and methods

2.1. Wheat bran

Wheat bran from durum wheat bran (*Triticum durum*). was supplied by a French industrial miller, the Panzani Group. This batch consists of fine bran, made up of smaller particles from the inner layers of the husk. It is richer in starch and protein due to its proximity to the aleurone layer.

2.2. Grinding operations

Durum wheat bran batches were milled using processes dominated by specific mechanical stresses (impact, shear, friction) at varying sieve sizes.

Impact mill – UPZ (Hosokawa-Alpine, type 100 UPZ, Augsburg, Germany): Grinding was performed at room temperature at 18,000 rpm using 500 µm and 300 µm sieves, with impact as the predominant stress mode.

Ultracentrifugal mill – ZM200 (Retsch, Germany): Operating at 18,000 rpm with 500 µm or 250 µm sieves, shear dominates while impact also occurs. Bran was pre-frozen, and chamber temperature was monitored to avoid structural alterations. Milled material was collected via a cyclone equipped with a filter to limit fine particle dispersion.

2.3. Conditioning samples at different relative humidities

Prior to ATR-FTIR, NMR relaxometry and solid-state NMR analysis, the ground samples were equilibrated at two relative humidity levels (58% and 86%) achieved

using saturated solutions of NaBr and KCl, respectively, in accordance with standardized sorption conditions. A conditioning time of 14 days was required to reach mass stability.

2.4. Bran characterization

2.4.1. Particle size measurement by laser diffraction

The particle size distribution of the ground samples was measured by laser diffraction using a Mastersizer 2000 equipped with a Scirocco 2000 dry dispersion unit Scirocco 2000 (Malvern Instruments, Worcestershire, UK). The particle size distribution is expressed as % of total particle volume. The median particle size (D_{50}) and span (D_{90}-D_{10}/D_{50}) were used as the primary descriptors. This measurement was performed only on ground material since the size of initial brans was outside the measurement range of the device. All measurements were performed in triplicate.

2.4.2. ATR-FTIR spectra

The FTIR spectra were collected in the 400-4000 cm−1 wavenumber range on a Bruker Vertex 70v Fourier Transform spectrometer (Bruker Optik GmbH. Germany) operating with a Globar source in combination with a KBr beamsplitter and a DigiTect DLaTGS detector with integrated preamplifier. The optical cell was a Golden Gate diamond ATR system. The spectra were recorded with a resolution of 4 cm−1, automatically adding 128 repetitive scans. Scans were corrected for the air contribution and were preprocessed using OPUS software (version 7.0) by performing a baseline correction, a 9 points smoothing and a vector normalization for taking into account the effective number of absorbers. Experiments were conducted on powders of native and ground brans previously equilibrated at 50% or 86% relative humidities in specific climatic chambers (at 25 °C). The spectra of freeze dried brans were subtracted following the direct difference method [9]. The resulting spectrum is supposed to correspond to interfacial hydration water. In ATR-FTIR, the parameter $R_{multimer}$ is defined as the ratio of absorbance maxima for two water states: $R_{multimer} = A_{3600} / A_{3200}$. The 3600 cm^{-1} band corresponds to weakly coordinated "multimer" water MW (0–1 hydrogen bonds), while the 3200 cm^{-1} band represents strongly coordinated "network water" NW (up to four hydrogen bonds). An increased $R_{multimer}$ indicates a higher proportion of weakly structured water interacting with the matrix.

2.4.3. Time-Domain NMR

T_2 measurements on powders were performed using a minispec 20-MHz Bruker spectrometer (Wissembourg, France). The temperature of samples at 20 °C was measured and controlled using a calibrated optical fiber. T_2 relaxation times were measured via the combined FID-CPMG sequence implementing 128 scans preceded by a 400 ms recycle delay. The FID duration was 141 µs. The echo time (TE) in the CPMG sequence was 0.05 ms for 2000 echoes. The fitting of FID-CPMG signals required the combination of exponential, Gaussian and SinC functions. The total NMR signal was well represented by a combination of a cardinal sinus function and a Gaussian broadening, followed by three or four exponential decreasing depending on the hydration level [10].

2.4.4. Solid-state NMR

A Bruker Avance NEO 400 WB spectrometer operating at a proton frequency of 400.13 MHz was used for all NMR spectra acquisition. The magic angle spinning (MAS) rate was set at 12 kHz. VCT-CPMAS ^{13}C NMR was performed using 160 contact times with 128 accumulations and a recovery time of 3 s. T_{CH}, T_{HH} and $T_{1\rho}^{H}$ parameters were determined as previous proposed [5].

3. Results and discussion

It is worth noting that, although similar grid sizes were used in both milling devices, the particle sizes measured at the outlet show significant differences as shown in table 1 (median diameters of 140.53 µm and 306.02 µm for the 300 µm sieve for ultracentrifugal and impact mill respectively for example). This highlights that, during deconstruction, the mechanical stresses specific to each mill (mainly shear in the centrifugal mill, and a combination of impact and shear in the impact mill) [11] influence the fragmentation mechanisms in different ways. Therefore, beyond the grid size alone, the nature of the applied stresses (impact, shear, compression) plays a key role in determining the resulting particle size distribution [4].

Table 1. Different parameters (D_{10}, D_{50}, and D_{90}) of the particle size distribution curves for wheat bran samples milled using ultracentrifugal and impact mills with different sieves.

	Ultracentrifugal mill		**Impact mill**	
	250 µm	500 µm	300 µm	500 µm
D_{10}	21.04	79.97	39.39	136.20
D_{50}	140.53	436.23	306.02	514.02
D_{90}	362.80	1001.37	651.85	1355.50

All ATR-FTIR spectra show three main absorption bands. The band at ~3600 cm^{-1} corresponds to weakly coordinated "multimer" (MT) water, forming few hydrogen bonds (0–1) and interacting mainly with the matrix. The ~3450 cm^{-1} band represents "intermediate water" (IW), with moderate structuring (2–3 hydrogen bonds), acting as a transition between disordered and structured states. The ~3200 cm^{-1} band corresponds to "network water" (NW), composed of strongly coordinated molecules (up to four hydrogen bonds), reflecting a well-organized hydrogen-bond network similar to highly structured or bound water. ATR-FTIR analysis revealed clear differences in the structure of water within ground durum wheat bran matrices, depending on the grinding conditions and relative humidity. The spectra obtained show a reproducible distribution of the three water populations (MW, IW, NW), with a higher overall intensity at 86% RH. Calculation of the $R_{multimer}$ parameter confirmed these observations, revealing a predominance of disturbed water (MW) under high humidity, and a more pronounced structure (NW) under NaBr conditions. These results

illustrate the sensitivity of water states to the microstructure induced by milling processes and to hydration conditions. Table 2 presents the values of the $R_{multimer}$ parameter, calculated for each experimental condition (grinder type, sieve size, relative humidity). This ratio reflects the balance between the populations of weakly structured water (MW) and strongly bound water (NW) in the matrix.

Table 2. Values of the Rmultimer ratio (A_{3600}/A_{3200}) and water uptake for each ground sample and relative humidity condition.

	Ultracentrifugal mill		**Impact mill**	
	250 µm	500 µm	300 µm	500 µm
Water uptake at RH 86%	8.7%	2.86%	8.27%	1.95%
$R_{multimer}$ RH 86%	1.38	1.09	1.12	1.28
$R_{multimer}$ RH 58%	0.87	1.16	1.12	1.16
Water uptake at RH 58%	-3.2%	-0.75%	0.61%	-2.28%

In Table 2, we report the water uptake of the samples under the different conditioning conditions. At low humidity (58%), the samples tend to lose water, except for the sample produced with the impact mill using a 300 µm grid.

Under conditioning at 86% relative humidity, all samples absorb water, and the obtained values appear to be mainly related to the grid size used, with only minor differences between the milling devices. These first observations highlight that the mechanical stresses generated by the mills, beyond particle size reduction, also affect differently the various tissues composing wheat bran, leading to different capacities for hydrogen bond formation. The state of water within this matrix can be described using the multimer ratio (R). An R value below 1 indicates a higher proportion of interactions between water molecules and the surrounding water molecules (network water NW), whereas an R value above 1 suggests that, for the same water content, water molecules interact more with the matrix (Multimer water MW). This parameter therefore provides insight into the accessibility of the matrix to water molecules and, potentially, to solvents used during extraction processes.

Analysis of the values reported in table 2 also makes it possible to identify the dominant water population under different conditions. Under a relative humidity of 86%, all samples exhibit $R_{multimer}$ values greater than 1, indicating a predominance of multimer water (MW). Under a relative humidity of 58%, one sample of ground wheat bran at 250 µm with ultracentifugal mill show values less than 1, in which network water (NW) becomes the dominant fraction. The functional groups and/or their accessibility can be altered by the grinding loading mode impacting the network water component situated at low wavenumbers.

As shown in Figure 1, for each sample, the kinetics were modeled, allowing the extraction of several parameters: T_{CH}, which characterizes interactions between macromolecules; T_{HH}, the spin diffusion time, which indirectly probes water–matrix interactions; and $T_{1\rho}{}^{H}$, which enables the assessment of the level of molecular order.

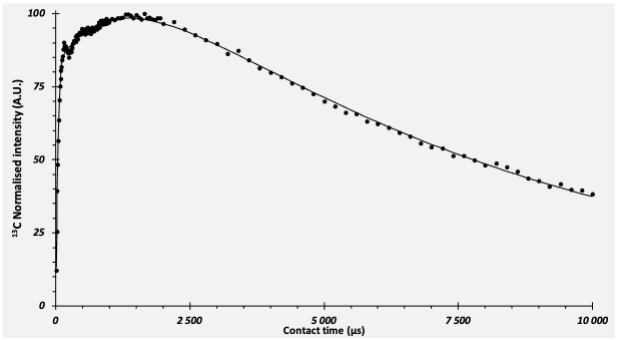

Figure 1. VCT profile of wheat bran milling with impact mill and conditioned at relative humidity of 59%. Each data point represents the signal intensity extracted from the ^{13}C CPMAS spectrum acquired at the corresponding contact time on the x-axis. Solid lines represent the results of modelling.

$R_{multimer}$ correlates with solid-state NMR parameters such as cross-polarization transfer time (T_{CH}) and spin diffusion time (T_{HH}) (Figure 2), reflecting macromolecular interactions and water structuring in polysaccharides, as well as with T_{23} from NMR relaxometry, characterizing intermediate water mobility. Although both parameters evolve in a similar manner, the direct linear correlations remain moderate (0.46–0.53), likely due to sample heterogeneity and differences in hydration levels.

Indeed, wheat bran is a complex matrix composed of various plant tissues. While it is of great interest for extraction processes, its structural complexity must be considered. During deconstruction, mechanical stresses affect these tissues differently, which is precisely what this study aimed to highlight.

However, the chemical groups revealed by this differential deconstruction, depending on the milling process, likely do not respond in the same way across the analytical techniques used (FTIR, solid-state NMR, and NMR relaxometry). This suggests that other types of correlations need to be explored.

Biochemical analyses are currently underway to complement this study and refine the observed correlations.

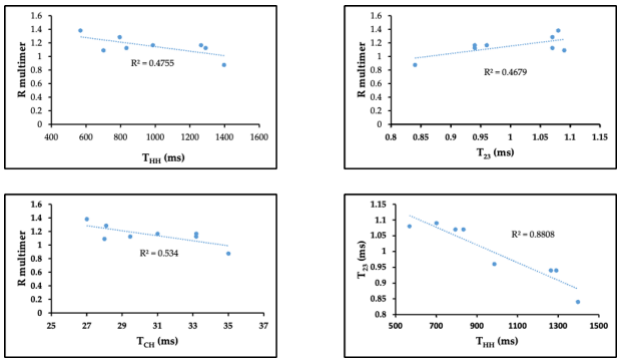

Figure 2. Observed interactions between Rmultimer measured by ATR-FTIR and T_{CH}/T_{HH} from solid-state NMR, as well as T_{23} from NMR relaxometry. All data obtained under the two relative humidity conditions were used.

4. Conclusion and perspectives

The complementary analysis done by ATR-FTIR and NMR showed results consistent with the observations of Barbar et al. (2023), who demonstrated a redistribution of water content depending on the grinding method and relative humidity. The link between more intense grinding (fine shearing) and an increase in multimere water is also consistent with the trends described by Cadden (1987), who had already suggested a correlation between particle fineness and the release of bound water in ground plant fibers. Complementary studies are needed to clarify the relation between the effect of the grinding mode on the dissociation of the tissues and on the accessibility of the constituents and their impact on the hydration properties. This will bring new elements to optimize the milling processability of wheat bran to target specific hydration properties as well as extraction efficiency by increasing solid–liquid surface area.

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