



# Hydration of broken carioca beans: Kinetics and changes in composition and techno-functional properties

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## ABSTRACT

Maceration of bean grains reduce antinutritional substances and cooking time. The hydration of broken beans differs from that of whole beans due to their larger surface area and the absence of seed coat resistance to water penetration. Therefore, the aim of this work was to investigate the effect of temperature on the hydration kinetics of broken carioca beans and the chemical composition, and techno-functional properties of macerated flour. The hydration curve of broken grains showed no lag phase due to their larger surface area and exposed interiors. The hydration time decreased with the temperature rise and was shorter for broken beans compared to whole grains, while the equilibrium moisture content was similar. The protein, ash, carbohydrate, and lipid content of flours did not differ significantly between untreated and macerated flours. Phytic acid and moisture content were reduced in the macerated flour. Techno-functional properties remained unchanged, however the macerated showed higher viscosity and setback values obtained by rapid visco analyzer and produced a firmer and more adhesive gel. Off-flavor compounds from aldehyde, alcohol, ketone, and furan classes were more prevalent in the macerated flour, probably due to increased oxidation during processing. The results presented in this work show how hydration affects broken carioca beans providing information for improving the processing efficiency and quality of carioca bean byproducts.

## 1. Introduction

The carioca bean, characterized by its light cream color and light brown streaks, is the most widely cultivated bean in Brazil (Bento et al., 2022). The Brazilian food industry has shown interest in using carioca bean as a food ingredient, mainly due to their low cost and high availability of non-standard grains. These include broken grains that result from processing and handling and hardened beans from storage under high temperature and humidity (Los et al., 2018, 2020). Halves and broken grains refer to healthy bean seeds that have been split into their cotyledons due to the rupture of the seed coat. These fragments, resulting from mechanical processing or handling (harvesting, drying, cleaning, and sorting), do not pass through a sieve with circular openings measuring 5 mm (Brasil, 2008). This byproduct can be milled and used as flour by the food industry since it preserves the same characteristics as whole beans and has a lower cost.

Bean-derived flours can be utilized in a wide range of products,

including leavened goods like bread and cakes, deep-fried snacks, baked items such as crackers and cookies, as well as beverages, meat products, and dressings (Nartea et al., 2023). Understanding the technological and physicochemical properties of this ingredient is essential to enhance food quality and meet consumer demands (Bento et al., 2022). Key technological properties studied for whole flours include rapid viscosity analysis (RVA), texture, water and oil retention capacity, emulsifying capacity, and foaming capacity. These properties are crucial for define potential ingredient applications and impact the processing and final characteristics of developed products (Bento et al., 2022; de Paiva Gouvêa et al., 2023; Du et al., 2014).

When processing beans, soaking is recommended to reduce antinutritional substances (Mubarak, 2005; Rawat and Saini, 2022) and is commonly used to reduce cooking time (Munthali et al., 2022; Stefan et al., 2014). This process, that consists in immersing the food in water, is a mass transfer operation involving diffusion, capillarity, and specific water flow pathways in foods (Miano et al., 2018c). The beans hydration

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kinetics depending on variety, composition, temperature, pH, and salt addition (Bento et al., 2021b; Miano et al., 2018; Oladele et al., 2018; Stefan et al., 2014). Kinetic constants are often determined using Peleg (1988a) and Kaptso et al. (2008) models to analyze water absorption behavior, providing insights into the rate and extent of hydration.

Despite the increasing use of broken beans, there remains a lack of studies on their hydration kinetics and their impact on flours produced from raw, broken carioca beans. Most existing research focuses on the hydration kinetics of whole beans (Miano et al., 2018b, 2019; Oladele et al., 2018) and the effects of soaking on cooking time, protein digestibility, and the reduction of antinutritional compounds (Fernandes et al., 2011; Stefan et al., 2014; Vanier et al., 2019). In terms of broken beans, Bento et al. (2021a) examined the effects of soaking on the physical and technological properties of pre-gelatinized flours. However, their hydration time was fixed at 6 h, and the hydration kinetics were not analyzed. No studies have specifically investigated the hydration kinetics and its influence on the physical-chemical composition, techno-functional properties and volatile profile of broken carioca beans.

Broken grains present increased surface area exposed to water and higher diffusion coefficient than whole seed (Prasad et al., 2010). Consequently, it is expected that broken carioca beans will exhibit different hydration kinetics compared to whole beans. Therefore, the aim of this work was to investigate the effect of temperature on the hydration kinetics of broken carioca beans and evaluate the soaking process effect on composition, techno-functional properties, and volatile compounds profile of broken carioca bean flour.

## 2. Material and methods

### 2.1. Material

The broken carioca beans (*Phaseolus vulgaris* L.) and soy oil were purchased on the local market (Campinas, Brazil). The microbiological and mycotoxin results of the sample is presented in the Supplementary material (Table S1). Bradford reagent, Dowex G-55 chloride form resin, and phytic acid were purchased from Sigma-Aldrich (St. Louis, USA). All other chemicals were of analytical grade and solutions were prepared with deionized water (Permuton, Curitiba, Brazil).

### 2.2. Hydration kinetics

The whole and halved grains were obtained from the same batch and the halves were carefully separated using a scalpel. Approximately 10 g of samples and 400 mL of with deionized water were used. The halves and whole beans were hydrated at 20, 30 and 40 °C controlled by an ECO Gold immersion thermostat with water circulation (Lauda DR.R. Wobser GMBH and Co. KG, Lauda-Königshofen, Germany) in individual containers from 5 min to 16 h. After the hydration process, the samples were removed from the solution, drained with the aid of a sieve and superficially dried with absorbent paper to remove surface water. The moisture content was determined by mass balance based on the mass of the hydrated product and initial moisture of the sample that were 14.93 and 12.65% d.b for half and whole beans, respectively. The hydration kinetics data of the grains were adjusted to Equations (1)–(3), described by Peleg (1988a), Kaptso et al. (2008) and Weibull (Cunha et al., 1998; Montanuci et al., 2015), respectively. The data were fitted to the mathematical models by using the Statistica 14 (Tibco, Palo Alto, USA) with a confidence level of 95% using the Levenberg–Marquardt algorithm.

$$M_t = M_0 + \frac{t}{k_1 + k_2 \times t} \quad (1)$$

$$M_t = \frac{M_\infty}{1 + \exp[k(t - \tau)]} \quad (2)$$

$$M_t = M_0 - \left\{ (M_0 - M_\infty) \times \left[ 1 - \exp \left( -\frac{1}{\beta} \right)^\alpha \right] \right\} \quad (3)$$

Where:  $M_t$ : dry basis moisture;  $M_0$ : initial moisture;  $M_\infty$ : equilibrium moisture content;  $t$ : hydration time;  $k_1$ : hydration rate constant;  $k_2$ : related to the equilibrium moisture;  $k$ : hydration rate constant;  $\tau$ : time required to achieve half saturation of the seeds;  $\alpha$ : shape parameter;  $\beta$ : scale parameter.

### 2.3. Preparation of untreated and macerated carioca bean flour

Untreated broken carioca bean flour (CBF) was obtained by ground in a knife granulator mill from the manufacturer Treu (Rio de Janeiro, Brazil) using 3.2 mm followed by 0.75 mm sieves. For the preparation of macerated carioca bean flour (MCBF), the grains were selected, washed in hypochlorite solution (1%) to sanitize the surface of the beans and left to soak in distilled water in a ratio of 1:5 for 3 h at 20 °C (equilibrium found based on hydration kinetics). After maceration, the beans were dried in an oven with air circulation at 50 °C and ground as described for CBF resulting in the macerated carioca bean flour (MCBF).

### 2.4. Physicochemical characterization of carioca beans

The moisture, protein, lipid, and ash contents were determined according to the methodologies described in AOAC (2009) and (IAL, 2008), and the carbohydrate content was calculated by difference. Phytic acid quantification was performed using the method of Latta and Eskin (1980), where phytic acid was concentrated by adsorption on an ion exchange column (Harland and Oberleas, 1977). Water activity was measured using a dew point hygrometer Aqualab Lite (Decagon Devices, Pullman, Washington, USA). The particle size of flour dispersed in ethanol was determined by laser diffraction (L950, Horiba Instruments, Inc., Kyoto, Japan). The content of damaged starch was obtained by the amperometric AACC approved method 76–33.01 (AACC, 2010) using the SD Matic equipment (Chopin, Villeneuve-la-Garenne, France). The color analysis of flours and protein concentrates were performed using a Minolta colorimeter (model CR 300, Konica Minolta, Tokyo, Japan), where  $L^*$  (lightness, ranging from 0 for black to 100 for white),  $a^*$  (green to red scale), and  $b^*$  (blue to yellow scale) parameters were determined.

### 2.5. Techno-functional properties

The technological functional properties of the carioca bean flours evaluated were: protein solubility (PS), water (WRI) and oil (ORI) retention index, emulsifying (EC) and foaming (FC) capacity. The PS was determined in flour suspension (1%) at pH 3 to 9 using NaOH or HCl. The suspension was homogenized for 30 min using a rotary shaker (Tecnal, Piracicaba, Brazil) and then centrifuged at 5000 rpm for 15 min (Hettich Centrifuge, Westphalia, Germany). The soluble proteins of the supernatant were quantified using the Bradford method (Bradford, 1976). Considering that all proteins are soluble at high pH, a control sample, representing 100% solubility, was prepared in 0.1 M NaOH (de Paiva Gouvêa et al., 2023).

The determination method for WRI (water retention index) and ORI (oil retention index), described by Anderson et al. (1969), was used with some modifications. To each 1g of flour, 25 mL of water or oil was added. The samples were stirred for 30 min using a rotary shaker (Tecnal, Piracicaba, Brazil) and then centrifuged (5000 rpm/15 min, Hettich Centrifuge, Westphalia, Germany). The WRI and ORI values were defined as the weight of water or oil absorbed per gram of the sample.

The emulsion and foam were prepared as described by de Paiva Gouvêa et al. (2023). The emulsion was prepared using 60 mL of flour suspension (0.3% of protein) at pH 7 and 20 mL of soy oil. The mixture was emulsified in an Ultra-Turrax (9500 rpm/1 min, probe S 25 KV-18

G, Ika Staufen, Germany). The emulsion was transferred to a test tube and analyzed using the Turbiscan MA 2000 (Formulation, Toulouse, France) at 25 °C for 30 min to determine creaming speed (CS). Emulsifying capacity (EC) was defined as the percentage of mass of the emulsified phase separated after centrifugation (5000 rpm/15 min). The foam was prepared using 30 mL of flour suspension at pH 7.0 (1.5% of protein) homogenized using an Ultra-Turrax at increasing speeds (6500 rpm/30 s, 9500 rpm/30 s, and 13500 rpm/1 min). Foaming capacity (FC) was defined as the percentage of foam volume after homogenization minus the initial sample volume divided by the initial sample volume.

## 2.6. Pasting and texture properties of bean flours

The pasting properties of the CBF and MCPF were analyzed using an RVA (Rapid Visco Analyzer, RVA 4500, Warriewood, Australia) according to the AACC approved method 76.21-01 (AACC, 2010). Samples (3.5 g) with moisture correction to 14% prepared in 25 mL of distilled water were heated from 50 °C to 95 °C, and then cooled from 95 °C to 50 °C. The gel obtained from the RVA analysis was kept in the aluminum cup, covered with PVC film, and stored at 5 °C for 24 h. The gel texture was analyzed using a Texture Analyser TAXT2i (Stable Micro Systems Ltd., Godalming, UK) with a cylindrical acrylic probe (25 mm high). The test conditions were as follows: pre-test and post-test speeds of 2 mm/s, a test speed of 0.8 mm/s, 40% strain, and a trigger force of 0.049 N. The texture parameters included hardness, adhesiveness, elasticity, and cohesiveness.

## 2.7. Volatile compounds profile

The headspace of CBF and MCBF samples was analyzed by solid phase microextraction, gas chromatography and mass spectrometry (HS-SPME-GC-MS) in an Agilent 8890 gas chromatograph/7010B spectrometer equipped with a PAL 3 autosampler (Agilent Technologies, Santa Clara, USA). A SPME (DVB/CAR/PDMS, Supelco, Bellefonte, USA) extraction was carried out in a 20 mL headspace vial containing on 0.5 g of sample suspended in 3 mL of saturated NaCl incubated at 50 °C for 30 min, with agitation at 250 rpm. The chromatographic separation conditions were as follow: from 40 °C to 250 °C in a DB-WAX column (60m × 0.25mm × 0.25μ) and helium (0.5 mL.min<sup>-1</sup>) as carrier. The mass spectra of separated volatiles compounds were tentatively identified by comparison with NIST 17 Library with the aid of MassHunter Unknowns software (Agilent Technologies, Santa Clara, USA).

## 2.8. Statistical analysis

The results of the measurements were presented as the mean ± standard deviation. The effect of temperature on the hydration kinetics parameters were evaluated by analysis of variances (ANOVA) followed by the Tukey test or Kruska Wallis followed by multiple comparisons of mean ranks at a 95% significance level with the aid of Statistica version 10.0 (StatSoft, Tulsa, Oklahoma, U.S.A.). A paired *t*-test or Wilcoxon was conducted using Microsoft Excel 2016 (Microsoft Corporation, Redmond, USA) to assess whether there was a significant difference between the macerated and untreated carioca bean flours techno-functional properties and volatile profile. Differences were considered significant at *p* < 0.05. The results of normality, homogeneity, and effect size are presented in Tables S3 and S4 of the Supplementary material.

## 3. Results and discussion

### 3.1. Hydration kinetics

Fig. 1 shows the hydration kinetics of halves and whole carioca bean in the temperatures of 20, 30 and 40 °C. Data is presented up to 10h of hydration for better visualization. The curves of bean halves in all temperatures and whole carioca beans at 30 and 40 °C presented a hyperbolic profile characterized by maximum hydration rate at the beginning of the process. A distinct behavior is observed for whole carioca beans at 20 °C and 25 °C described in other works which have presented a sigmoidal profile (Miano et al., 2018b; Oladele et al., 2018). This difference in the whole beans curve shape may be attributed to the initial moisture content (Miano et al., 2018a) and the cultivar of carioca bean used (Miano et al., 2018c). For whole beans at 20 °C the onset of hydration is slow due to the low permeability of the seed coat and slow absorption of water by the grain mass (lag phase). With the increase in the temperature (30 and 40 °C) whole beans hydrated faster and the lag phase was not observed. For half beans, hydration begins as soon as the grains come into contact with water and the surface area is larger, accelerating the hydration process.

Table 1 presents the results of percentage of variance explained (*R*<sup>2</sup>), the RMSE (Root Mean Square Error) and the carioca half and whole beans hydration constants using the Peleg, Kaptso, and Weibull models. The three mathematical models were selected to facilitate comparison with existing literature and to ensure consistency under the same conditions. Both models presented *R*<sup>2</sup> > 0.98 and small RMSE indicating adequate correlation between experimental and predicted data by models used. The smallest RMSEs were obtained for the Weibull model. It can be observed by the kinetic constants obtained by both models used that the hydration process becomes faster when the temperature is

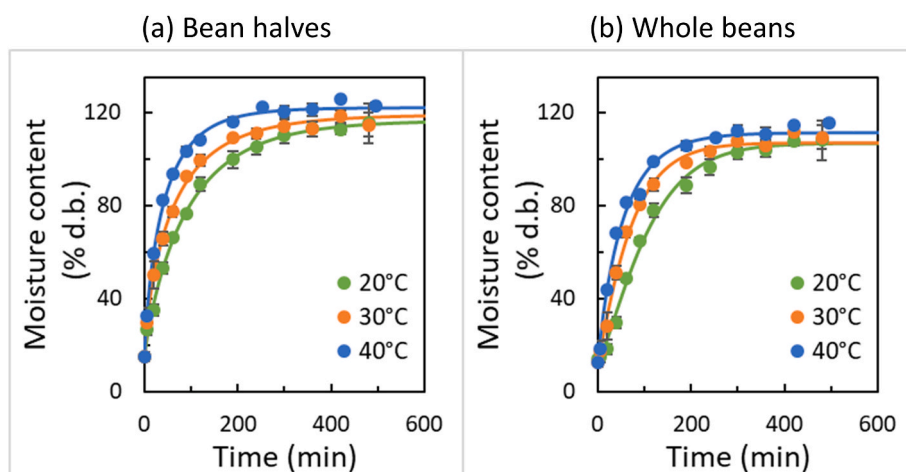


Fig. 1. Hydration kinetics of halves (a) and whole beans (b) adjusted to the Weibull model.

**Table 1**

Parameters of hydration kinetics curve adjusted to the Peleg, Kaptso and Weibull models at different temperatures for halves and whole beans.

	Bean halves			Whole beans		
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
<b>Peleg</b>						
$k_1$ (min % <sup>-1</sup> )	0.6 ± 0.1 <sup>ab</sup>	0.4 ± 0.0 <sup>ab</sup>	0.2 ± 0.0 <sup>b</sup>	1.0 ± 0.1 <sup>a</sup>	0.6 ± 0.1 <sup>ab</sup>	0.4 ± 0.0 <sup>ab</sup>
$k_2$ (× 10 <sup>-3</sup> % <sup>-1</sup> )	8.7 ± 0.4 <sup>ab</sup>	8.9 ± 0.1 <sup>ab</sup>	8.7 ± 0.1 <sup>a</sup>	8.3 ± 0.1 <sup>b</sup>	9.1 ± 0.2 <sup>ab</sup>	9.3 ± 0.0 <sup>a</sup>
$M_{\infty}$ (%)	130.7 ± 5.7 <sup>ab</sup>	127.6 ± 1.3 <sup>ab</sup>	129.7 ± 1.3 <sup>ab</sup>	133.0 ± 0.8 <sup>a</sup>	122.1 ± 2.0 <sup>ab</sup>	119.7 ± 0.4 <sup>b</sup>
$R^2$	0.9953 ± 0.0017 <sup>AB</sup>	0.9854 ± 0.0030 <sup>B</sup>	0.9956 ± 0.0013 <sup>A</sup>	0.9854 ± 0.0030 <sup>AB</sup>	0.9854 ± 0.0030 <sup>B</sup>	0.9879 ± 0.0033 <sup>BC</sup>
RMSE	3.30 ± 0.49 <sup>BC</sup>	2.97 ± 0.18 <sup>BC</sup>	3.19 ± 0.53 <sup>C</sup>	6.20 ± 0.68 <sup>A</sup>	5.91 ± 1.52 <sup>A</sup>	5.16 ± 0.72 <sup>AB</sup>
<b>Kaptso</b>						
$k$ (× 10 <sup>-2</sup> min <sup>-1</sup> )	2.4 ± 0.2 <sup>c</sup>	3.2 ± 0.3 <sup>b</sup>	4.45 ± 0.0 <sup>a</sup>	2.4 ± 0.1 <sup>c</sup>	3.3 ± 0.2 <sup>b</sup>	4.1 ± 0.2 <sup>a</sup>
$\tau$ (min)	53.1 ± 5.3 <sup>b</sup>	36.8 ± 2.7 <sup>c</sup>	27.0 ± 1.1 <sup>d</sup>	74.4 ± 2.6 <sup>a</sup>	47.9 ± 2.6 <sup>b</sup>	34.9 ± 1.1 <sup>cd</sup>
$M_{\infty}$ (%)	111.1 ± 3.2 <sup>ab</sup>	114.0 ± 1.3 <sup>ab</sup>	119.3 ± 0.5 <sup>a</sup>	103.9 ± 0.7 <sup>b</sup>	104.8 ± 1.3 <sup>ab</sup>	107.9 ± 0.6 <sup>ab</sup>
$R^2$	0.9889 ± 0.0048 <sup>BC</sup>	0.9931 ± 0.0010 <sup>A</sup>	0.9829 ± 0.0004 <sup>CD</sup>	0.9931 ± 0.0010 <sup>C</sup>	0.9931 ± 0.0010 <sup>A</sup>	0.9818 ± 0.0026 <sup>D</sup>
RMSE	5.05 ± 1.06 <sup>AB</sup>	5.85 ± 0.35 <sup>A</sup>	6.30 ± 1.08 <sup>A</sup>	3.36 ± 0.50 <sup>ABC</sup>	5.33 ± 0.06 <sup>AB</sup>	6.34 ± 0.47 <sup>A</sup>
<b>Weibull</b>						
$\beta$ (min)	96.7 ± 13.4 <sup>ab</sup>	65.0 ± 1.0 <sup>ab</sup>	43.8 ± 2.0 <sup>b</sup>	114.5 ± 3.1 <sup>a</sup>	74.7 ± 6.4 <sup>ab</sup>	53.9 ± 1.4 <sup>ab</sup>
$\alpha$	0.9 ± 0.1 <sup>cd</sup>	0.8 ± 0.1 <sup>d</sup>	0.8 ± 0.0 <sup>cd</sup>	1.3 ± 0.1 <sup>a</sup>	1.1 ± 0.1 <sup>ab</sup>	0.9 ± 0.0 <sup>bc</sup>
$M_{\infty}$ (%)	117.1 ± 4.1 <sup>ab</sup>	119.1 ± 1.5 <sup>ab</sup>	122.5 ± 0.7 <sup>a</sup>	106.6 ± 0.9 <sup>b</sup>	107.2 ± 0.6 <sup>ab</sup>	110.1 ± 0.7 <sup>ab</sup>
$R^2$	0.9974 ± 0.0020 <sup>A</sup>	0.9966 ± 0.0025 <sup>A</sup>	0.9973 ± 0.0014 <sup>A</sup>	0.9964 ± 0.0012 <sup>A</sup>	0.9938 ± 0.0028 <sup>A</sup>	0.9930 ± 0.0026 <sup>AB</sup>
RMSE	2.38 ± 0.94 <sup>C</sup>	2.65 ± 0.99 <sup>C</sup>	2.48 ± 0.66 <sup>C</sup>	3.07 ± 0.56 <sup>BC</sup>	3.78 ± 0.88 <sup>ABC</sup>	3.92 ± 0.71 <sup>BC</sup>

Note: RMSE: Root Mean Square Error. The Peleg equilibrium moisture was obtained by equation  $M_{\infty} = M_0 + 1/k_2$ . Samples with the same lowercase letter in a line do not differ significantly according to Tukey test or multiple comparisons of mean ranks ( $p > 0.05$ ). Averages followed by capital letters do not differ statistically for the same temperature according to Tukey test ( $p > 0.05$ ).

higher.

The  $M_{\infty}$  of the carioca bean calculated by Peleg equation varied from 120 to 133% (d.b.), while the Kaptso and Weibull models yielded a  $M_{\infty}$  of 104–119 and 106–122% (d.b.), respectively. The different  $M_{\infty}$  is due to the type of model applied. The Peleg model produces a hyperbolic curve, capturing rapid initial water absorption followed by a gradual approach to equilibrium. The Kaptso model describes a sigmoidal curve, reflecting an initial lag phase, rapid water uptake during exponential growth, and eventual stabilization at equilibrium (Kaptso et al., 2008; Miano et al., 2018b; Peleg, 1988b). The Weibull model predict both sigmoidal and hyperbolic behavior (Cunha et al., 1998; López et al., 2017). The  $M_{\infty}$  indicates the water absorption of approximately eight times the initial moisture content, which is comparable to the equilibrium moisture range of 112–132% reported for whole carioca beans (Miano et al., 2018a, 2018b, 2019).

The  $k_1$  values found by Peleg model adjustment were higher for whole beans (1.0–0.4 min/%) compared to halves beans (0.6–0.2 min/%) indicating a smaller rate of mass transfer. This is due to the available surface area to water absorption, i.e. smaller grains absorb water faster (Montanuci et al., 2015). Besides, the split grains have a smaller amount seed coat, which is one of the main factors limiting water absorption (Abu-ghannam and Mckenna, 1997; Oliveira et al., 2013). A decrease in the  $k_1$  occurred with the temperature rise showing higher rate of water absorption at higher temperatures as reported in other works. This is related to the increase in the rate of diffusion due to the enhanced seed coat's plasticity, reduced fluid viscosity and expanded grain pores (Li et al., 2020; Montanuci et al., 2015; Oliveira et al., 2013; Prasad et al., 2010).

Although sigmoidal behavior was observed only for the whole beans at 20 °C, the Kaptso model was fitted to the data to allow comparison under the same conditions. The  $k$  obtained by Kaptso model adjustment represents the hydration rate constant which indicates how quickly water is absorbed by the grains. Values of  $k$  found in this work (0.02–0.04 min<sup>-1</sup>) did not differ significantly between whole grains and halves at the same temperature, while for the same sample it increased with increasing temperature. The results are in range of those reported in the literature for carioca bean (0.011–0.024 min<sup>-1</sup>) (Miano et al., 2018c, 2019).  $\tau$  represents the time required to achieve half of the maximum hydration. In this study, the  $\tau$  values varied from 27 to 74 min are lower than that reported for whole beans, which ranges from 76 to 240 min (Miano et al., 2018a, 2018b, 2019). Half beans hydrated more quickly than whole beans, an expected result due to the absence of the

seed coat, which acts as a barrier to water penetration. As expected, the increase in temperature decreased the hydration time. The reduced hydration time is beneficial for industrial processes, as it decreases processing costs and minimizes the degradation of some substances such as phenolic compounds (Mba et al., 2019).

For the Weibull parameters, the  $\beta$  value decreased as the temperature increased, indicating a reduction in hydration time. In the Weibull model, the scale parameter  $\beta$  represents the rate of the moisture uptake process (reciprocal to the rate constant) and corresponds to the time required to achieve approximately 63% of the total moisture uptake. The shape parameter  $\alpha$  serves as a behavior index, reflecting the mechanism governing the process (López et al., 2017). A  $\alpha$  higher than 1 indicate a sigmoidal curve, while a  $\alpha$  smaller than 1 indicate a hyperbolic curve. In this study,  $\alpha$  was greater than 1 for whole grains at 20 °C and 30 °C, suggesting greater resistance to hydration during the initial phase. For the other conditions,  $\alpha$  was less than 1, indicating a faster hydration process.

Despite the hydration at 20 °C being slower, this condition was chosen to obtain MCBF since it is a milder condition for preserving the techno-functional properties and volatile profile. The broken grains were hydrated for 3h, a time chosen based on the value of value  $\beta$  (97 min) and the hydration curve.

### 3.2. Physicochemical and techno-functional properties

Table 2 shows the physicochemical composition of CBF and MCBF. The lower moisture, phytic acid content, and particle size and higher L\* value were observed for MCBF when compared to CBF. The other parameters did not show significant differences on a dry basis. The MCBF showed a lighter color compared to the untreated beans because the hulls were partially removed during maceration. The damaged starch content and water activity did not present difference ( $p > 0.05$ ) between the treatments, demonstrating that the grinding was carried out in a controlled way independent of the maceration process. The particle size of CBF was larger than those from the MCBF. This may have occurred due to the lower moisture and hulls content of the macerated beans, leading to greater grain hardness and favoring the grinding.

The content of phytic acid reported in the literature for carioca bean varies in the range from 0.02 to 1.3% depending on the cultivar and storage conditions (Bento et al., 2023; De Almeida et al., 2017; Maria et al., 2002) that is in accordance with the results of this study. A decrease in the phytic acid content occurred for MCBF, that is attributed



**Table 2**

– Physical-chemical characteristics of untreated (CBF) and macerated bean flour (MCBF).

Parameter	CBF	MCBF
Moisture (%)	15.36 ± 0.07 <sup>a</sup>	9.27 ± 0.07 <sup>b</sup>
Carbohydrate (%)	70.08 ± 0.31 <sup>a</sup>	69.17 ± 0.06 <sup>a</sup>
Protein (%)	24.81 ± 0.21 <sup>a</sup>	25.60 ± 0.12 <sup>a</sup>
Lipid (%)	1.43 ± 0.10 <sup>a</sup>	1.57 ± 0.04 <sup>a</sup>
Ash (%)	3.69 ± 0.01 <sup>a</sup>	3.65 ± 0.01 <sup>a</sup>
Phytic acid (%)	0.88 ± 0.07 <sup>a</sup>	0.65 ± 0.09 <sup>b</sup>
L*	89.59 ± 0.24 <sup>a</sup>	93.71 ± 0.29 <sup>a</sup>
a*	1.91 ± 0.04 <sup>a</sup>	1.26 ± 0.04 <sup>a</sup>
b*	10.94 ± 0.08 <sup>a</sup>	10.40 ± 0.19 <sup>b</sup>
Water activity	0.355 ± 0.002 <sup>a</sup>	0.356 ± 0.004 <sup>a</sup>
Damaged starch (%)	2.63 ± 0.12 <sup>a</sup>	2.45 ± 0.02 <sup>a</sup>
D50 (μm)	51.5 ± 3.9 <sup>a</sup>	36.2 ± 3.1 <sup>b</sup>

Note: moisture, protein, lipid, ash, and phytic acid are expressed in dry basis. D50 corresponds to the median of the distribution. Samples with the same letter in a row do not differ significantly according to the *t*-test or Wilcoxon ( $p > 0.05$ ).

to its leaching into the hydration water since this substance presents high water solubility. This may result in an increase in nutritional quality of MCBF since phytic acid binds to essential minerals like calcium, iron, and zinc, and proteins reducing their bioavailability and hindering nutrient absorption (Maria et al., 2002; Nartea et al., 2023).

Fig. 2 shows the results of particle size distribution, protein solubility, emulsion (EC) and foaming (FC) capacity, emulsion creaming speed (CS), oil (ORI) and water (WRI) retention index for CBF and MCBF. Both flours showed a tri-modal particle size distribution, with major peaks located at 100 μm and 30 μm, and a minor peak at 2–3 μm. This result is similar to other pulses flours and can be attributed to protein bodies

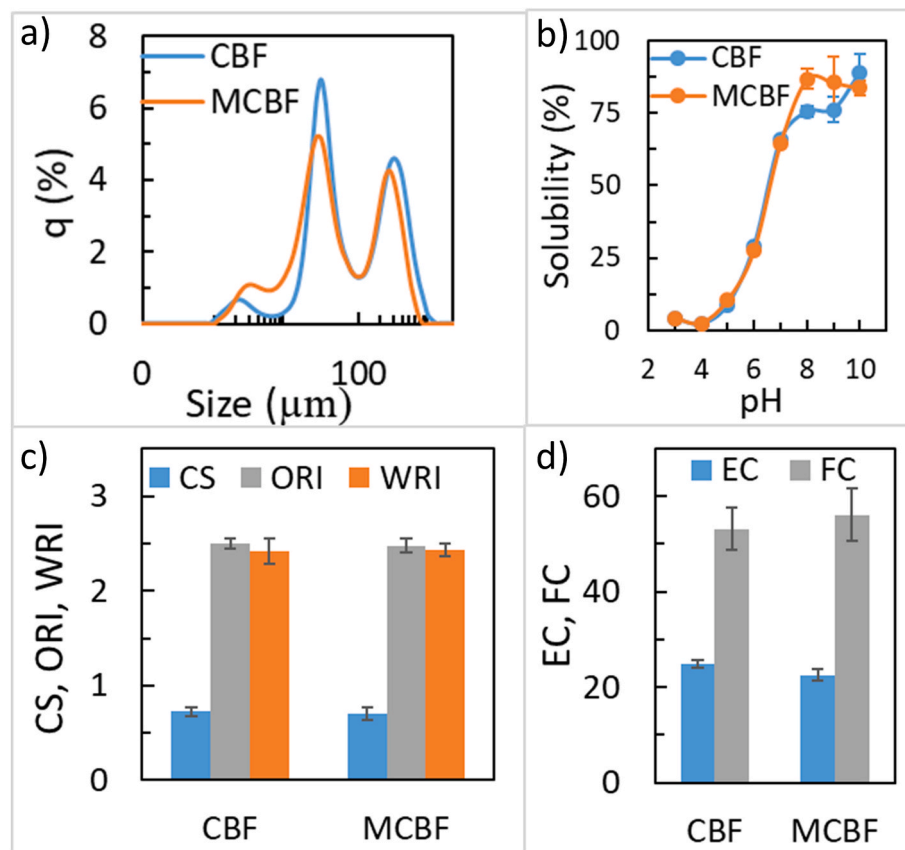
(1–5 μm), starch granules (15–40 μm), and whole cells or cell fragments (larger than 40 μm) (Sivakumar et al., 2022).

The solubility in function of the pH curves showed a similar profile for both flours. A low solubility occurred at pHs 3 to 5 ( $\leq 10\%$ ), intermediate solubility at neutral pH ( $\sim 65\%$ ) and high solubility at alkaline pHs as typically observed for other pulses. The water and oil retention index were close for CBF and MCBF and there was no difference ( $p > 0.05$ ) between them. Similar protein solubility and water and oil retention index were reported by de Paiva Gouvêa et al. (2023) for carioca bean whole flour. There was no significant difference ( $p > 0.05$ ) between emulsion and foam properties of both flours. This result shows that the maceration does not impact on these functional properties that can be attributed to similar physical-chemical composition and no impact on the protein and starch structures.

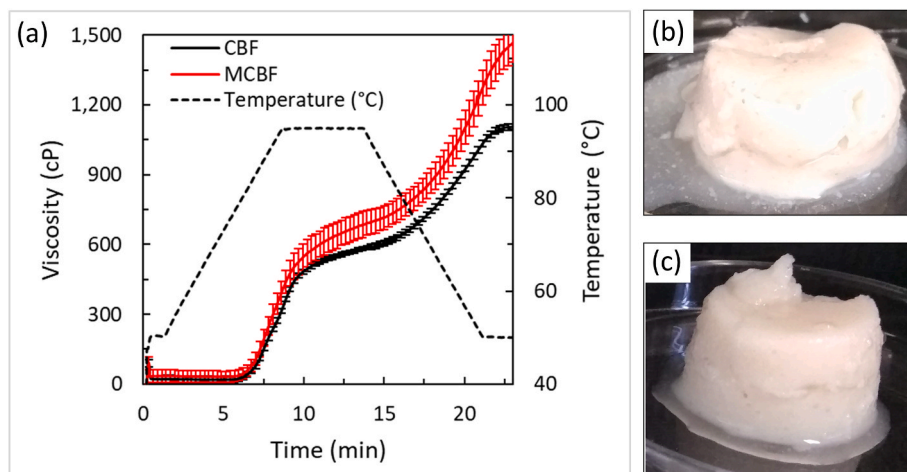
### 3.3. Pasting and texture properties

Fig. 3 shows the viscosity profile curve and visual appearance of the gels obtained by RVA after refrigerated storage of bean flours. The flours showed an increase in viscosity in function of heating and cooling and no viscosity break in both flours. This result demonstrates that the carioca bean starch granule presents greater resistance to heating and shearing, i.e. carioca bean flour pastes have greater stability, as also observed by other authors (Bento et al., 2022). These results can also be attributed to the smaller particle size and lower amount of gelation interfering substances, such as fibers from hulls, that were partially eliminated by the maceration.

Table 3 shows the pasting and texture parameters obtained for CBF and MCBF. Since no peak was observed, results of trough, breakdown and setback are not presented. The samples presented similar peak and a



**Fig. 2.** Particle size distribution (a) and protein solubility in function of pH (b) curves for carioca bean flour without treatment (CBF) and macerated (MCBF). The functional properties emulsion creaming speed (CS - %BS/min), oil (ORI) and water (WRI) retention index are presented in Figure c. The emulsion (EC) and foaming (FC) capacity expressed in percentage are in Figure d. Samples did not differ significantly according to the *t*-test ( $p > 0.05$ ) for CS, ORI, WRI, EC and FC.



**Fig. 3.** Viscosity profile (a) and visual appearance of the gels formed after storage under refrigeration for 24 h of untreated (CBF) (b) and macerated (MCBF) (c) carioca bean flours.

**Table 3**

– Pasting and texture parameters of gels from untreated (CBF) and macerated (MCBF) carioca bean flours.

Parameter	CBF	MCBF
<i>RVA</i>		
Peak viscosity (cP)	571 ± 8 <sup>a</sup>	672 ± 54 <sup>a</sup>
Final viscosity (cP)	1107 ± 13 <sup>b</sup>	1468 ± 80 <sup>a</sup>
Pasting temperature (°C)	81.6 ± 0.3 <sup>a</sup>	81.0 ± 0.2 <sup>a</sup>
<i>Texture</i>		
Hardness (N)	3.33 ± 0.21 <sup>b</sup>	4.47 ± 0.05 <sup>a</sup>
Adhesiveness (N.s)	2.09 ± 0.05 <sup>b</sup>	6.12 ± 0.33 <sup>a</sup>
Springiness	0.94 ± 0.03 <sup>a</sup>	0.97 ± 0.04 <sup>a</sup>
Cohesiveness	0.38 ± 0.03 <sup>a</sup>	0.37 ± 0.01 <sup>a</sup>

Note: Samples with the same letter in a row do not differ significantly according to the *t*-test or Wilcoxon ( $p > 0.05$ ).

higher final viscosity was observed for MCBF. The pasting temperature of both flour was around 81 °C that is higher than carioca bean purified starches that vary from 73 to 78 °C (Vanier et al., 2019). This is due to the presence of other substances that compete with the starch for water (e.g. proteins, cellulose) and is in accordance with values found for other pulses flours (Du et al., 2014). Besides, the high amount of amylose (around 30%) compared to cereals (around 10%) increase the pasting temperature (Bento et al., 2022).

The flour gels textural parameters evaluated were hardness, adhesiveness, springiness, and cohesiveness, corresponding to the maximum force during the first compression, area below the baseline, the ability to recover shape after deformation, and the ratio of force areas in the first and second compressions, respectively (Ghribi et al., 2015). The gel hardness were similar to values reported by Bento et al. (2022) for whole carioca bean flours that associated the high values to the high amylose content that recrystallize after cooling. This can be confirmed by the visual appearance and syneresis of the gels obtained (Fig. 3b and c). In this work, the maceration increased the gel hardness and adhesiveness. The last parameter (adhesiveness) is correlated with the surface characteristic and influenced by the combined effect of adhesive and cohesive forces, as well as viscosity and viscoelasticity (Adhikari et al., 2001), affecting the machinability of the product.

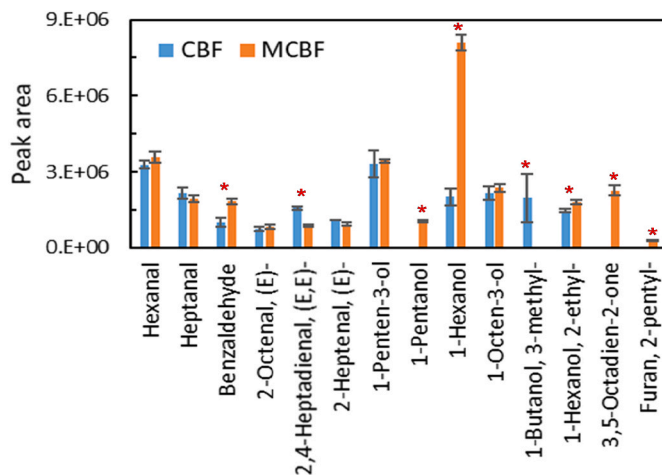
This result is correlated to the higher final viscosity observed in RVA results and the content decrease in some compound that could impair the gel formation, such as phytic acid and compounds of the hulls.

### 3.4. Volatile compounds profile

It was identified 33 and 38 volatile compounds in CBF and MCBF,

respectively, as presented in Supplementary material, Table S2. Of these, the compounds related to off-flavors are shown in Fig. 4. The mass spectra of these compounds were tentatively identified by comparison with the NIST 17 library, and belong to aldehydes, alcohols, ketones and furans classes. The same classes of compounds is commonly reported in literature as beany flavor and found in other pulses and legumes in general (Oomah et al., 2007). The aldehydes compounds, the main class found, presented similar peak areas for both samples include hexanal, described as having cut-grass and green notes; heptanal, associated with dry fish aromas; (E)-2-octenal and (E)-2-heptenal, which impart fatty, green, and cucumber-like aromas. The alcohols include 1-penten-3-ol and 1-octen-3-ol, described as giving beany, green, and mushroom qualities; 3-methyl-1-butanol, contributing balsamic notes; and 2-ethyl-1-hexanol, which adds a green aroma (Wang et al., 2021).

MCBF presented higher amount of benzaldehyde, 1-pentanol, 1-hexanol, 3,5-octadien-2-one and 2-pentyl-furan, that are associated to almond, wax, green, fat and beany off-flavors descriptors. CBF showed a higher amount of (E,E)-2,4-heptadienal and (E)-2-heptenal that is associated to fatty and fishy off-flavors (Wang et al., 2021). The off-flavors occur mainly due to oxidation of unsaturated free fatty acids and the degradation of amino acids during seed development, storage, and transformation (Karolkowski et al., 2021). Therefore, the soaking triggered the oxidation of fatty acids increasing the off-flavor



**Fig. 4.** Off-flavors peak areas found for carioca bean flour without any treatment (CBF) and macerated (MCBF). Samples with asterisk represent significant difference according to *t*-test ( $p < 0.05$ ).

compounds. For example, He et al. (2023) attributed the increase in 1-hexanol content during soaking in chickpeas and mung beans to the oxidation of linoleic acid.

#### 4. Conclusion

This work aimed to study the hydration kinetics of broken carioca beans and evaluate its compositional changes and techno-functional properties. Bean halves and whole bean at 30 and 40 °C hydration curve did not present the lag phase and a smaller hydration time when compared to the whole bean was observed. This is attributed to the higher surface area and no need to penetrate the seed coat since the interior of the broken grains is exposed and faster hydration kinetics of whole beans at 30 and 40 °C. As expected, the increase in temperature from 20 to 40 °C accelerated the hydration process. The flours obtained from untreated and macerated samples showed no significant differences in protein, ash, carbohydrate, or lipid content; however, a reduction in phytic acid and moisture was observed in the macerated flour. No differences were observed in emulsion, foaming, or water and oil holding capacities, while macerated flour exhibited higher final viscosity and setback, producing a firmer and more adhesive gel. Macerated flour showed a higher concentration of off-flavors, likely due to more extensive processing, which facilitated oxidation during the hydration and drying stages. Therefore, broken carioca beans soaking offers advantages such as shorter processing time and improved nutritional quality without negatively impacting techno-functional properties.

#### CRediT authorship contribution statement

**Elaine Kaspchak:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Eduardo Vicente:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Elizabeth Harumi Nabeshima:** Writing – review & editing, Visualization, Validation, Methodology, Investigation, Formal analysis. **Maria Teresa Bertoldo Pacheco:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition. **Mitie Sonia Sadahira:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, Data curation.

#### Declaration of competing interest

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

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jfoodeng.2025.112537>.

#### Data availability

Data will be made available on request.

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