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**Emerging approaches to improve barley malt processing and quality:
ultrasound-assisted hydration and ethanol pre-treatment to drying**

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Abstract

This work aimed to evaluate how two emerging technologies impact the malting process and the quality of barley malt: ultrasound-assisted hydration and ethanol pre-treatment to drying. All three steps of malting (hydration, germination, and drying), as well as the resulting malt's quality indicators, were evaluated. Conventional and ultrasound-assisted (25 kHz; 91 W/L, 20 °C) hydration were carried out, followed by germination, ethanol (99.5%) pre-treatment (immersion 30 min, 25 °C), and convective drying (50 °C, 1 m/s). Texture analysis demonstrated that the different stages of the malting process modify the structure and composition by increasing or decreasing the compression force in the grain. The ultrasound-assisted hydration improved the second hydration stage, where hydration resistances were greater, reducing hydration time by 38%; moreover, ultrasound accelerated the germination step with root growth 1.17 times greater. During drying, ultrasound-assisted hydration followed by ethanol pre-treatment, reduced drying time by 38.5% (barley) and 17.8% (malt). Both evaluated technologies, therefore, intensify the malting process. In addition, it was demonstrated that their use increased the alpha (9%) and beta-amylase (7%) activity in malt and modified paste and gel-forming properties of barley and malt flours. Therefore, these results suggest that the use of ultrasound improved hydration and germination processes, and ethanol pre-treatment accelerated the drying process because of improved mass transfer, both without negative impact on malt quality.

Keywords: Mass transfer, Ultrasound processing, Hydration, Malting process, Process intensification.

1. Introduction

Barley is one of the most produced cereals in the world and the most important raw material for malt production, which is used as the main ingredient for beer and whisky production (Carvalho et al., 2021b) and also an emerging ingredient for bread making (Polachini et al., 2023). Malt production consists of three main steps: steeping/hydration; germination and drying. These three steps are time-consuming; therefore, it is interesting to explore improved process alternatives to accelerate the stages, without negatively affecting the malt properties.

During malt production, the hydration is responsible for promoting the increase in the barley moisture from 10-12% (in wet basis, w.b.) until 40-47% (w.b.). Commonly, the hydration is carried out at temperatures from 15-20 °C for 2 to 4 days (Rani and Bhardwaj, 2021). Although higher temperatures lead to faster water uptake, it increases the risk of microbial contamination. This step is essential to break the dormancy of the grain, carrying nutrients and molecules from the external layers of the grain to the inner endosperm, initiating biochemical reactions that will activate the biological phase and, consequently, the germination.

In the course of germination, the enzymes are formed or activated and promote the hydrolysis of the starchy endosperm and other macromolecules, such as proteins and fibers. The products of the hydrolysis will be nutrient for the development of acrospire and rootlets. Germination is starting the plant development; however, for malt production, the main objective is the synthesis of enzymes and only a partial degradation of the endosperm, transforming it from a hard to a soft (friable) structure. Therefore, the germination is stopped by drying after 3 to 6 days of process.

Drying also ensure the malt stability, reducing the moisture from about 40% to 5-7% (w.b.), while preventing the enzymes denaturation. It also promotes the formation of important characteristics, such as color and flavor. Generally, the drying process is conducted rising the temperature from 50-80 °C for around 21 to 24 hours. For some kinds of malt, where different color and flavor are desirables, the drying temperature can

be rise, reaching 180-200 °C. Nevertheless, for malts where the diastatic power is essential, the drying temperatures are milder, due to the sensibility of the enzymes that provide this characteristic, such as the alpha and beta-amylases. (Briggs and Briggs, 1978; Ullrich, 2010; Mallett, 2014; Carvalho et al., 2018; Rani and Bhardwaj, 2021; Kumar et al., 2023).

In the last years, ultrasound and an ethanol pre-treatment have been applied to accelerate food drying (Llavata et al., 2020). Ultrasound is an emerging technology, which due to mechanisms such as cavitation, sponge effect, microjets, and others, can modify the structure of the products and improve the heat and mass transfer during food processing. It has being applied to improve several operations in food processing, including the hydration or drying of barley (Carvalho et al., 2018; Borsato et al., 2019; Shafaei et al., 2019; Song et al., 2019) and wheat (Guimaraes et al., 2020) grains. Drying can be improved by the pre-treatment of samples with ethanol (by immersion, 25 °C for 5-30 min). The surface tension differences between ethanol and water promotes the moisture outflux and ethanol influx in the product (Guedes et al., 2021), in addition to the osmotic effect and higher vapor pressure, which, after pre-treatment, accelerates the drying process (Carvalho et al., 2020). Consequently, the combination of both technologies can improve the malting process, although it was not evaluated until now.

Therefore, this work aimed to evaluate the utilization of ultrasound-assisted hydration of barley followed by ethanol pre-treatment for drying barley malt, evaluating the effect on the process itself and some quality parameters of the barley and malt (rootlets growth during germination, enzymatic activity, texture and pasting properties of flours).

2. Material and Methods

2.1. Raw material

Barley (*Hordeum vulgare* cv.), two-row variety *Andrea*., provided by the Cooperativa Agraria – Agraria Malte (Guarapuava, PR, Brazil), was used in the experiments. Before use, the grains were cleaned and selected to remove foreign materials and broken grains and then stored under refrigeration. To determine initial moisture, the grains were milled using an analytical mill (Model A11, IKA, Germany), sieved (0.5 mm of the screen) and examined in a moisture analyzer (MX-50, A&D Company, Japan), presenting a moisture of $10.07 \pm 0.07\%$ in wet basis (w.b.).

2.2. Malting

2.2.1. Barley hydration

The hydration of the barley grains was carried out in two ways: the conventional, static method (ST), and assisted by high-intensity ultrasound (US) (Figure 1). Approximately 400 g (± 0.03 g) of barley grains were placed in a tray of stainless-steel mesh (20 x 20 x 5 cm and mesh with 0.46 mm wire and 2 mm between wires).

The hydration process was carried out until the grains reached the moisture necessary for germination, of 41.2% (w.b.). This moisture content and hydration temperature were chosen based on breaking the dormancy and actual industrial uses to optimize the germination step (Briggs and Briggs, 1978; Mallett, 2014).

Table 1 shows the description of all evaluated treatments.

For ST hydration, the tray with barley grains was inserted in a bath with 4 L of distilled water maintained at 20 °C. For US-assisted hydration, the tray was placed into an ultrasonic bath (Q 13/25, Ultronique, Brazil) which works at constant frequency of 25 kHz and volumetric power of 91 W/L (determined by the calorimetric method as described by Cárcel et al. (2007)). The ultrasound was applied during the entire hydration process and the temperature was kept at 20 ± 1 °C using heat exchangers to cool the water. This temperature was selected since at temperatures higher than 20 °C the ultrasound effect on water absorption is less evident (Shafaei et al., 2019), as well as there is a possible negative impact on malt quality (Borsato et al., 2019).

To obtain the hydration kinetics, at specific times, the tray with barley grains was removed from the water, drained, and superficially dried to remove the excess water, weighed, and returned to the distilled water. The moisture content (M_t) over the process time (t) was obtained by a mass balance considering the initial moisture content (M_0) and the increase in barley grains weight due to absorption of water. After pre-tests, the solid matter transferred from the barley grains to the hydration water was assumed to be negligible.

2.2.2. Germination

After reaching the moisture content ($41 \pm 1\%$ w.b. or approx. 0.7 g/g d.b), the grains were submitted to germination. The hydrated grains were placed in plastic trays capped with plastic film to avoid excessive water evaporation while promoting gas exchange. The capped trays were placed into an incubator chamber at 16 ± 1 °C for 84 hours (3.5 days). During the germination process, the grains were homogeneously distributed to avoid the formation of blocks that can difficult the gas exchange and the heat transfer; water was sprinkled daily in the samples to maintain the moisture content.

An aliquot of grains was separated during the germination process to monitor the rootlets growth. This monitoring was made for 96 hours (4 days), registering daily images of 10 random grains of each treatment during the process. The images were captured including a scale which was used as a measurement reference. The grains and rootlets growth were measured with the software CorelDRAW (Version 2018, Corel Corporation, Canada) in the images obtained every day during the germination process. All the rootlets present in each grain were measured and expressed as the sum of their length.

2.2.3. Ethanol pre-treatment and drying

Ethanol pre-treatment and the subsequent drying process were carried out with two materials: the hydrated barley (obtained after hydration, before germination) and with the green malt (obtained after hydration and germination). The drying process was

performed after the hydration process of barley to evaluate the effect of the germination in characteristics such as the structure, and to evaluate in isolation the effects of the ultrasound-assisted hydration and ethanol pre-treatment. To evaluate the effect of pre-treatment with ethanol on the subsequent drying process, approximately 150 g of hydrated barley and green malt were immersed in 1 L of ethanol (99.5% Food Grade) for 30 min at 25 °C. After pre-treatment time, the grains were removed from ethanol, drained, and superficially dried with paper towel to remove the excess of ethanol. Then, the grains were placed into trays (15 cm in length; 15 cm in width; and 5 cm in height) of stainless steel with a 0.71 mm wire screen and 2.5 mm aperture for convective drying. Drying was conducted in an oven (MA 035, Marconi, Brazil) with air circulation of 1.0 ± 0.1 m/s, measured by a hot wire thermoanemometer (405i, Testo, Germany), at a temperature of $50.1 \pm 0.5^\circ\text{C}$.

The sample surface temperature was monitored and registered by thermal images using an infrared camera (Testo 865, Testo, Germany) with 0.95 of emissivity. The thermal images were analyzed using the software IRSOFT (Version 4.5, Testo SE & Co, Germany).

Drying was conducted until the grains reached constant weight, in four replicates. At specific times, the sample was quickly removed from the oven, the weight was recorded in a precision scale and the sample was returned to the oven. The drying kinetics was obtained by mass balance, from the sample weight (m_t) over the drying time (t) and the initial and final moistures (M_0 and M_∞). In the treatments that include ethanol, since there was an influx of ethanol into the samples during ethanol pre-treatment, the moisture throughout the drying time includes not only water but also ethanol that remains at each drying time (t) (Rojas and Augusto, 2018). However, it is important to mention that previous studies demonstrated that the inlet of ethanol occurs at a surface level and that it can be eliminated mainly in the first stages of drying (Rojas and Augusto, 2018; Carvalho et al., 2021a). The initial and final moisture contents of the samples were measured at 105 °C using a moisture analyzer (MX-50, A&D Company, Japan) after

milling about 20 g of grains in an analytical mill (Model A11, IKA, Germany). The samples were analyzed in triplicate.

After finishing the malt drying, the rootlets were removed from the dried grains, because they present high hygroscopicity, which can compromise the stability and quality of the malt (Briggs and Briggs, 1978; Mallett, 2014). The malt obtained with the different treatments was stored in airtight containers in a cool, dry place.

2.3. Malt properties

2.3.1. Enzymatic activity

Alpha- and beta-amylase activities were determined according to method proposed by Bernfeld (1955) for the produced malts, as well as, for the barley grains, to evaluate the effect of different treatments. The grains were finely ground in an analytical mill (Model A11, IKA, Germany) and sifted (0.5 mm screen) before extraction and reaction.

Malt extract: the extraction of enzymes was made by weighting 1 g of sample, adding in 20 mL of NaCl solution 0.5%, and placing it in an agitation bath at 20 °C and 200 rpm for 2 hours. After agitation, the suspension was filtered (filter paper 90 g, Química Moderna, Brazil) and the extract was frozen until the use.

Substrate: the substrates were solutions of 1% soluble starch (Êxodo científica, Brazil) diluted in phosphate buffer 0.02 M (pH 6.9) containing 0.0067 M of NaCl for alpha-amylase determination, and in acetate buffer 0.016 M (pH 4.8) for beta-amylase determination.

DNS reagent: the DNS reagent was prepared from the dilution of Sodium Hydroxide (Labsynth, Brazil) solution 2 M, Sodium and Potassium Tartrate (Qhemis, Brazil) and 3,5-Dinitrosalicylic Acid (Dinâmica Química, Brazil).

Maltose standard curve: The standard curve was obtained with Maltose (Sigma-Aldrich, Brazil) solution at concentration of 0 (only water), 0.1, 0.2, 0.4, 0.8, 1, 2 and 4 g/L. 0.5 mL of different concentration maltose solution was placed in falcon tubes and

0.5 mL of DNS acid was added and the tube was placed in a boiling bath at approximately 100 °C for 5 minutes for the reaction between the DNS acid and the maltose (standard reducing sugar) to color formation. Then, 4 mL of distilled water was added, the tubes were agitated in a vortex and the absorbance was read at 540 nm in a spectrophotometer (Femto, Model 600S, São Paulo, Brazil).

The enzymatic reaction was carried out according to the method described by Bernfeld (1955), placing 0.25 mL of the starchy substrate (for both alpha- and beta-amylases) and 0.25 mL of the malt extract to react for 3 minutes at 20 °C in a falcon tube of 15 mL. After the reaction, 0.5 mL of DNS acid was added to interrupt the enzymatic reaction, and the tube was placed in a boiling bath at approximately 100 °C for 5 minutes. Then, 4 mL of distilled water was added, the tubes were agitated in a vortex and the absorbance was read at 540 nm in the same way as the standard curve of maltose.

The activities of alpha- and beta-amylases were calculated by using Equation 1, adapted from Osman (2002):

$$U = \frac{C_{maltose}}{t} \times \frac{TV}{AV} \times \frac{EV}{m_{malt}} \times F \quad (1)$$

Where U is the enzymatic activity, which corresponds to the mass of maltose equivalent, in mg, released by 1 g of malt, during the reaction time at 20 °C ($\text{mg}_{\text{maltose}}/\text{g} \cdot \text{min}$). $C_{maltose}$ is the concentration of equivalent of maltose, obtained from the standard curve, in mg/mL; TV is the total volume during the reaction, in mL; AV is the malt extract aliquoted volume, in mL; EV is the total volume for the extraction process, in mL; m_{malt} is the mass of malt used for extraction, in g; and F is the dilution factor, which was equal to 1.

2.3.2. Texture analysis

Texture analyses were performed in two moments: i) in the grains during the malt production, and ii) in the gels formed with barley flours. For these purposes, a Texture Analyzer (TA.XT Plus, Stable Micro System Ltd., England) with a load cell of 50 kg-f (490.03 N) was used.

During the malting process, the texture was evaluated for the barley grains and malt before and after convective drying. The grains were compressed until a strain of 50% of their thickness with 1 mm/s velocity, using a 35 mm aluminum cylindrical probe (P/35R). From each treatment, 10 replicates were performed for each condition.

The barley and malt flours were gelatinized in the RVA analysis (section 2.3.3), and the obtained pastes were gelled at 8 °C for 24 h by storing them in plastic cups (40 mm diameter and 20 mm height) in a desiccator with water to avoid dehydration. The malt flour did not form gels, reflecting the changes in composition and structure after germination. Therefore, only the gels made with barley grains were evaluated in relation to their texture. The firmness of the obtained gels was measured by a compression test using a cylindrical probe (P100, 100 mm of diameter) to compress the sample 75% at 1 mm/s. The gel firmness was determined as the maximum force achieved during the assay.

2.3.3. RVA analysis

The apparent viscosity of barley and malt flour suspensions was evaluated in a Rapid Visco Analyzer (RVA-4, Newport Scientific Pvt. Ltd., Australia, with the Thermocline for Windows software, version 3.0).

For barley flour, 4 g of flour (14% w.b.) was mixed with 25 g of distilled water, and the suspension was analyzed under constant shear on a programmed heating, retention, and cooling cycle. The suspensions were initially held at 50 °C for 1 min, heated to 90 °C at 10.8 °C/min, and kept at 90°C for 5 min, being then cooled to 50 °C at 8 °C/min, and kept at this temperature for 1 min. The pasting parameters were then obtained, based on the suspension and paste apparent viscosity (evaluated in mPa·s, where 1 mPa·s = 1 cP). After, the pastes were gelled and analyzed as described in section 2.3.2.

For malt flour, the same methodology was employed. However, because with 4 g of malt flour the formation of paste was not observed due to the presence of enzymes

that hydrolyzed the starch and other components, it was necessary to increase it to 7 g of malt flour (14% moisture in wet basis) in 21 g of distilled water (Balet et al., 2019).

2.4. Mathematical description

Mathematical functions were used to describe two steps of malt production: i) hydration and ii) drying.

2.4.1. Hydration process

Empirical models were used to describe the hydration process, fitting them to the experimental data. The Peleg Model (Peleg, 1988), represented by Equation (2), is commonly used to describe processes of hydration of food materials,

$$M_t = M_0 + \frac{t}{k_1 + k_2 t} \quad (2)$$

where M_t is the moisture content (g/g d.b.) at the time t (min) of hydration. M_0 is the initial moisture content (g/g d.b.). k_1 (min·g/g d.b.⁻¹) is the constant rate (related to the inverse of initial water absorption rate) and k_2 (g/g d.b.⁻¹) is the constant of capacity (inversely related to the equilibrium moisture reached during the process).

Considering the observed behavior and the adjustment of Peleg Model, a second model was used to describe hydration, which describes the hydration in two parallel stages, as proposed by Miano et al. (2017). This model is represented by Equation (3).

$$M_t = (M_\infty - M_0)[p(1 - \exp(-k_a t)) + (1 - p)(1 - \exp(-k_b t))] + M_0 \quad (3)$$

Where M_∞ is the equilibrium moisture content (g/g d.b.); p is the fraction of water absorbed by the barley kernel in the fast or short process; and k_a and k_b are global mass transfer parameters at the first and second phases of the process, in min⁻¹.

2.4.2. Drying process

The mathematical modelling of drying process for both hydrated barley and green barley malt was made by the Page Model (Equation 4).

$$MR = \frac{M_t - M_\infty}{M_0 - M_\infty} = \exp(-k_p t^n) \quad (4)$$

where k_p is the drying rate parameter, min^{-n} ; and n is the dimensionless drying parameter.

Although the Page model is empirical, Simpson et al. (2017) proposed a fractional analysis of it, giving them some interpretation based on the anomalous diffusion model. Therefore, the k parameter can be associated with the diffusivity and geometry of the sample and the n parameter describes the “type of diffusion” ($n < 1$ as sub-diffusion and $n > 1$ as super-diffusion), which in turn can be related to the sample microstructure and mechanisms of mass transfer.

2.4.3. Regressions

The adjustments of the models on Equations 2, 3 and 4 to experimental data were performed using the solver tool from Excel (version 22, Microsoft Company, USA), through the GRG non-linear method with convergency of 0.0001. The goodness of fit was evaluated by the determination coefficient (R^2), by the Mean Relative Error (MRE) and the Root Mean Square Error ($RMSE$), equations (5) to (7).

$$R^2 = 1 - \frac{\sum_i (y_i - \bar{y}_i)^2}{\sum_i (y_i - \hat{y}_i)^2} \quad (5)$$

$$MRE = \frac{100}{n} \sum_i^n \left| \frac{y_i - \hat{y}_i}{y_i} \right| \quad (6)$$

$$RMSE = \sqrt{\sum_i^n \left| \frac{(y_i - \hat{y}_i)^2}{n} \right|} \quad (7)$$

where y_i is the experimental value; \hat{y}_i is the predicted value; and \bar{y}_i is the average value of the analyzed data.

2.5. Experimental design and statistical analysis

Hydration, germination, and drying processes were carried out four times and the analyses were made at least in triplicate. The analysis of variance (ANOVA) was carried out with a significance level of 5%. To determine significant differences between the

means of the treatments, Tukey test was applied. Statistical analysis was carried out in Statistica (v.13, StatSoft. Inc., USA).

3. Results and Discussion

3.1. Grain texture during processing

The texture of barley grains is related to the structural and compositional characteristics of endosperm, where starch, β -glucan, proteins, and their interactions determine the hardness or friability of the grain (Rani and Bhardwaj, 2021). Grain texture can influence other processing properties such as grinding energy, particle size, water absorption, hydration time, among others (Walker and Panozzo, 2016). Figure 2 presents the maximum force for grain compression along different steps of malt production. From the compression analysis, it was possible to infer changes in the structure and composition of the grain over the different steps of processing.

The barley grain, as expected, presented the highest compression force, $151,1 \pm 24.4$ N, reflecting the intact structure and small plasticity of the dry tissues and cell walls. After hydration, the compression force was reduced by 66% and 72% for the static and ultrasound-assisted hydrations, respectively. The entry of water into the grain, filling the extracellular spaces and, posteriorly, enters the endosperm cell and promotes the structure softening, which was more pronounced when ultrasound was applied.

During germination, hydrolytic enzymes (glucanases, proteases, and amylases) are biosynthesized and released into the inner endosperm for depolymerization of the endosperm cell wall, polysaccharides, and proteins (Rani and Bhardwaj, 2021). Since barley hardness is mainly determined by the endosperm cell wall thickness and starch-protein binding (Nair et al., 2011), the action of these enzymes promotes changes in the microstructure of the grain, transforming the hard into friable endosperm. This can also be observed by comparing the compression force of the hydrated barley grains (Figure 2B) with the green malt (Figure 2C), which presented a reduction of approximately 76%.

Friability is considered an important property of the malt, which can be used to determine the modification of the cell wall of malt grains, from the principle that the malt poorly modified is very hard and difficult to grind (Rani and Bhardwaj, 2021). Carvalho et al. (2021b) also evaluated the compression force during barley germination (conventional process), observing a reduction of approximately 70% during germination, evidencing the modifications that occur in the grains during this step.

During drying, by removing water, a certain level of compression force was recovered in the samples, although this recovery was lower in the germinated samples. This could be evidenced by comparing the compression force of *in natura* barley grain with that of dried barley (Figure 2D) and dried malt (Figure 2E), where the compression force decreased up to 10% and 61%, respectively. Evaluating the effect of the treatments, in dry barley it is observed that the ultrasound effect, evident after hydration, disappears with drying, with no difference among treatments (Figure 2D). On the contrary, in malt (Figure 2E) a slight reduction (~ 5%) in the compression force was observed in the treatments where ultrasound was applied (M-US and M-US+E). This could indicate that ultrasound-assisted hydration favored enzymatic activity in the endosperm either by stimulating the biosynthesis of hydrolytic enzymes such as amylases (evidenced in Figure 9) or by promoting their release in the endosperm.

Therefore, the compression force results after hydration, germination, and drying demonstrated that changes in texture are not only due to the increase or decrease of water after hydration or drying, respectively, but they are also mainly due to modifications in structure and composition that occur during germination - which are irreversible. In addition, mechanisms of action of the ultrasound, such as the cavitation, and the sponge effect, can contribute to structural modification and metabolic stimulation in the grain – which can make the grains more friable and facilitate the mass transfer unit operations, as evaluated as follows.

3.2. Malt processing

3.2.1. Mechanism of water transport and hydration kinetics

Water transfer during the hydration process is mainly determined by the structure of the barley grain, water availability and temperature, of which the limiting factor is the inherent structure of the barley. Therefore, to better understand the behavior of hydration kinetics, it is first important to know how water transfer occurs in the structure of the barley grain.

The hydration of barley grains was attributed to occurring in two parallel stages of water transfer one occurring first and faster than the other, similar to the described by Miano et al. (2017) in corn kernels. Figure 3 shows a representation of the entry and distribution of water during rehydration in the barley grain, considering the tissues of the barley structure (Freeman and Palmer, 1984) and previous studies of the hydration mechanism of barley (Turner et al., 2019). The first stage of hydration occurs quickly, mainly through tissues that lack external layers such as the micropyle, which lacks testa (external tissue after the pericarp in the form of a protective membrane) and presents a less compressed pericarp. Therefore, water would enter by capillarity through the micropyle much faster than other areas. Then, the water will be directed towards the germ cells (embryo). Another area through which water could have entered in the initial stage of the process is through the ventral furrow, which also lacks testa (Freeman and Palmer, 1984). At the same time, at this stage, the husk cells in the whole grain will have begun to absorb water.

As the hydration process time increased, and according to what was described by McEntyre et al. (1998), the water already located in the germ cells will continue to migrate into the scutellum and then into the crushed cells layers. Simultaneously, the water that began entering the husk cells will continue to migrate into the pericarp, subsequently towards the testa and aleurone. Finally, the water transport that occurred through different routes will converge in the endosperm starting a second hydration stage, where an increase in moisture content occurs slowly and for long hydration times. This continuous increase in moisture, even in long hydration times can be attributed to

modifications that happen in the grain (Carvalho et al., 2018) during the hydration, reactions occur mainly by the action of enzymes, promoting the endosperm degradation and consequent formation of soluble sugars, resulting in higher entrance of water in the grain.

The effect of ultrasound application on barley hydration, as well as the adjustment of Peleg and Miano-Ibarz-Augusto models, are shown in Figure 4. This hydration kinetics behavior was also reported by Carvalho et al. (2018) during ultrasound-assisted barley hydration.

Although the Peleg model was commonly used to represent grain hydration processes, this model did not result in a good fit for the barley hydration (R^2 lower than 0.91 and MRE higher than 7.3%) (Figure 4A and Table 2). In contrast, it was observed that the MIA model presented better adjustment to experimental data of barley hydration, with R^2 higher than 0.998 and MRE lower than 1% (Table 2). Therefore, this suggests that the hydration of barley is not exactly asymptotic as proposed by the Peleg model, but rather occurs in two stages as proposed by the MIA model coinciding with the water transfer stages described above.

The B-US presented a slightly lower value for p parameter (MIA model), 0.3859 ± 0.0070 in comparison with a value of 0.4317 ± 0.0076 for the B-ST. However, it is important to highlight that the parameter p , which represents the water absorbed in the faster/shorter period of the process, is related to the equilibrium moisture. Therefore, because the equilibrium moisture (M_{eq}) of the B-US was higher, despite the p parameters being different in value (Table 2), the same amount of water (0.28 g of absorbed water/g) was absorbed in the first stage by both processes. The application of ultrasound did not affect the first or faster stage, of the hydration process (no differences in its kinetics parameter of MIA model, k_a). This is probably because this process is already fast, being difficult to improve.

On the other hand, ultrasound promoted higher absorption of water in the hardest stage of the process where the process resistances are greater, and the water absorption

is slow (kinetics parameter of MIA model, k_b). The water absorbed in the second hydration stage, when the ST process was used, was 0.36 g water absorbed/g d.m, while when the ultrasound-assisted process was used, it was 0.45 g water absorbed/g d.m. This improvement can be due to different mechanisms. As hydration time increased, the composition and structure were modified, resulting in softer tissues – as was described in section 3.1, which can favor the ultrasound action by facilitating the “sponge effect” and reducing the waves reflection. Additionally, the formation of microchannels is an important effect of ultrasound application which can improve the mass transfer (Miano, Alberto Claudio et al., 2016) and, in this case, not only in hydration properly, but in subsequent steps of malt production, as drying.

The hydration time to reach the desired moisture of 0.7 g/g (d.b.) was 14.6 h; similarly, Montanuci et al. (2013) showed barley took approximately 15 h to reach the moisture of 0.7 g/g (d.b.) at 20 °C. The water absorption by barley grains during rehydration was improved by the ultrasound application. As shown in Figure 4B, to reach the moisture of 0.70 g/g (d.b.), the application of ultrasound during the hydration reduced the processing time by 38%. Borsato et al. (2019) reported a reduction in barley hydration time of 33.3% when ultrasound was applied at 35 °C. In addition, Carvalho et al. (2018) and Guimaraes et al. (2020) also reported that the use of intermittent high-intensity ultrasound probe system can improve grain hydration, reducing the process time by 30 - 36% for barley and wheat.

Therefore, ultrasound can be used as an efficient tool to reduce the hydration time of barley. In addition, it is important to highlight that due to these mechanisms, ultrasound was not only able to increase the amount of water in barley grains but also could impact the further steps of malting, which has not been studied so far. Consequently, this work also evaluated the effect of ultrasound-assisted hydration of barley on its germination and drying.

3.2.2. Germination

Figure 5 shows rootlet (*RL*) and grain (*GL*) lengths during the germination process. The grain length remained practically constant during the germination, with approximately 0.85 - 0.90 cm, while there was a high rootlet growth, reaching 1.20 ± 0.35 and 1.40 ± 0.34 cm, for B-ST and B-US samples, respectively.

The ratio, given by the relation between the rootlet length and the grain length (*RL/GL*), is routinely used in malt industries to evaluate the germination process. The rootlet size of 1.5-2 times the grain length is considered to stop the germination and avoid the excessive hydrolysis of the endosperm (Schwarz and Li, 2010). In the present work, at the end of the germination process, a significantly higher *RL/GL* ratio was found for the B-US (1.62 ± 0.41) compared to the B-ST (1.35 ± 0.39) samples. In fact, the application of ultrasound resulted in the emergence of the rootlets right after the hydration process, at time 0 of germination.

Guimaraes et al. (2020) showed the application of ultrasound did not affect the final percentage of germinated wheat grains, while Miano et al. (2015) reported that ultrasound reduced the hydration time without affecting the germination and vigor of barley seeds. Furthermore, Miano, A. C. et al. (2016) reported that ultrasound not only accelerated the hydration of mung beans but also improved the germination due to two main mechanisms: the improvement of mass transfer and, consequently, the transport of water, gases and nutrients, and the activation of germination enzymes. In the case of barley malting, the improvement of mass transfer can also improve the transport of gibberellic acid, an important natural hormone precursor of germination.

Therefore, the use of ultrasound assisting the hydration process is a promising alternative to accelerate the germination process of barley, since at the end of the hydration process the metabolic activity in the grains has already begun, demonstrated by the early emergence of the rootlets. The impact of the subsequent drying, therefore, must be evaluated.

3.3. Convective drying

The kinetics of convective drying of barley and green malt, which were hydrated using static (ST) and ultrasound-assisted (US) methods, submitted or not to pre-treatment with ethanol, are shown in Figure 6. Therefore, three factors were evaluated to affect drying: the application of ultrasound during hydration, the malting process, and the pre-treatment with ethanol. Page model presented good adjustment to the experimental data of barley and malt drying, with R^2 higher than 0.99, and RMSE and MRE lower than 4.2 and 4.5%, respectively (Table 3).

The application of ultrasound during hydration resulted in a subtle effect on the drying process, suggesting a small reduction in the drying time, mainly for the barley, as shown in Figure 6C and Figure 7A, but with no statistical significance ($p > 0.05$). The major effect observed in the barley and malt drying was due to the pre-treatment with ethanol, which promoted a higher reduction in the processing time (Table 3).

Figure 7 shows the drying time to reach the moisture of 20, 15, 10 and 7% (w.b.) for the barley and malt grains, calculated using the parameters of the Page model.

For both barley and malt, the pre-treatment with ethanol was effective in reducing the time to reach 20% (w.b.) of moisture. This faster reduction for moisture contents below 20% is important due to the temperature sensibility of some compounds such as enzymes. Then, further drying is needed to stabilize the malt.

In fact, Figure 8 shows that the samples pre-treated with ethanol presented lower initial temperatures and faster heat-up, reaching higher temperatures earlier. This behavior is related to the higher vapor pressure of ethanol, and consequent ease of evaporation, and the absorption of energy from the surface of the sample for this phase change from liquid to vapor (Carvalho et al., 2020; Santos et al., 2021). Moreover, at same moisture contents, the surface temperature of the grains pre-treated with ethanol was lower, and the higher differences between samples with and without the pre-treatment with ethanol can be observed in higher moisture contents. Mainly, for the barley malt, this can be interesting because some enzymes, such as beta-amylase, are more sensitive to the temperature at higher moisture levels. Then, keeping the

temperature lower in this period can preserve the enzymatic activity of the malt – as described in the next sections.

Malt drying is conducted until smaller moistures, such as close to 7%. The pre-treatment with ethanol reduced the time to reach the moisture of 7% (w.b.) and the ethanol effect was again higher for barley grains. Regarding the control barley sample (B-ST), ethanol pre-treatment (B-ST+E) reduced the time by 26.2%, the ultrasound-assisted hydration (B-US) reduced the time by 11.7% and the ultrasound-assisted hydration followed by ethanol pre-treatment (B-US+E) reduced the time by 31.2%. For malt drying, the effect of ultrasound-assisted hydration (M-US) was lower, reducing the time by 10.3%. The pre-treatment (M-ST+E) and ultrasound-assisted hydration followed by ethanol pre-treatment (M-US+E) reduced the drying time by 17.0 and 17.2%, respectively.

This lower effect of ultrasound observed in the malt drying, can be attributed to the germination step between hydration and drying, already promoting big structural changes in the grain. This was evidenced in section 3.1 by the evaluation of grain's texture, where the modifications produced by germination were much greater than those produced by ultrasound, and the latter were overshadowed.

3.4. Impact of different strategies of malt production on malt quality

The activity of both alpha and beta-amylases, for the different treatments, is shown in Figure 9.

The alpha and beta-amylases activity in the dried barley were not affected by any applied treatment when compared to the *in natura* grain (IN). For *in natura* and dried barley grains, the alpha-amylase activity varied from 11.40 ± 1.40 to 14.80 ± 1.01 mg/g and the beta-amylase activity varied from 9.51 ± 0.67 to 15.14 ± 0.27 mg/g. However, when ethanol pre-treatment was applied to hydrated barley (B-ST+E, B-US+E), a slight decrease in amylase activity was observed compared to samples without ethanol (B-ST, B-US). Regarding the effect of ethanol on amylase enzymes, it has been reported that it

is dependent on the concentration of ethanol, where low concentrations favor reversible or irreversible inactivation, while high concentrations prevent calcium ionization of the active enzyme, favoring stability of α -amylase activity (Shirzadpour et al., 2015). Therefore, the decrease in the activity of amylase enzymes observed (Figure 9) were probably not related to the inhibitory effect of ethanol, but rather to an extraction effect of the surface enzymes, which at this stage of the process (after hydration) are not yet released into the inner endosperm.

As expected, the malt presented higher values of alfa-amylase activity than the barley grain, varying between 44.82 ± 2.5 and 49.39 ± 3.79 mg/g. Furthermore, the utilization of ultrasound during hydration increased the alpha-amylase activity in malt, regardless of the use of ethanol as pre-treatment, by approximately 7% for M-US and 9% for M-US+E, thus reaffirming that this increase in enzymatic activity influenced the decrease in the compression force of the malt (as described in section 3.1).

The behavior of beta-amylase activity was similar to alpha-amylase.

Yaldagard et al. (2007) also reported an increase in alpha-amylase activity of barley grains submitted to a pre-treatment with probe system ultrasound-for 5, 10 and 15 min at 30 °C and posteriorly submitted to malting. Borsato et al. (2019) also reported an increase in diastatic power, which is related to alpha- and beta-amylases, with the application of ultrasound during the barley hydration at 40 °C.

The increase in the activities of both amylases can be related to the modifications promoted by the ultrasound in the structure and metabolism of the grains, promoting the biosynthesis of enzymes.

It is important to mention that during the malting process, amylase enzymes are not the only ones responsible for structural and compositional modifications. According to what is described by Rani and Bhardwaj (2021), throughout the malting process, the enzymes that act first are the enzymes that hydrolyze the cell walls (such as Endo- β -(1-3,1-4)-glucanases) allowing the release of amylase enzymes (α - and β -amylases) and proteolytic enzymes, which rapidly increase their activity during the first stages of

germination. The complex activity of this entire enzyme system can be reflected in the effects on the pasting properties of barley and malt flour described below (Punia, 2020).

Figure 10 shows the analysis of barley and malt flours carried in the Rapid Visco-Analyzer (RVA). In this assay, the flour aqueous suspensions are heated and cooled to induce gelatinization and the initial gelling. The apparent viscosity evaluation over this assay complements the information regarding the modification in structure and enzymatic activity, discussed above.

The hydration of barley grain and subsequent drying reduced the apparent viscosity of the flour suspension (Figure 10A and Table 4) and decreased the compression force of the formed gels (Figure 10B). The Peak Apparent Viscosity (PAV) was reduced by 9 (B-ST), 6 (B-ST+E), 21 (B-US) and 16% (B-US+E), when compared with IN sample. Similarly, Trough Apparent Viscosity (TAV) was reduced by 30, 27, 45 and 41% and Final Apparent Viscosity was reduced by 15, 14, 33 and 29%, for the respectively aforementioned treatments. The compression force of the formed gels was, on average, 25% lower in comparison with IN sample, however, without significant difference between other the treatments (B-ST, B-ST+E, B-US, B-US+E), which can be due to hydrolyzing activity that already occurs with the hydration process. Barley grain naturally presents enzymes such as alpha (in minor quantity) and beta-amylases, proteases, and β -glucanases (Mayolle et al., 2012; Rani and Bhardwaj, 2021). Moreover, the hydration process, as mentioned before, is responsible for breaking the dormancy of the grain, starting its metabolism and enzymatic activity. The action of α - and β -amylases enzymes depend on the temperature, both amylases have optimal temperature for action, 65 to 75 °C for α - and 60 to 65 °C for β -amylases (Laus et al., 2022). Additionally, the hydrolyzation of malt starch by the amylases is conditioned by its gelatinization, which can occur at temperatures around 62 °C; however, it can vary with the type, composition, and characteristics of the malt starch (Langenaeken et al., 2019). Therefore, the heating during the assay promotes this hydrolytic action of enzymes in macromolecules, forming smaller chain molecules and reducing sugars,

decreasing the capacity of gelatinization, and gelling with consequent diminution in the apparent viscosity of the paste and compression force of the gel, respectively. This phenomenon is observed when the barley and malt flour are compared. In the malt flour, due to the higher action of the enzymes, the starchy endosperm is much more hydrolyzed and did not present the capacity to form gel.

The application of ultrasound during the hydration (B-US and B-US+E in Figure 10A) reduced the apparent viscosity by 21% and 16%, respectively. Considering that it was previously observed that ultrasound does not affect significantly the activity of amylase enzymes (Figure 9), the decrease in apparent viscosity could be because the ultrasound applied during hydration could promote the activity of other types of enzymes such as cell wall hydrolases, which are the first to exert their activity by digesting components of the cell wall that have high viscosity such as β -glucans (Rani and Bhardwaj, 2021).

Cui and Zhu (2020) reported the effect of application of ultrasound on the pasting properties of commercial wheat flour. The apparent viscosity was reduced with the application of the ultrasound and, increasing in the application time (from 2 to 12 hours), promoted higher reduction on the apparent viscosity, attributing the reduction in the crystallinity and creating defects on granules, which can promote the penetration of water and reduction of the pasting properties. Instead of most of the studies evaluate the application of ultrasound on the flour or extracted starch, in the present work, even evaluating the whole flour, it was possible to observe similar effect of the ultrasound application, reducing the pasting properties and corroborating with the hypothesis of modification on structure of the product.

On the other hand, the treatment with ethanol resulted in a slight increase in apparent viscosity. This could be because ethanol extracted small amounts of enzymes and/or inhibited the enzymatic activity. In fact, Figure 9 shows that the treatments with ethanol are the ones that presented the lowest amylase enzyme activity.

For malt flour, pasting properties values were lower than those properties of barley, being more evidenced in treatments with ultrasound, where regarding M-ST the apparent viscosity was reduced by 21% and 14% for M-US and M-US+E, respectively. These results agreed with the results of the enzymatic activity of amylases (Figure 9), which was higher for the treatments with ultrasound-assisted hydration. Amylases hydrolyzed starch from endosperm into fermentable sugars, which were responsible for the observed poor pasting properties and inability to form a gel.

This reduction could be interesting for further applications of the malt in beverages, for example, as it can facilitate the mashing step, where the enzymes, which had increased activity by ultrasound, hydrolyze the starch, which also presented higher modification and could be easily accessed.

In summary, ultrasound-assisted hydration improved the hydration and germination processes (accelerating both processes), while pre-treatment with ethanol helped to accelerate drying without negative effects on the activity of the malt enzymes. In this regard, it was observed that with the use of ultrasound, there was an increase in the enzymatic activity of amylases and a decrease in paste properties in the malt flour, which indicated that there was a greater production of fermentable sugars, being beneficial for the subsequent processes of production of alcoholic beverages.

Although further studies need to be carried out for scale up, since malt processing usually involves large amounts of product, the ultrasound is considered a non-destructive, low-cost, and relatively simple technique to improve the process. However, there are some difficult in relation to the homogeneity of the cavitation effect, mainly in large scales (Arruda et al., 2021). The utilization of a system similar to the ultrasonic bath system to assist the hydration of barley, since this process occurs in tanks, could be reliable using several ultrasonic transducers in different points of the tank, ensuring higher homogeneity and improved action of this technology.

The ethanol pre-treatment also could be easily applied, placing the product in a tank with ethanol, which demands shorter times of pre-treatment to provide significant

reduction in the drying time, which is the stage which requires the most energy in malt processing. However, expanding investigations in relation to the conditions of the pre-treatments, costs and reutilization of the ethanol are needed, since this is the first study applying this pre-treatment in malt, and, additionally, complementary research exploring other conditions of processing, aiming to optimize even more the malt production.

Therefore, , ultrasound and ethanol can be suitable technologies to be applied to the malt production - highlighting the ethanol pre-treatment to drying is a very simple and relatively cheap technique to be employed, showing interesting results regarding reduction of drying time and low-temperature maintenance of the malt when the product is more sensible, at the beginning of the process.

4. Conclusions

This work evaluated the effect of ultrasound-assisted hydration of barley grains and the pre-treatment to drying using ethanol in the malting process and malt quality.

The texture of barley and malt grains showed the changes in the structure and composition that occur throughout the different stages of the malting process, where the application of ultrasound during hydration and germination makes the grain more friable (compression force decreases). The use of ultrasound-assisted hydration favored the second stage of hydration, where the inherent structure of the grain is the limiting factor, allowing an increase in the amount of water absorbed and reducing the time necessary to reach the required moisture in the grains (0.70 g/g d.b.) by 38%. During germination, ultrasound-assisted hydration accelerated the process and increased rootlet length. On the other hand, by using ultrasound-assisted hydration followed by ethanol pre-treatment, the drying time was reduced by 31.2% and 17.2% to achieve a moisture content of 7% (w.b) during the drying of barley and malt respectively. Additionally, the use of ultrasound increased the α -amylase enzyme activity in malt by up to 9% and decreased the paste properties such as the apparent viscosity of the barley and malt flour by up to 21%. In summary, the results demonstrated that ultrasound improved

hydration, and increased the enzymatic activity of alpha and beta amylases, which agreed with what was observed in the texture, germination and pasting properties and the pre-treatment with ethanol reduced significantly the drying time, being an interesting alternative to reduce the energy consumption of the malt processing. Furthermore, it is recommended to better explore the effect of ultrasound on the distribution of water inside the grain during hydration, as well as on the activity of other types of enzymes, in addition to amylases, and other grains whose germination is desired. Scale up and economical evaluations are also suggested.

Nomenclature

AV = malt extract aliquoted volume [mL] (Equation 1)
 B = Barley
 $C_{maltose}$ = concentration of equivalent of maltose [g/L] (Equation 1).
d.b. = Dry basis (g water/g dry matter).
 E = Ethanol pre-treatment.
 EV = total volume for the extraction process [mL] (Equation 1)
 F = Dilution factor (Equation 1).
 IN = *In natura*, raw barley grain.
 k_a = global mass transfer parameter at the first stage of the process [min^{-1}] (Equation 3).
 k_b = global mass transfer parameter at the second stage of the process [min^{-1}] (Equation 3).
 k_1 = Constant rate of Peleg model [$\text{min} \cdot \text{g} / \text{g} \text{ db}^{-1}$] (Equation 2).
 k_2 = Constant of capacity of Peleg model [$\text{g} / \text{g} \text{ db}^{-1}$] (Equation 2).
 k_p = Drying rate parameter of Page model [min^{-n}] (Equation 4).
 M = Malt.
 M_t = Moisture content along processing time (t) (Equation 2 and 4).
 MR = Dimensionless moisture ratio (Equation 4)
 M_0 = Initial moisture content (Equation 2 and 4).
 M_∞ = Equilibrium moisture content [$\text{g} / \text{g} \text{ d.b.}$] (Equation 3 and 4).
 m_{malt} = mass of malt used for extraction [g] (Equation 1).
 n = dimensionless drying parameter of Page model (Equation 4).
 p = is the fraction of water absorbed in the fast or short process (Equation 3).
 ST = Static or conventional hydration method.
 TV = total volume during the reaction [mL] (Equation 1)
 U = enzymatic activity [mg of maltose equivalents/g of malt] (Equation 1).
 US = Ultrasound-assisted hydration method.
w.b. = Whet basis (g water/g sample).

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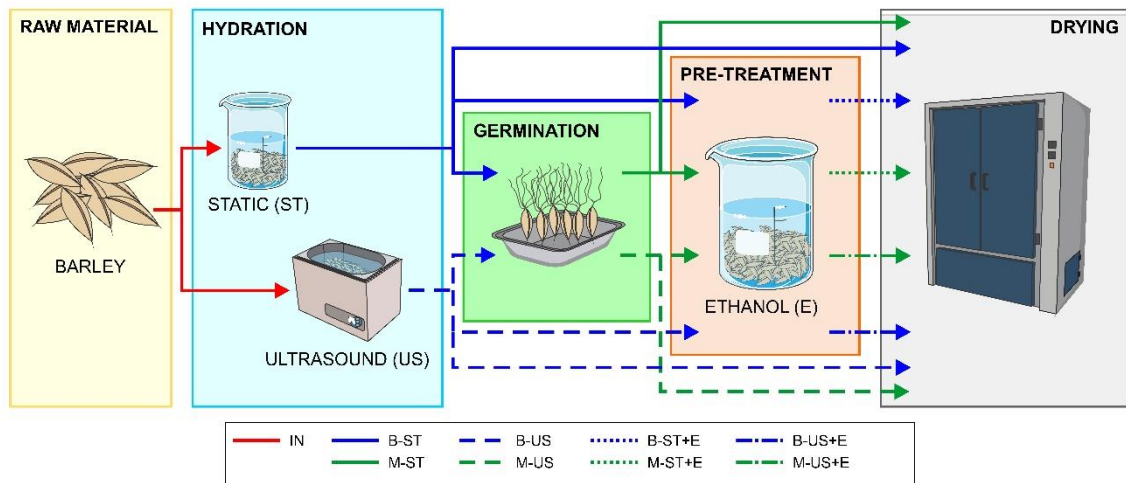


Figure 1. Illustrative representation for barley and malt processing with static (ST) and ultrasound-assisted (US) hydration, pre-treatment with ethanol (E) and convective drying (CD). The description of each treatment code is shown in Table 1.

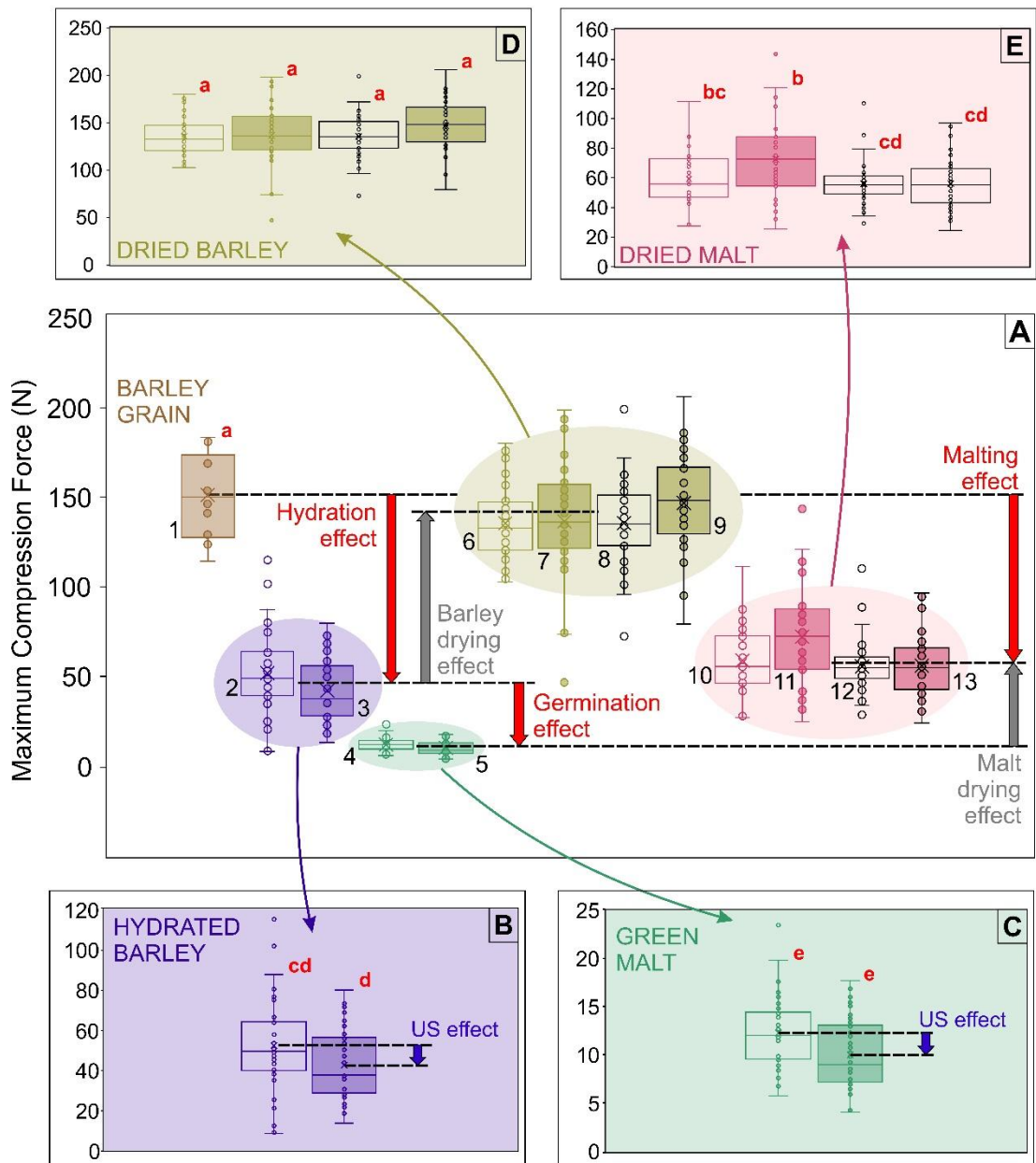


Figure 2. A) Maximum force (in N), to compress the barley and malt grains through the malting process. Highlighting the hydrated barley (B), green malt (C), dried barley (D) and dried malt (E) and the effects of each processing step. (Where 1: IN; 2: B-ST; 3: B-US; 4: M-ST; 5: M-US and, after drying, 6: B-ST; 7: B-ST+E; 8: B-US; 9: B-US+E; 10: M-ST; 11: M-ST+E; 12: M-US; 13: M-US+E).

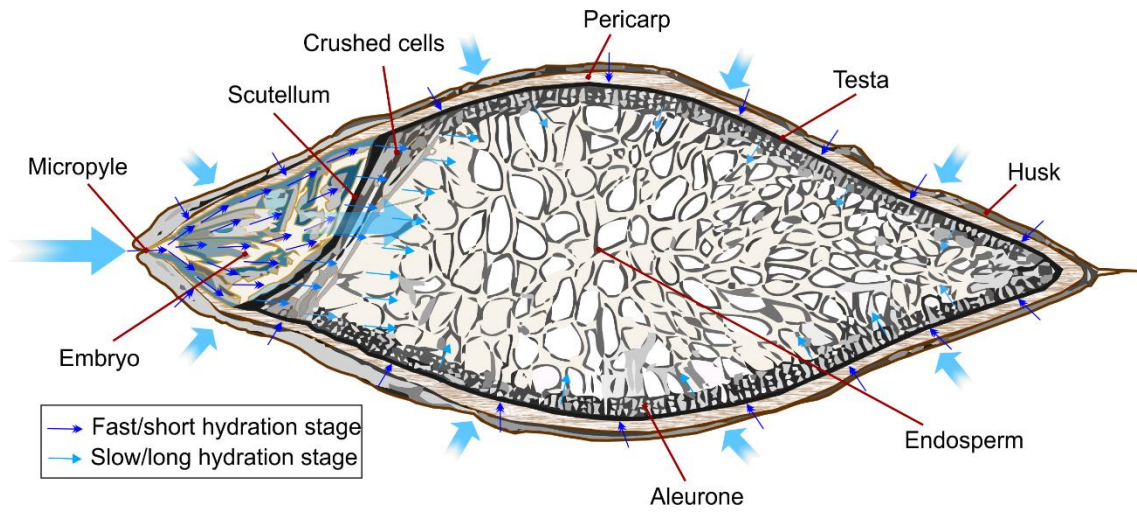


Figure 3. Representation of tissues and water transfer stages during hydration of barley grain.

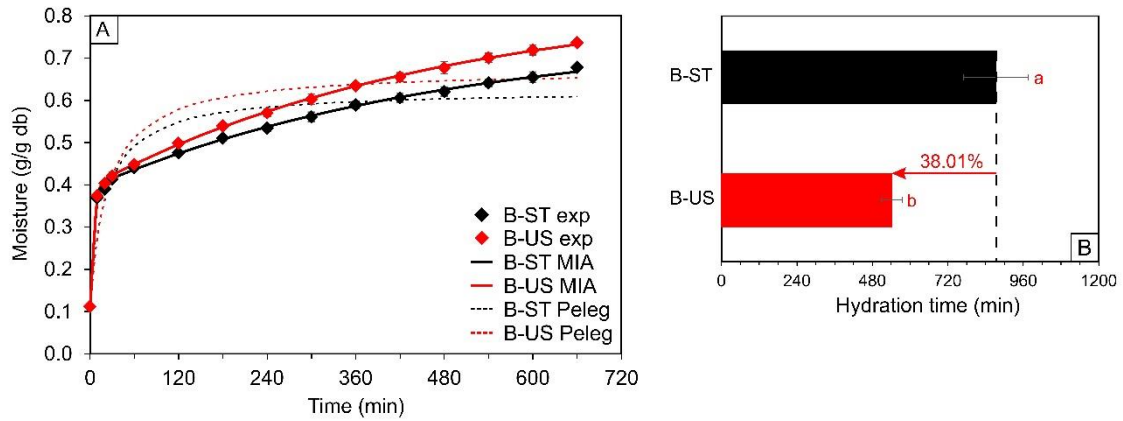


Figure 4. (A) Hydration kinetics of barley with static method (ST) and assisted by ultrasound (US). Average \pm standard deviation. The curves are the Peleg (dashed, Equation 2) and Miano-Ibarz-Augusto (continuous, Equation 3) models. (B) hydration time, predicted with MIA model, to reach the target barley grain moisture of 0.70 g/g in dry basis. Average \pm standard deviation, the different letters represent significant differences ($p < 0.05$) between the conditions.

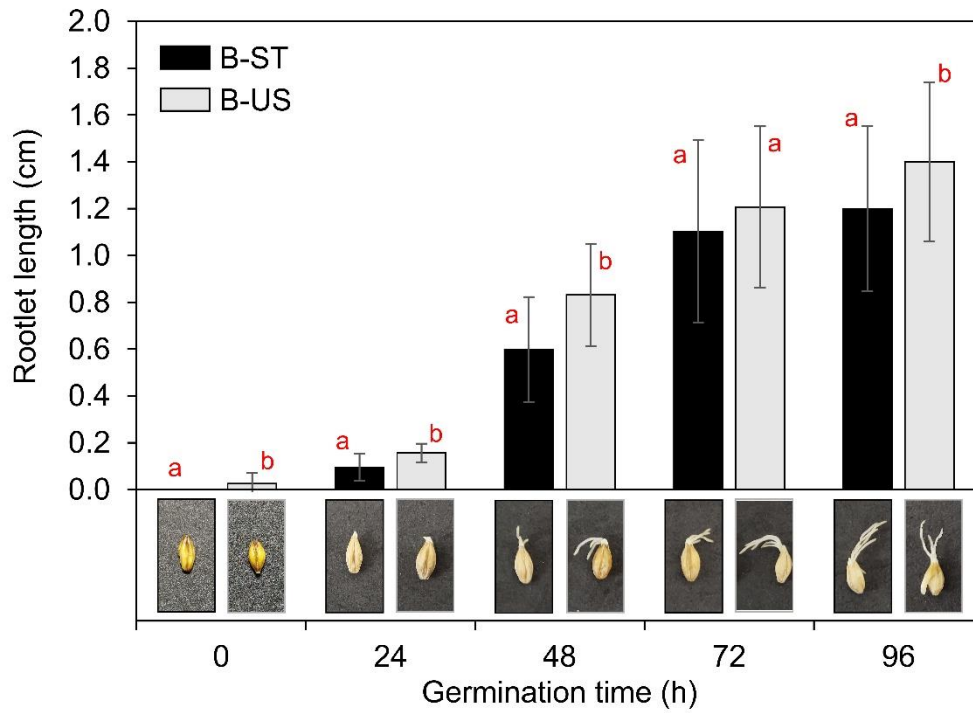


Figure 5. Rootlet length during the germination represented by the black (B-ST) and grey (B-US) bars (Average \pm standard deviation). *Different letters represent significant differences ($p < 0.05$) between the conditions.

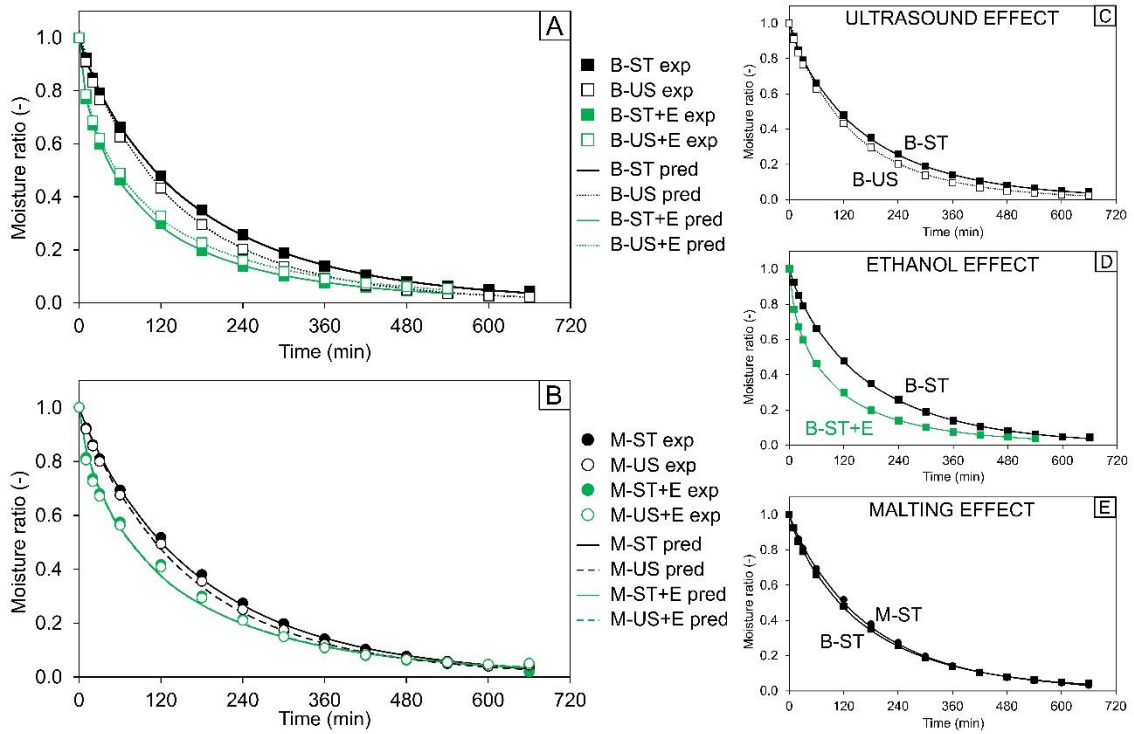


Figure 6 – Kinetics of convective drying of barley and green malt at 50 °C and 1 m/s. Effect of hydration assisted by ultrasound and pre-treatment with ethanol for drying. *Dots represent the experimental data and curves represent the Page Model.

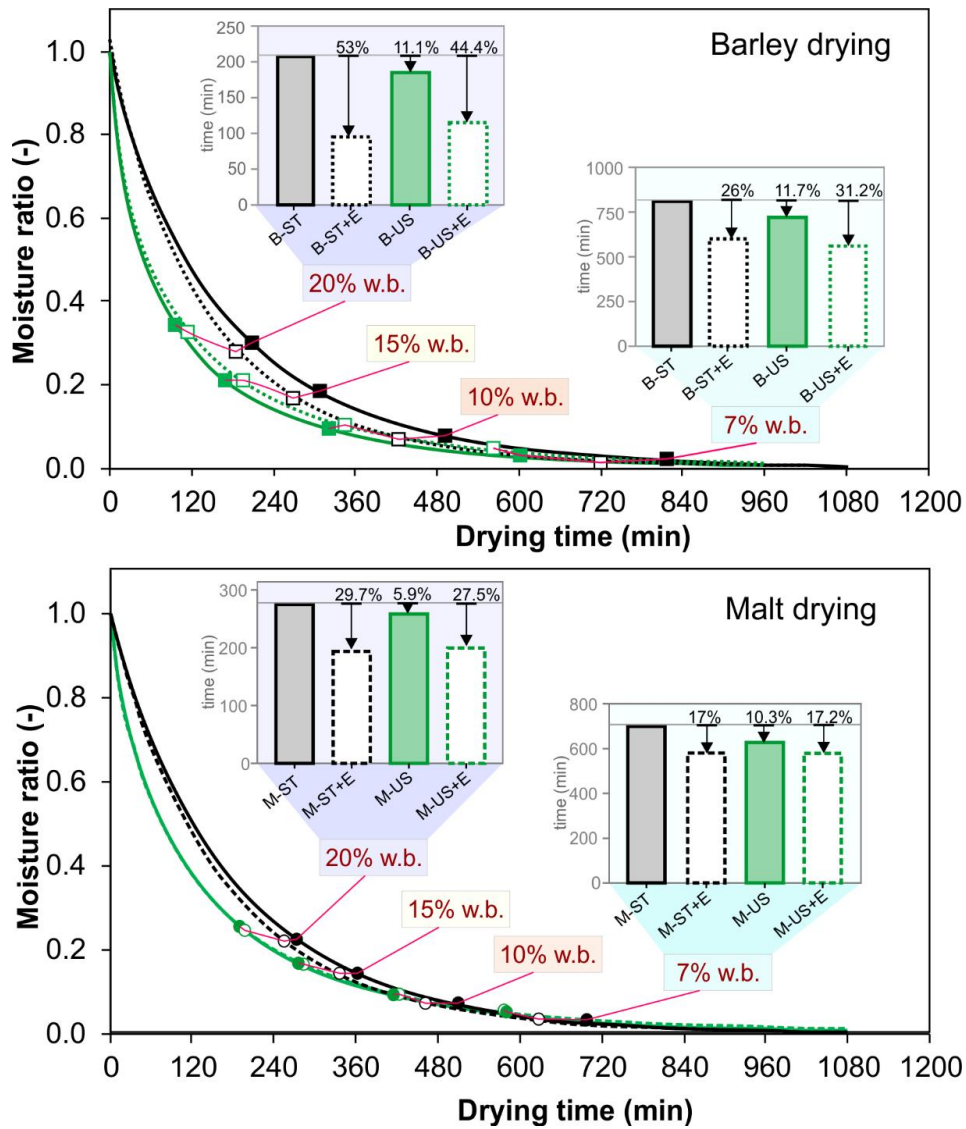


Figure 7. Drying time to reach the moisture of 20, 15, 10 and 7% in wet basis (w.b), during drying of (A) barley and (B) malt grains. Inserted graphs detail the reductions in drying time for moisture of 20% and 7% compared to controls.

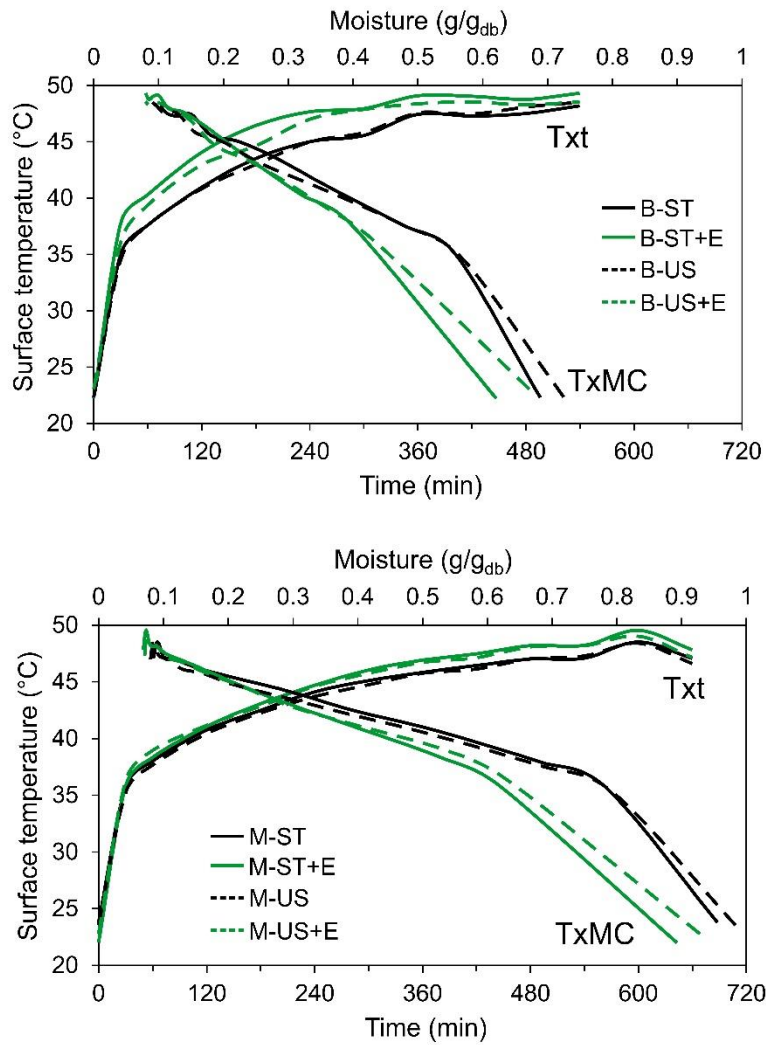


Figure 8. Surface temperature (T) and moisture content (MC) over the drying time (t) of barley and malt.

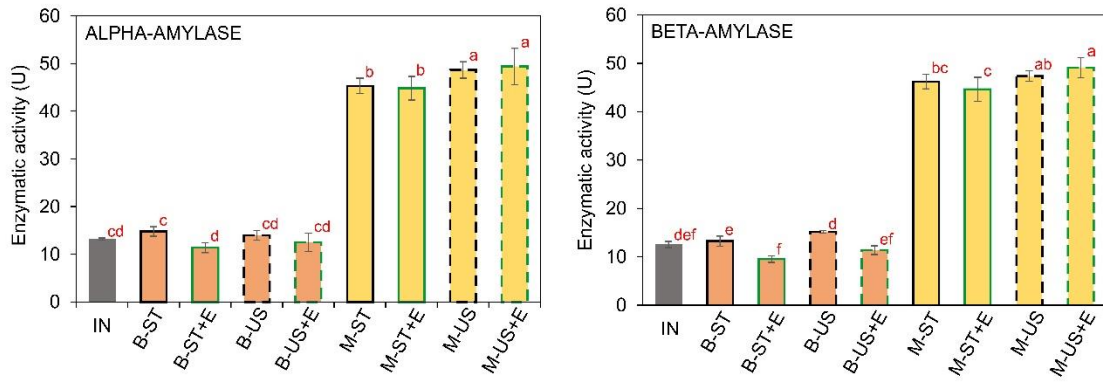


Figure 9. Alpha-amylase and Beta-amylase activities on barley and malt. Different letters represent significant difference ($p < 0.05$) among the treatments. Table 1 presents the description of the codes for each treatment.

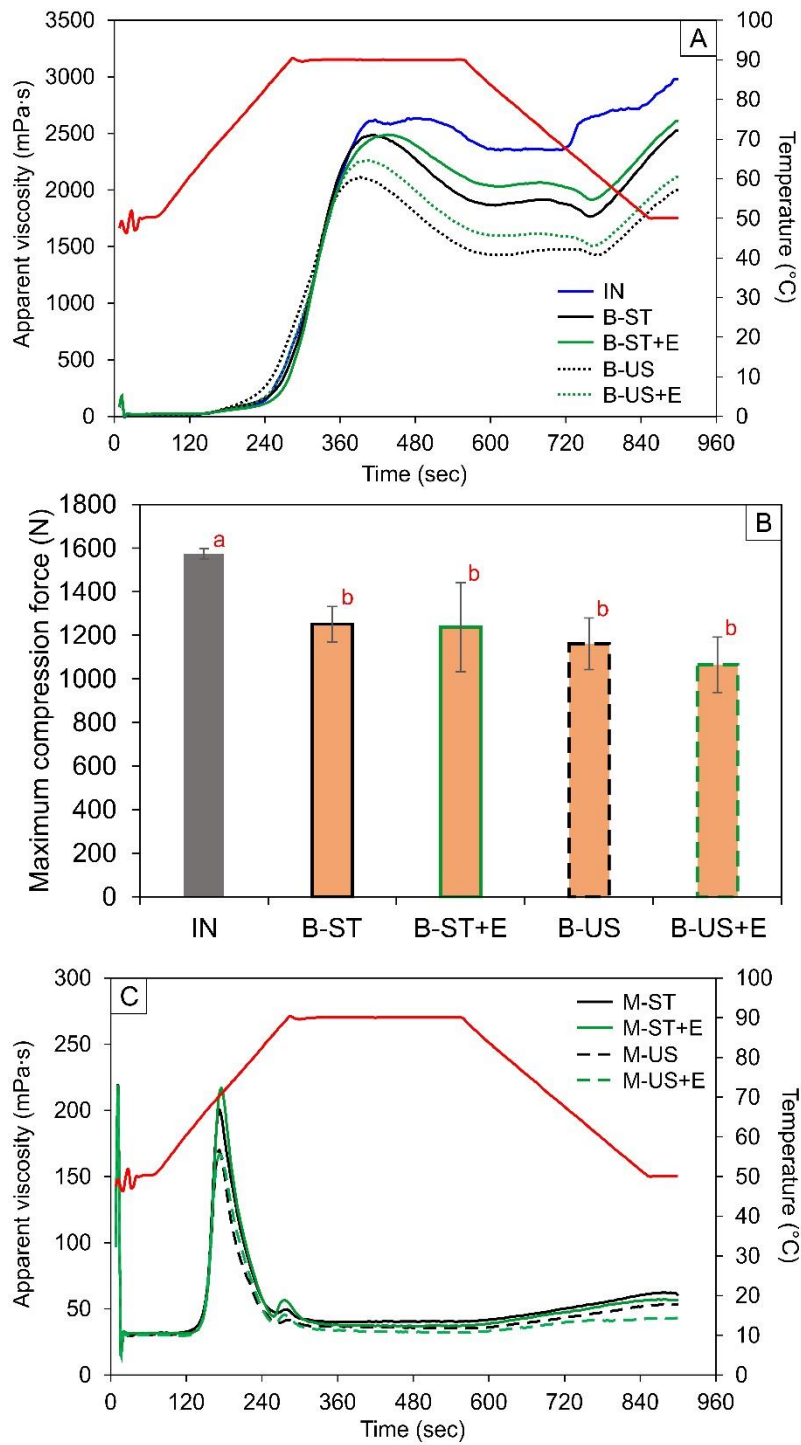


Figure 10. (A) Pasting profile of barley flour; (B) Maximum compression force (in N) of barley flour gels; and (C) Pasting profile of malt flour.

Table 1. Description of the performed treatments.

Treatment code	Description
IN	In natura barley
B-ST	Barley hydrated with conventional, static method (ST)
B-ST+E	Barley hydrated with conventional, static method (ST) and pre-treated with ethanol (E).
B-US	Barley with ultrasound-assisted hydration.
B-US+E	Barley with ultrasound-assisted hydration and pre-treated with ethanol (E).
M-ST	Malt produced from B-ST barley.
M-ST+E	Malt produced from B-ST+E barley.
M-US	Malt produced from B-US barley.
M-US+E	Malt produced from B-US+E barley.

Table 2 – Adjustment parameters of Peleg and Miano, Ibarz & Augusto (MIA) models to experimental data of barley hydration.

Model	Parameter	B-ST	B-US
<i>Peleg</i>	k_1	40.88(1.84) ^a	43.48(2.98) ^a
	k_2	1.952(0.074) ^a	1.784(0.027) ^b
	R_0	0.0245(0.0011) ^a	0.0231(0.0016) ^a
	M_{eq}	0.6250(0.0195) ^b	0.6727(0.0085) ^a
	R^2	0.9040	0.8960
	$RMSE$ (%)	4.54	5.28
	MRE (%)	7.37	8.31
<i>MIA</i>	p	0.4317(0.0076) ^a	0.3859(0.0070) ^a
	k_a	0.2202(0.0152) ^a	0.2235(0.0147) ^a
	k_b	0.0021(0.0001) ^a	0.0021(0.0001) ^a
	M_{eq}	0.7620(0.013) ^b	0.8457(0.0207) ^a
	R^2	0.9987	0.9993
	$RMSE$ (%)	0.5154	0.4240
	MRE (%)	0.7024	0.5207

Data are represented as average (standard deviation). *Different letters in the same line represent significant differences in the model parameters for the hydration ST and US, obtained by ANOVA followed by the Tukey test ($p < 0.05$).

Table 3 – Adjustment of Page Model: model parameters and adjustment parameters.

Page Model parameters				
Treat	MC_0 [g/g d.b.]	MC_{eq} [g/g d.b.]	k [min⁻ⁿ]	n [-]
B-ST	0.6891(0.0298) ^{bc}	0.0633(0.0064) ^{ab}	0.0111(0.0018) ^c	0.8809(0.0238) ^a
B-US	0.7251(0.0105) ^b	0.0672(0.0064) ^a	0.0115(0.0021) ^c	0.9053(0.0236) ^a
B-ST+E	0.621(0.027) ^c	0.0591(0.0059) ^{abc}	0.0528(0.056) ^a	0.66(0.0157) ^{bc}
B-US+E	0.6722(0.0183) ^{bc}	0.0466(0.0089) ^{abc}	0.0527(0.0103) ^a	0.6465(0.0419) ^c
M-ST	0.9558(0.074) ^a	0.049(0.0143) ^{abc}	0.0079(0.0017) ^c	0.9377(0.0389) ^a
M-US	0.9833(0.0491) ^a	0.0473(0.0221) ^{abc}	0.0076(0.002) ^c	0.9639(0.0140) ^a
M-ST+E	0.8931(0.0559) ^a	0.0354(0.0129) ^{bc}	0.0302(0.0068) ^b	0.7307(0.0433) ^b
M-US+E	0.9285(0.0408) ^a	0.0322(0.0121) ^c	0.0321(0.0093) ^b	0.7213(0.0596) ^{bc}
Adjustment parameters				
Treat	R^2 [-]	RMSE [%]	MRE [%]	
B-ST	0.9998	0.6154	0.9148	
B-ST+E	0.9995	0.4619	1.2286	
B-US	0.9996	0.4668	1.1602	
B-US+E	0.9995	0.4781	1.7559	
M-ST	0.9992	1.0257	2.0238	
M-ST+E	0.996	1.9148	4.2278	
M-US	0.999	1.1548	2.3428	
M-US+E	0.9964	1.9058	4.1477	

*Average(standard deviation). **Different letters in the same column represent significant differences ($p < 0.05$) between means of treatments.

Table 4. Pasting properties of barley and malt flours.

	PAV [mPa·s]	TAV [mPa·s]	BD [mPa·s]	FAV [mPa·s]	SB [mPa·s]	PT [°C]
IN	2702.7 (78.8) ^A	2689.0 (29.6) ^A	13.7 (58.3) ^A	2977.3 (17.9) ^A	288.3 (26.6) ^C	83.83 (0.03) ^{AB}
B-ST	2464.3 (289.19) ^A	1882.4 (99.9) ^B	581.9 (234.2) ^B	2529.6 (121.1) ^A	647.2 (32.8) ^A	85.18 (1.30) ^{AB}
B-ST+E	2529.1 (494.5) ^A	1960.1 (250.0) ^B	569.0 (257.6) ^B	2571.8 (301.0) ^A	611.7 (53.3) ^A	86.14 (0.90) ^A
B-US	2125.3 (355.3) ^A	1474.0 (232.8) ^C	651.3 (123.5) ^B	2571.6 (1996.9) ^B	522.9 (65.3) ^B	80.37 (2.37) ^C
B-US+E	2266.8 (323.2) ^A	1580.0 (219.2) ^C	686.8 (106.0) ^B	2112.8 (263.5) ^B	532.8 (44.6) ^B	83.36 (1.22) ^B
M-ST	158.1 (17.6) ^{ab}	55.38 (5.40) ^a	102.8 (17.9) ^{ab}	62.00 (5.18) ^a	6.63 (0.74) ^a	66.91 (0.47) ^a
M-ST+E	172.3 (31.6) ^a	52.14 (5.61) ^a	120.1 (31.7) ^a	56.71 (6.05) ^a	4.57 (2.76) ^{ab}	67.50 (0.81) ^a
M-US	125.6 (11.8) ^b	47.88 (4.76) ^{ab}	77.8 (14.1) ^b	53.13 (4.26) ^a	5.25 (1.04) ^{ab}	67.33 (1.28) ^a
M-US+E	136.7 (14.7) ^{bc}	40.29 (9.69) ^b	96.4 (16.8) ^{ab}	43.00 (10.42) ^b	2.71 (2.43) ^b	67.65 (1.42) ^a

PAV: Peak apparent viscosity; TAV: Trough apparent viscosity; BD: Breakdown; FAV: Final apparent viscosity; SB: Setback; PT: Pasting temperature.