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Functional, thermal, and pasting properties of cooked carioca bean (*Phaseolus vulgaris* L.) flours

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ABSTRACT

This study verified if cooking presoaked beans in the steam of autoclave improves the pasting properties, texture profile, water-solubility (WSI), emulsifying capacities of aged carioca bean' flours. The carioca beans flour presented high content of protein (20.7 –22.3 g·100g^{-1}), resistant starch (RS) (8.3 – 31.1 g·100g^{-1}), and dietary fiber (TDF) (18.9 – 23.7 g·100g^{-1}), and the cultivar Notavel presented the highest content of total dietary fiber and resistant starch for both cooked and raw flour. The pretreatment promoted an increase in TDF (8.8%, cultivar Dama) and a decrease in RS (19.5%, 33.4%, and 47.0% for cultivars Imperador, Gol, and Bola Cheia, respectively). Regarding the pasting properties, the heating process promoted a reduction in the values of peak viscosity, final viscosity, breakdown, and setback for all carioca bean cultivars. The other parameters, i.e., gel hardness, WSI, emulsifying capacity, and stability also presented a significant decrease in the cooked flours. So, the pretreatment promoted a total or/partially starch pre-gelatinization and the denaturation of the proteins of the flours which might increase their acceptability for food development.

1. Introduction

Dry bean (*Phaseolus vulgaris* L.) is an important crop worldwide due to their nutritional value and because they contribute to the food security of low-income people in underdeveloped countries. In 2019, Brazil was the third of the world's largest producers of dry beans, with an estimated production of 2.9 million tons, in an area of around 2,600,000 ha (FAO, 2019). Dry beans are a product of great economic and social importance in Brazil because it is an economic alternative for agricultural exploitation in small farms in a large amount of Brazilian rural regions. That is, family farming is responsible for the production of 70% of national beans (considering all types of beans) (Silva, 2017). The carioca bean - grains with a light cream color and with the presence of light brown streaks - is the most cultivated in Brazil. They look slightly like pinto beans, except for the stripes instead of spots in the tegument and the smaller size of the grains.

Due to the seasonality of bean production in Brazil and other countries, the storage of carioca beans is necessary to maintain bean supply throughout the year. Nevertheless, improper storage conditions cause undesirable changes of carioca beans, e.g., the browning of the integument (Bento, Ferreira, Bassinello, & Oomah, 2021c; Bento et al., 2020). So, after harvesting, grains of the carioca type quickly lose their commercial value because some genotypes darken very quickly due to chemical changes, related to the oxidation of proanthocyanidin (Bento et al., 2021d; Coelho et al., 2020). This depreciation is because the consumers reject dark grains since it is associated with old grains and with a long cooking time (Bento et al., 2021c; Bento et al., 2020). The aged carioca beans that quickly darkens and consequently lose their commercial value can be used as ingredients in food formulation. So, making flour from aged carioca beans can contribute to the sustainability of the bean production chain since the use of the bean flour could add value to the aged bean. Similarly, flour from broken beans (i.e., the bean byproduct) is useful for food development since they present a similar nutritional value compared to the whole grain (Bento et al., 2021b; Gomes et al., 2015).

The heat treatment of pulses to produce flours can change the technological properties of the flours, for example, it reduces the value of the breaking and final viscosities and the tendency to retrograde (Sun et al., 2018). In our previous studies we showed that making flour from cooked beans allows the development of food staff with high sensorial acceptance and depending on the type of bean (e.g., colorful beans or black and carioca byproduct) the flour may be adequate for differ-

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ent food development (Bento et al., 2021a; Bento et al., 2021b). This happens because different bean genotypes present distinct amounts of protein, dietary fibers, resistant starch, and chemical profile which influence their technological properties, i.e., water and oil absorption, emulsification, water solubility, and gelation properties (Gupta, Chhabra, Liu, Bakshi, & Sathe, 2018; Lin & Fernández-Fraguas, 2020; Ramírez-Jiménez, Reynoso-Camacho, Mendoza-Díaz, & Loarca-Piña, 2014). The flour made from colorful bean presoaked in water (6 h) and cooked in the steam of autoclave (5 min) presented a higher amount of resistant starch and lower viscosities values (Bento et al., 2021a). Thus, these flours from pretreated beans were advantageous for food systems application when high levels of supplementation with pulse components are desired without causing a major texture discrepancy (Bento et al., 2021a; Felker, Kenar, Byars, Singh, & Liu, 2018). Unfortunately, there is limited research on the impact of their major elements on the functional characteristics of flours and the physicochemical properties of carioca bean flours, which are primordial for the further development of food products made with bean flours (Romero & Zhang, 2019).

Considering the importance of the technological properties of flour for the further development of food products made with carioca bean flours, studies that propose the development of aged carioca bean flours from cooked grains and their physicochemical evaluation are justified. They would provide information about technological properties changes and help with the use of bean flours by industries, improving the nutritional quality of processed foods, and still would attend to specific consumer's demands. Therefore, the present study aimed to verify if cooking presoaked beans in the steam of autoclave improve the pasting properties, texture profile, water-solubility, emulsifying capacities of aged carioca bean flours.

2. Material and methods

2.1. Plant material

Dry bean from the commercial carioca group were selected from the Active Germplasm Bank of Embrapa Arroz e Feijão, in Santo Antônio de Goiás, Goiás State, Brazil: BRSMG Madrepérola (Ma), TAA Dama (Da), BRS Notável (No), IAC Imperador (Im), TAA Gol (Gol) and TAA Bola Cheia (BC). The grains were cultivated in the experimental fields of Embrapa Arroz e Feijão, on the Capivara farm, in the same municipality. After harvesting and drying of beans in an oven with forced air circulation (40 °C) (final moisture ± 12.0%) (the moisture was determined using a dielectric moisture analyzer (Grainer II PM-300, Kett Electric Laboratory)), the beans underwent cleaning operations, purge, and manual selection of grains. After quartering for sample homogenization, they were stored in low-density polyethylene bags, in portions of 1 kg (triplicate, three biological samples for each bean cultivars) for 3 months, in a place with ambient lighting at 25 °C.

2.2. Flour preparation

To obtain the flour from raw grains, the beans were washed into running water and then dried, in an oven (Nova Ética, 400/5, Brazil) at 60 °C with air circulation, for 1 - 2 hours (until final moisture of 10-12%). Afterward, the beans were ground in a hammer mill with a sieve of 20 mesh. For cooked flour, the washed grains were soaked for 6 hours in water (1:2 w/v), and then the washed beans were placed in 1 L beakers without the addition of water and then cooked with the steam from the autoclave (121 °C·at 1.1 kg·cm^2) (Prismatec, CS, Brazil) for 5 min (Bento et al., 2021a). After that, the cooked grains were dried in an oven (60 °C) with air circulation for 8 - 12 hours (until final moisture of 10-12%), and then it was ground in a hammer mill. Three repetitions of each carioca bean flour were obtained (raw and cooked) and showed similar granulometry, with particle sizes between 106 μm and 425 μm. A flowchart describing the flour preparation is presented in Supplementary Fig. 1.

2.3. Protein content, total dietary fiber (TDF), and resistant starch (RS)

The nitrogen content by the micro-Kjeldahl method and then multiplied by a factor of 6.25 to obtain the crude protein content, according to AOAC (2016), method number 979.09. The TDF was determined using a standardized enzymatic-gravimetric method (K-TDFR Kit, obtained from Megazyme International Ireland, Bray, Ireland), according to method number 985.29 (AOAC, 2016). RS content of bean flour was determined using an RS assay kit (cat. no. K-RSTAR, obtained from Megazyme International Ireland, Bray, Ireland), with some modifications. Briefly, pancreatic α-amylase and amyloglucosidase were added directly to 100 mg of bean flour in 50 mL test tubes, and tubes were incubated at 37 °C for 16 h with shaking (100 rpm). After the addition of ethanol and centrifugation, the supernatant (nonresistant starch - NRS) was removed and the precipitate was homogenized using a magnetic stirrer. To solubilize RS, 2 M KOH was added to the homogenized precipitate on the ice bath. Sodium acetate buffer (1.2 M, pH 3.8) was added and incubated with amyloglucosidase to convert the solubilized RS to glucose. The glucose content of the RS fraction was determined by the glucose oxidase/peroxidase reagent (GOPOD) method.

2.4. Pasting properties and gel hardness

The sample (3.5 g with adjusted moisture of 14 g·100g^{-1}) with 25.0 mL of distilled water were analyzed in a Rapid Visco Analyser (Perten Instruments, RVA 4500, Macquarie Park, Australia), using the flour method (RVA Method 5, Version 4, March 2010). The suspension was kept at 25 °C for 2 min, heated (14 °C·min^{-1}) at 95 °C and kept at this temperature for 3 min, and cooled (14 °C·min^{-1}) at 25 °C. The pasting properties evaluated were paste temperature, peak viscosity, final viscosity, breakdown, and setback, expressed in centipoise (cP). After being subjected to the Rapid Visco Analyzer, the samples were kept refrigerated (7 °C) overnight, and later they were analyzed with a texturometer (TA HD Plus Stable Micro Systems, Surrey, England). The gel hardness was measured with a 20 mm cylindrical probe at a temperature of 25 °C according to Wani, Sogi, Wani, Gill, and Shivhare (2010), with a test speed of 0.5 mm·s^{-1}, a pre-test speed of 1.0 mm·s^{-1}, a post-test speed of 10.0 mm·s^{-1}, with force contact depth of 10 gf, and with probe penetration distance/depth of 6 mm.

2.5. Thermal properties

The thermal properties were determined using a differential scanning calorimeter (TA Instruments, Q20, New Castle, UK). The samples (2 mg, dry weight) were weighed in aluminum containers, suitable for the equipment. Distilled water (6 μL) was added, and the sample holders were sealed in a specific press. These were kept for 12 h at room temperature and heated in the range between 35 and 120 °C, at a heating rate of 10 °C·min^{-1}. From the obtained curve, the temperature of peak gelatinization and vitrea transition was calculated using the TA Universal Analysis application (TA Instruments, New Castle, UK).

2.6. Water solubility index and the water and oil absorption index

The water solubility index (WSI) and the water absorption index (WAI) were determined according to the method described by Anderson, Conway, Pfeifer, and Griffin Junior (1969). The samples (2.5 g) were weighed into previously tared centrifuge tubes and 30 mL of distilled water was added. The tubes were shaken in a water bath for 30 min at 25 °C and then centrifuged at 3000 *g* for 15 min. The supernatants were carefully removed into 10 mL volumetric flasks. The WAI was calculated using Eq. (1), and the result was expressed in g of precipitate per g of dry matter. To determine the oil absorption index (OAI), the same methodology with adaptations was also used, since the water was replaced by soybean oil. The WSI was calculated from the ratio between

Table 1
Protein, total dietary fiber, resistant starch, and total starch content in dry weight (g·100g^{-1}) of different raw and cooked carioca bean flour.

Flours	Protein	Total dietary fibers	Resistant starch
Da	20.76 ± 0.58 b	18.89 ± 0.17 e	29.00 ± 1.48 ab
Da_C	-	20.55 ± 0.06 cd	31.11 ± 1.59 a
No	20.90 ± 0.15 b	23.05 ± 0.33 a	27.60 ± 1.41 ab
No_C	-	23.72 ± 0.37 a	29.63 ± 1.51 ab
Ma	22.31 ± 0.34 a	21.49 ± 0.53 bcd	9.10 ± 0.46 f
Ma_C	-	20.88 ± 0.45 cd	8.30 ± 0.42 f
Im	21.52 ± 0.44 ab	21.20 ± 0.40 bcd	27.76 ± 1.40 ab
Im_C	-	20.80 ± 0.44 cd	22.34 ± 1.14 c
Gol	21.39 ± 0.29 ab	21.72 ± 0.61 bc	26.14 ± 1.33 b
Gol_C	-	22.50 ± 0.55 ab	17.41 ± 0.89 d
BC	21.28 ± 0.28 ab	20.37 ± 0.74 cd	26.76 ± 1.36 b
BC_C	-	20.93 ± 0.29 d	14.18 ± 0.21 e

*Means of three determinations ± standard deviation. Different letters on the same column represent the statistical difference (p <0.05). Beans are described as **No** and **No_C** (Notavel), **Im** and **Im_C** (Imperador), **Gol** and **Gol_C** (Gol), **BC** and **BC_C** (Bola Cheia), **Da** and **Da_C** (Dama) and **Ma** and **Ma_C** (Madreperola), where the '**C**' indicates cooked flours.

the mass of the dry residue of the supernatant (evaporation residue) and the sample weight multiplied by 3 (indicating the correction for the total supernatant volume since only 10 mL of the 30 mL was used) and the result expressed in g·100 g^{-1} Eq. (2).

$$\text{WAI} = \frac{\text{Precipitate weight}}{\text{Sample weight (d.w.)}} \quad (1)$$

$$\text{WSI} = \left\{ \left[\frac{\text{Evaporation residue}}{\text{Sample weight (d.w.)}} \right] 3 \right\} 100 \quad (2)$$

2.7. Emulsifying capacity and stability

The sample (0.35 g) was weighed into a graduated centrifuge tube (10 mL) and 2.5 mL of distilled water was added. The tubes were shaken in a vortex for 30 seconds and then 2.5 mL of corn oil was added. After, the tubes were vortex for 90 s and then centrifuged at 500 *g* for 5 min (Kaur & Singh, 2005). The emulsifying activity was calculated by dividing the volume of the emulsified layer by the total volume before centrifugation. The stability of the emulsion was determined, following the same procedure to determine the emulsifying activity. However, before centrifuging the samples, they were subjected to heat treatment at 85 °C for 15 min and centrifuged after cooling. Emulsion stability was expressed as the percentage of the remaining emulsifying activity after heating.

2.8. Statistical analyses

All results were obtained in triplicate, are presented as means ± standard deviation. Levene test was applied to verify the variance homogeneity (normality test), and the data were evaluated by the ANOVA (analysis of variance), followed by the Tukey test ($p < 0.05$). A general description of the data was obtained by Principal Component Analysis (PCA) of the normalized data based on Pearson's correlation matrix provided by XLSTAT software (Addinsoft, 2021).

3. Results and discussion

3.1. Protein, dietary fiber, total starch, and resistant starch content

The protein content presented a slight variation between the cultivars. The flours of the cultivar Ma showed the highest value of protein (22.31 g·100g^{-1}), while the cultivar No was the lowest one (20.90 g 100 g^{-1}) (Table 1). Bean's protein content is comparable to pea (18.7–22.3 g·100g^{-1}), lentil (25.1 g·100g^{-1}), and faba bean (26.5 g·100g^{-1}) (Abdel-Aal, Ragaee, Rabalski, Warkentin, & Vandenberg, 2018; Byanju, Hojilla-Evangelista, & Lamsal, 2021; Young et al., 2020). Besides, bean protein provides health benefits due to the presence of bioactive peptides that acts in anti-inflammatory responses, metabolism of protein and carbohydrate, antioxidant, and immune system modulation (Alves et al., 2021; Luna-Vital, Mojica, González de Mejía, Mendoza, & Loarca-Piña, 2015).

Carioca beans also presented high content of dietary fiber, between 18.89 to 23.7 g·100g^{-1}. The flour of beans is a source of fiber, and it had more fiber than lentil (4.11 g·100g^{-1}), green pea (6.51 g·100g^{-1}) (Byanju et al., 2021), and yellow pea (16.5 g·100g^{-1}) (Setia et al., 2019). The thermal pretreatment did not influence the TDF, with exception of the flours of cultivar Da that presented an increase in TDF in the cooked flour (Table 1). This increase in dietary fiber is due to protein–fiber complexes formed by chemical modification caused by the cooking process (Wang, Hatcher, Toews, & Gawalko, 2009). Many of the nutritional benefits from consuming beans have been largely accredited to their dietary fiber content (Vergara-Castañeda et al., 2010).

The flours of the cultivar Da showed the highest content of resistant starch (29 g·100g^{-1}), whereas the cultivar Ma had the lowest one (9 g·100g^{-1}) (Table 1). These results are low than those found for Pinto bean and black bean (around 35 g·100g^{-1}) (Escobedo, Mora, & Mojica, 2019). However, most of the flour of raw beans presented more resistant starch than the yellow pea (2 g·100g^{-1}) (Vatansever, Rao, & Hall, 2020), and cooked lentils (3.0 g·100g^{-1}) (Johnson et al., 2015). The content of RS starch may be influenced by several factors, such as the composition of the bean flour (e.g., the fibers content) and the starch characteristics (i.e., the crystallinity of starch) since starch with high content of amylose tends to make the major amount of RS related to their chain-length. Additionally, the enzymatic content of the bean flour influences the content of RS since the natural RS present in plant material is due to the enzymatic de-branching of the amylose and amylopectin branch (Hung, Vien, & Lan Phi, 2016). RS present low digestibility and are composed of soluble and insoluble fibers and non-digestible sugars which is fermented by gut microbiota in the colon. The fermentation of RS by these microorganisms produces short-chain fatty acids, such as butyric acid. These acids are known to improve several biological mechanisms such as modulate postprandial lipemia and blood pressure control (Barber, Kabisch, Pfeiffer, & Weickert, 2020; Mullins & Arjmandi, 2021; Reverri et al., 2015; Vergara-Castañeda et al., 2010).

The pretreatments decreased the RS content of the flours of cultivars Im, Gol, and BC. Other research also observed a reduction in the RS when the grains were soaked before cooking (Santiago-Ramos, Figueroa-Cárdenas, Véles-Medina, & Salazar, 2018). The cooking process of beans causes starch gelatinization which increases the starch digestibility and upon cooling they form retrograded starch (less digestible) (Liu, Ragaee, Marcone, & Abdel-Aal, 2020). However, the formation of less digestible starch is dependent on the starch composition (i.e., amylose and amylopectin ratio) of the bean cultivar. Moreover, the formation of RS due the recrystallisation of the starch fractions can be improved by an additional heating/cooling treatment (Ramírez-Jiménez et al., 2014; Ramírez-Jiménez, Reynoso-Camacho, Tejero, León-Galván, & Loarca-Piña, 2015).

3.2. Pasting properties and gel hardness

The pasting temperature of the raw bean flours was between 80.7 – 84.1 °C and the flour of cultivar BC presented the highest one (Table 2). Other flours of pulses also presented high pasting temperatures, e.g., yellow pea (79.3 °C) (Waduge et al., 2017), and kidney bean (89.4 – 94.9 °C) (Wani, Andrabi, Sogi, & Hassan, 2020). The high pasting temperatures are due to the presence of non-starch components (i.e., proteins, oligosaccharides, cellulose, etc.). These compounds compete with the starch for water, which reduces the water availability increasing the pasting temperature. Besides, the RS contributes to a higher resistance to swelling and rupturing (Lin & Fernández-Fraguas, 2020; Romero &

Table 2
Pasting properties and gel hardness of different raw and cooked carioca bean flour.

Flours	Paste temperature (°C)	Peak viscosity (cP)	Breakdown (cP)	Final viscosity (cP)	Setback (cP)	Gel hardness (N)
Da	83.90 ± 0.15b	944.0 ± 30.5b	18.7 ± 7.3c	1274.0 ± 36.6de	348.7 ± 3.2c	1.76 ± 0.26bc
Da_C	-	48.3 ± 1.5g	2.7 ± 0.5d	74.3 ± 1.5j	28.7 ± 0.6g	0.03 ± 0.00e
No	83.72 ± 0.63b	952.0 ± 6.6b	22.0 ± 4.4c	1282.7 ± 10.4d	352.7 ± 10.7c	1.85 ± 0.32bc
No_C	87.37 ± 0.38a	245.0 ± 11.8de	20.0 ± 3.0c	507.3 ± 17.9g	282.3 ± 9.1d	0.72 ± 0.03d
Ma	82.32 ± 0.26c	1005.3 ± 37.2b	35.3 ± 9.9bc	1363.7 ± 29.2c	393.7 ± 23.1c	2.09 ± 0.15b
Ma_C	-	93.0 ± 3.0fg	11.3 ± 2.3d	189.3 ± 2.5i	107.7 ± 1.1f	0.01 ± 0.00e
Im	80.73 ± 0.04d	932.5 ± 0.7bc	49.5 ± 0.7b	1450.5 ± 4.9b	567.5 ± 6.4b	2.05 ± 0.12bc
Im_C	83.17 ± 0.60bc	304.3 ± 15.6d	25.3 ± 3.2c	672.0 ± 34.2f	393.0 ± 19.7c	0.84 ± 0.01d
Gol	78.77 ± 0.60e	1376.7 ± 107.5a	65.0 ± 13.5a	1987.3 ± 35.4a	695.7 ± 30.4a	3.04 ± 0.05a
Gol_C	-	190.2 ± 14.8ef	21.0 ± 7.0c	385.0 ± 62.9h	192.0 ± 55.1e	0.05 ± 0.00e
BC	84.10 ± 0.35b	832.5 ± 3.5c	36.5 ± 2.1b	1204.0 ± 1.4e	408.0 ± 1.3c	1.68 ± 0.13c
BC_C	-	67.0 ± 1.0g	5.0 ± 0.8d	118.0 ± 5.0ij	56.0 ± 4.0fg	0.02 ± 0.00e

*Means of three determinations ± standard deviation. Different letters on the same column represent the statistical difference ($p < 0.05$). Beans are described as **No** and **No_C** (Notavel), **Im** and **Im_C** (Imperador), **Gol** and **Gol_C** (Gol), **BC** and **BC_C** (Bola Cheia), **Da** and **Da_C** (Dama) and **Ma** and **Ma_C** (Madreperola), where the '**C**' indicates cooked flours.

Zhang, 2019). Additionally, flours of pulses contain a high amount of amylose (around 30%) compared to cereal (around 10%). The high content of amylose might result in a high gelatinization temperature due to the orientation of amylose chains relative to one another, or strong interactions between starch chains, which increases the stability of the granules to rupture under mechanical agitation (Frohlich et al., 2021; Li, Prakash, Nicholson, Fitzgerald, & Gilbert, 2016; Lin & Fernández-Fraguas, 2020). These aforementioned factors raise the minimum temperature to cook the bean flours as well as the temperature at which the viscosity begins to increase during the heating process.

The pretreatment of the grains promoted a starch pre-gelatinization, and this phenomenon was more evident on the flours of Da_C, Ma_C, Gol_C, and BC_C because it did not present a paste temperature (Table 2). The flours of cultivar No_C and Im_C presented a paste temperature, which indicates that these grains were not completely cooked during the heat pretreatment. Therefore, its flour retains part of the native starch granules since it was not completely pregelatinized.

The beans flours presented a range for peak viscosity between 48.3 - 1376.7 cP, and the raw flour presented the highest one compared to the flours of cooked beans (Table 2). This result is comparable to the peak viscosity of fava bean (1152 cP), yellow pea (1544 cP), and pea (1542 cP) flours (Frohlich et al., 2021; Vatansever et al., 2020; Young et al., 2020). The breakdown, the difference between the maximum and minimum viscosities at constant temperature (95 °C), is associated with gel stability. Therefore, lower breakdown suggested that the paste is more stable during cooking (Zhang et al., 2019). The content of amylose and the extent of amylose leaching also influence the breakdown of pulses flours. Thus, the raw flour of cultivars Ma, Im, and Gol might show a high amount of amylose since these presented the highest viscosity values (Table 2). The final viscosity presented a range between 1204 – 1987 cP for raw bean flour, and between 74 – 672 cP for cooked bean flours. The setback oscillated between 28 and 695 cP, where the raw flour presented the highest values (e.g., Ma, Im, and Gol). Low values of setback represent a small tendency to retrogradation, i.e., the starch molecules have low mobility which retains the water into the gel matrix (Demiate et al., 2016; Li et al., 2016). The differences observed in pasting properties between the bean cultivars are a result of their starch composition (ratio of amylose and amylopectin), starch crystallinity, and the content of non-starch components (Frohlich et al., 2021; Lin & Fernández-Fraguas, 2020; Romero & Zhang, 2019).

In general, the flours of cooked beans presented low values of viscosity compared with the raw ones (Table 2, Supplementary Fig. 2). This is because the starch granules of these samples were previously gelatinized, at least part of them (Simons & Hall Iii, 2018). Consequently, the partial depolymerization of amylose and amylopectin promoted by the heating process produces short linear and branched chains. This happens in both crystalline and amorphous regions of the granule starch reducing the gel-forming power, swelling capacity, and viscosity values (Hung et al., 2016).

The gel hardness, which represents the compressive strength, presented a variation between 0.01 – 3.04 N, where the highest values were observed in the raw flour (Table 2). This property is related to the retrogradation of the flour. Thus, flours with high content of amylose present a high setback and gel hardness due to the recrystallization of amylose molecules (Weber, Collares-Queiroz, & Chang, 2009). So, the high gel hardness of cultivars Ma, Im, and Gol also suggest that these cultivars present a high amount of amylose. The heat pretreatment reduced the gel hardness due to starch pre-gelatinization.

3.3. Thermal properties

The flours from raw beans exhibited two endotherm peaks (Table 3, Supplementary Fig. 3), the first one corresponding to starch gelatinization and the second one to protein denaturation and the melting of amylose-lipid complexes (Santiago-Ramos et al., 2018). The peak temperatures (around 80 °C) of raw flours were higher than those reported for other pulses, i.e., faba bean (73 – 75 °C), lentil (70 – 71 °C), and pea (72 – 73 °C) (Abdel-Aal et al., 2018). The temperature of gelatinization is influenced by the starch composition and the presence of non-starch compounds. Which explains the difference between the beans with the other pulses as well as between different bean cultivars. The presence of the non-starch compound in the bean flour is responsible for the low enthalpy energy (Table 3) compared to the isolate bean starch (13 - 15 $J{\cdot}g^{-1}$) (Demiate et al., 2016). Some cooked flours did not present the first endotherm peak, which is following the paste properties results, showing that the starch of the flours from cultivars Da_C, Ma_C, Gol_C, and BC_C were pregelatinized during the cooking process (Table 2 and 3, Supplementary Fig. 4). For the cooked flours Im_C and Da_C the first endothermic peak presented an increase of temperature compared to their raw flours. This occurred due to the presence of retrograded starch which usually needs more temperature to start forming a gel.

Both sorts of flours (raw and cooked) from all studied bean cultivars presented the second endothermic peak (between 90 and 108 °C) (Table 3), which is due to the melting of amylose-lipid complexes due to the existence of them in flour from beans (Santiago-Ramos et al., 2018; Wani et al., 2020). At this range of temperature also occurs the denaturation of proteins since the peak denaturation temperatures of albumins and vicilin are 87 – 98 °C and 98.8 °C, respectively (Santiago-Ramos et al., 2018). Therefore, the differences between the bean cultivars in the temperature and the enthalpy energy may be due to the protein composition of the cultivars as well as the contents of amylose and lipids.

Table 3
Thermal properties of flour of raw and cooked beans from different cultivars: **No** and **No_C** (Notavel), **Im** and **Im_C** (Imperador), **Gol** and **Gol_C** (Gol), **BC** and **BC_C** (Bola Cheia), **Da** and **Da_C** (Dama), and **Ma** and **Ma_C** (Madreperola), where the '**C**' indicates cooked flours.

Flours[1]	Peak 1				Peak 2			
	T_{onset} (°C)	T_{peak} (°C)	T_{end} (°C)	ΔH (J g^{-1})	T_{onset} (°C)	T_{peak} (°C)	T_{end} (°C)	ΔH (J g^{-1})
Da	75.56 ± 0.15 b	80.34 ± 0.08 bc	88.03 ± 1.74 b	2.43 ± 0.63 abc	92.79 ± 0.08 b	97.14 ± 0.07 b	102.25 ± 0.01 b	1.17 ± 0.05 b
Da_C	-	-	-	0.00 ± 0.00 f	91.46 ± 0.24 b	96.29 ± 0.48 b	103.01 ± 2.37 b	1.66 ± 0.78 ab
No	75.70 ± 0.03 b	80.47 ± 0.33 bc	85.91 ± 0.96 c	1.68 ± 0.58 cd	99.84 ± 0.23 a	102.30 ± 0.10 a	107.47 ± 0.15 a	1.87 ± 0.01 ab
No_C	78.33 ± 0.15 a	85.26 ± 0.18 a	94.60 ± 0.95 a	1.32 ± 0.01 de	94.69 ± 1.59 b	98.86 ± 1.64 b	103.79 ± 1.38 b	0.62 ± 0.12 c
Ma	74.25 ± 0.22 c	79.84 ± 0.05 c	86.46 ± 0.43 b	2.41 ± 0.43 abc	93.21 ± 0.10 b	96.23 ± 0.01	102.67 ± 0.27 b	2.14 ± 0.20 a
Ma_C	-	-	-	0.00 ± 0.00 f	92.55 ± 1.21 b	97.25 ± 1.16 b	101.83 ± 2.04 b	1.13 ± 0.24 b
Im	77.01 ± 1.14 a	80.17 ± 0.64 bc	87.77 ± 0.15 b	2.98 ± 0.55 ab	99.96 ± 0.01 a	102.52 ± 0.10 a	107.30 ± 0.05 a	1.56 ± 0.01 b
Im_C	76.76 ± 0.14 ab	81.55 ± 0.63 b	89.80 ± 2.18 b	1.96 ± 0.23 bcd	92.74 ± 0.78 b	97.19 ± 0.20 b	102.66 ± 0.61 b	1.53 ± 0.24 b
Gol	74.77 ± 0.59 bc	79.57 ± 0.98 c	87.36 ± 0.87 b	2.92 ± 0.28 a	93.33 ± 1.23 b	97.38 ± 2.70 b	102.52 ± 2.25 b	1.29 ± 0.16 b
Gol_C				0.00 ± 0.00 f	93.20 ± 0.87 b	97.27 ± 0.91 b	102.54 ± 1.11 b	0.72 ± 0.06 c
BC	76.34 ± 0.24 ab	80.36 ± 0.37 bc	86.21 ± 0.37 b	1.45 ± 0.19 de	99.74 ± 0.33 a	102.43 ± 0.47 a	107.27 ± 0.51 a	1.72 ± 0.24 ab
BC_C	-	-	-	0.00 ± 0.00 f	92.09 ± 1.06 b	96.16 ± 0.84	100.99 ± 1.36 b	0.77 ± 0.15 c

Results are presented as the mean of three replicates ± standard deviation;[1]Flours: raw and cooked (presoaked beans cooked for 5 min). $\mathbf{T_{onset}}$: Onset temperature; $\mathbf{T_{peak}}$: Peak temperature; $\mathbf{T_{end}}$: Conclusion temperature. Different letters in the columns show statistical differences between the preparation method (p<0.05).

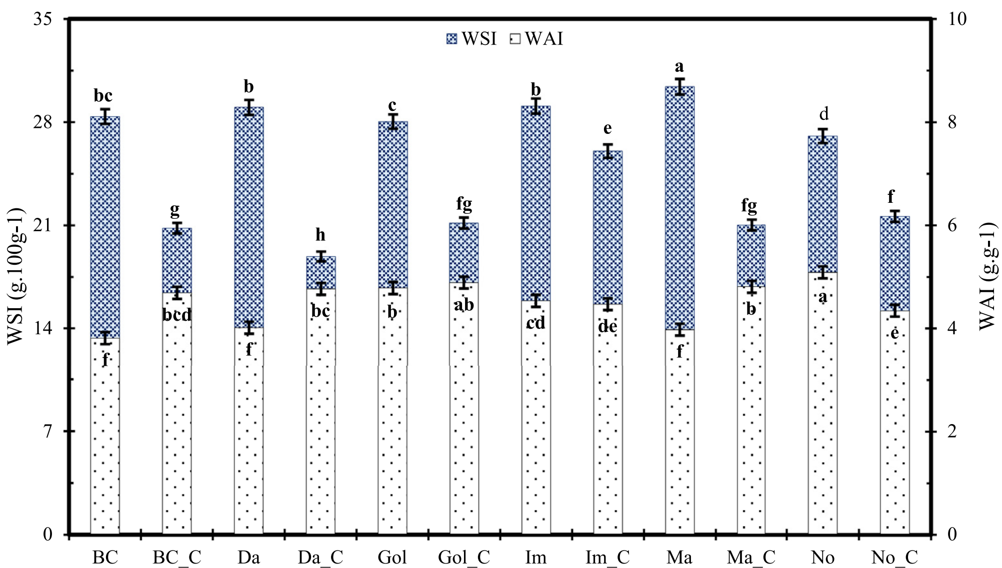

Fig. 1. Water solubility index (WSI) and water absorption index (WAI) of raw and cooked flours of different carioca bean cultivars. Beans are described as **No** and **No_C** (Notavel), **Im** and **Im_C** (Imperador), **Gol** and **Gol_C** (Gol), **BC** and **BC_C** (Bola Cheia), **Da** and **Da_C** (Dama), and **Ma** and **Ma_C** (Madreperola), where the '**C**' indicates cooked flours.

3.4. Water and oil absorption and water solubility

The water solubility index (WSI) varied between 27 – 30 g·100g^{-1} and the flours from cultivars Ma presented the maximum value and the cultivar No had the lowest one (Fig. 1). The bean flour solubility is mainly influenced by their protein composition and is related to the hydrophobicity of their amino acids (Boye, Zare, & Pletch, 2010; Los, Demiate, Prestes Dornelles, & Lamsal, 2020). The heat treatment promoted a reduction in the WSI for all bean cultivars (Fig. 1). These reductions might be due to the protein denaturation which changes the protein solubility, as well as to the starch gelatinization that modifies the cellular medium which might entrap the protein fraction (Alfaro-Diaz et al., 2021). Solubility is a critical factor to consider when developing products based on beans since some bean proteins have low solubility in their original state. Proteins with low solubility promote the formation of very thick suspensions after hydration, which are not suitable for making soups nor for producing low viscosity drinks such as milk substitutes (Vogelsang-O'Dwyer, Zannini, & Arendt, 2021). On the other hand, flours with low values of WSI are appropriate for pasta and baked products development (Bento et al., 2021b).

The water absorption index (WAI) is the ability of the flour to entrap water into its molecular structure. The WAI varied between 3.9 – 5.1 g·g^{-1} and the flours from cultivar No presented the maximum value and the cultivars Ma, Da, and BC the lowest ones (Fig. 1). The results were higher than those found for raw kidney bean flour (1.21–1.53 g·g^{-1}) (Wani et al., 2020). The WAI is affected by the ratio of hydrophilic proteins and carbohydrates amounts in the flours since their strong bonds of the hydrogens of the polar or charged side chains are responsible for contributing to the increased capacity to absorb water (Prasad, Singh, & Anil, 2012). The pretreatment increases the WAI, except for the flour from No_C which presented a reduction in WAI (Fig. 1). The increase in WAI observed in the flour of cooked beans is a consequence of the protein denaturation, which exposes some earlier hidden peptide bonds and polar side chains resulting in an increased ability to trap and keep hold water molecules. Additionally, the heat process promotes starch gelatinization, which also could increase WAI due to the greater loss of molecular order and crystalline structure (Lin & Fernández-Fraguas, 2020).

The oil absorption index (OAI) varied between 2.1 – 1.9 g·g^{-1} and the flours from cultivars BC presented the maximum value and the cultivar Gol had the lowest one (Fig. 2). These results were higher than those found for chickpea flour (0.62 g·g^{-1}) (Gupta et al., 2018). The OAI of the flour is related to the ability of the protein to link with the fat molecules, which is a very important characteristic, since the fat acts as a flavor retainer and increases the food palatability. Electrostatic and

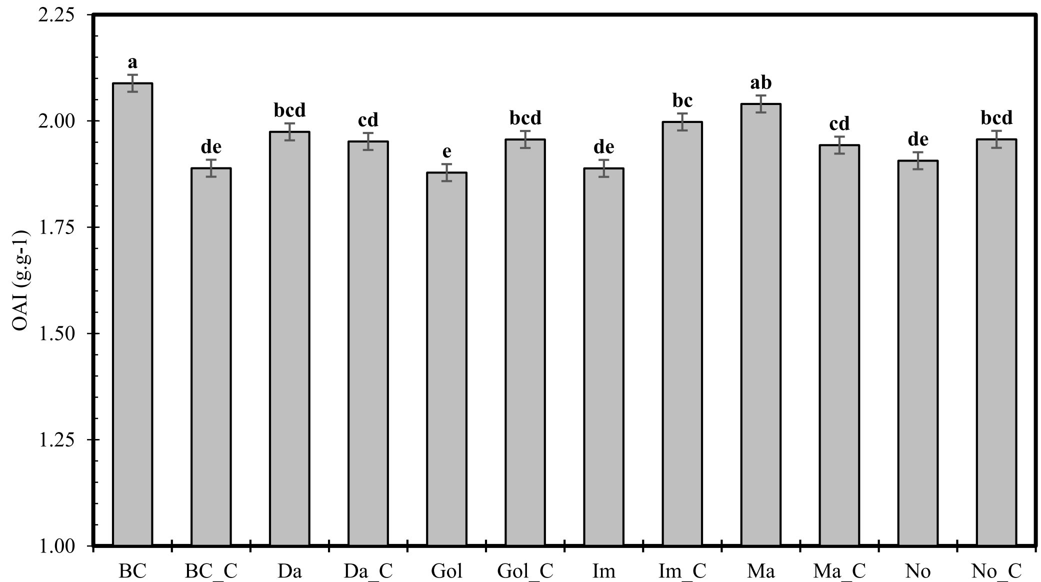

Fig. 2. Oil absorption index (OAI) of raw and cooked flours of different carioca bean cultivars. Beans are described as **No** and **No_C** (Notavel), **Im** and **Im_C** (Imperador), **Gol** and **Gol_C** (Gol), **BC** and **BC_C** (Bola Cheia), **Da** and **Da_C** (Dama) and **Ma** and **Ma_C** (Madreperola), where the '**C**' indicates cooked flours.

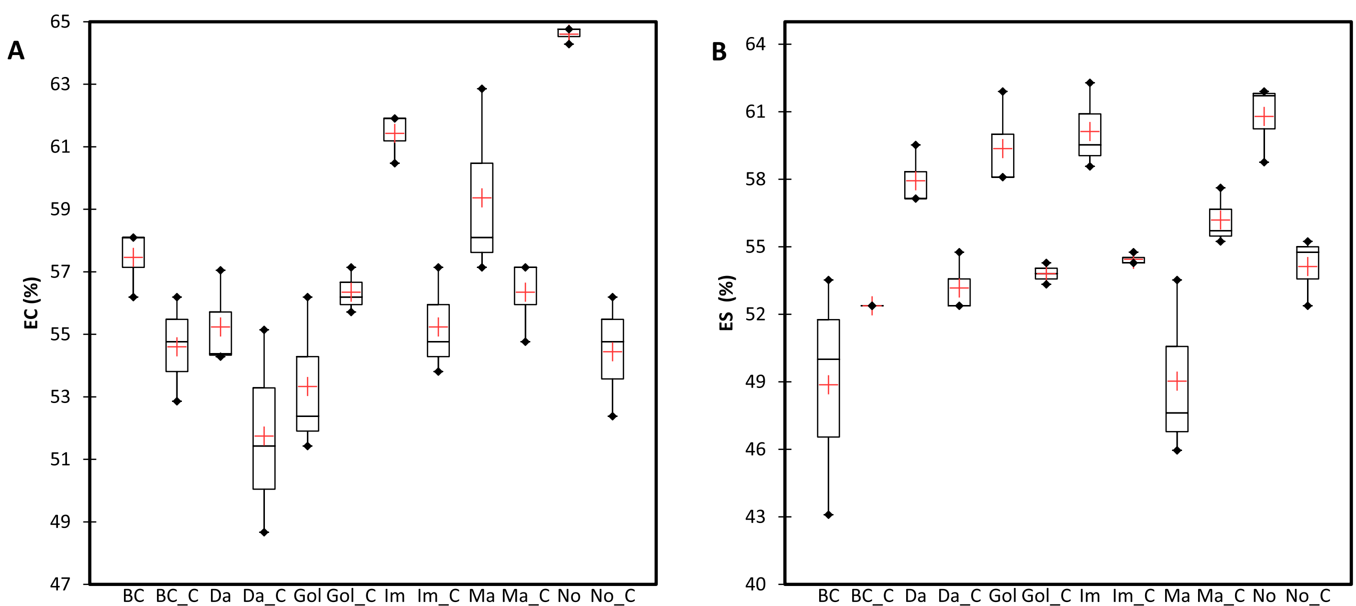

Fig. 3. Emulsify capacity (EC) (A) and emulsion stability (ES) (B) of raw and cooked flours of different carioca bean cultivars. Beans are described as **No** and **No_C** (Notavel), **Im** and **Im_C** (Imperador), **Gol** and **Gol_C** (Gol), **BC** and **BC_C** (Bola Cheia), **Da** and **Da_C** (Dama), and **Ma** and **Ma_C** (Madreperola), where the '**C**' indicates cooked flours.

hydrogen bonds are the forces involved in the lipid-protein interaction. The water and oil binding capacity of food proteins depends on intrinsic factors such as amino acid composition, protein conformation, and surface polarity or hydrophobicity (Vaidya, Solanke, & Gaware, 2016). The heat treatment promoted a slight reduction in OAI on the flour from BC and Ma cultivars, a slight increase in OAI on the flours of Gol and Im, and it was not able to affect the OAI of the flours from No and Da cultivars (Fig. 2). An enhanced OAI would be due to a higher amount of non-polar groups at the protein surface in contact with the neighboring oil (Lin & Fernández-Fraguas, 2020). The reduction of OAI observed in the cooked flours from BC and Ma can be interesting in the point of health since they may be used in fried products to provide reduced fat content and calories (Gupta et al., 2018).

3.5. Emulsifying properties

The emulsifying capacity (EC) ranged between 51 to 64%, with the raw flour from cultivar No presenting the highest value and the cooked flour Da_C the lowest EC (Fig. 3). The formation of emulsions is mainly due to the reduction in the interfacial tension of oil droplets in aqueous systems and electrostatic repulsion among them (Wani et al., 2020). The dissimilarity for EC among the cultivars is due to the hydrophilic/hydrophobic proportions of amino acids in the major storage proteins present in these seeds (Foschia, Horstmann, Arendt, & Zannini, 2017; Gupta et al., 2018). The polysaccharides help to stabilize it by increasing viscosity. So usually, pulses proteins with high solubility have high foaming capacity, emulsification, and gelatinization (Boye et al.,

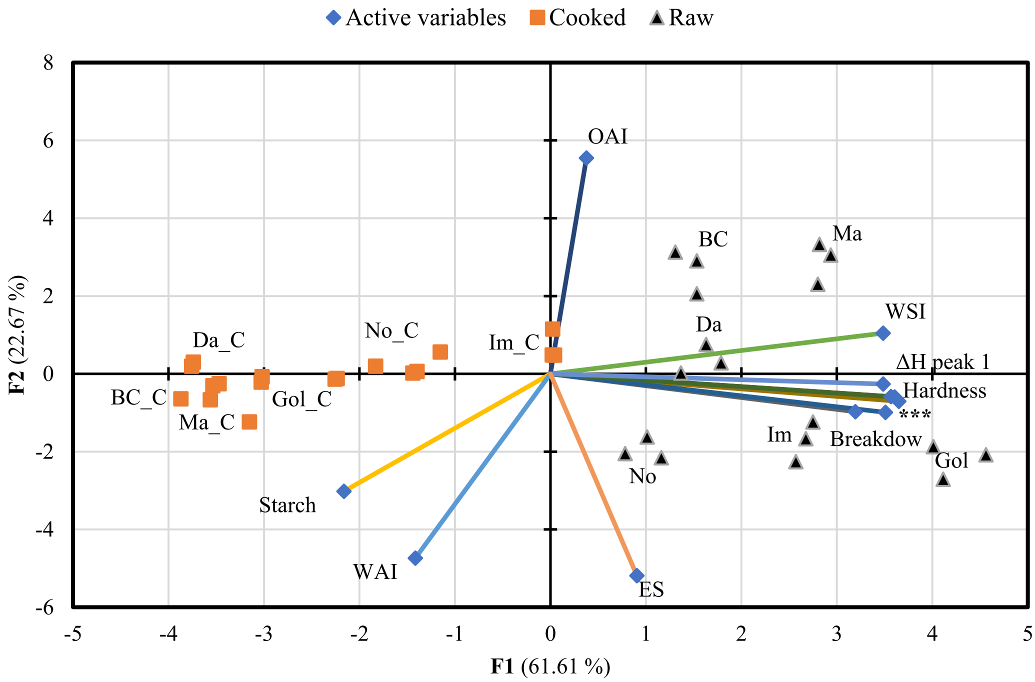

Fig. 4. Principal component analyses of the technological properties of raw and cooked flours of different carioca bean cultivars. Beans are described as **No** and **No_C** (Notavel), **Im** and **Im_C** (Imperador), **Gol** and **Gol_C** (Gol), **BC** and **BC_C** (Bola Cheia), **Da** and **Da_C** (Dama) and **Ma** and **Ma_C** (Madreperola), where the '**C**' indicates cooked flours. OAI: oil absorption index; WSI: water solubility index; ***: peak viscosity, final viscosity, and setback; ES: emulsion stability; WAI: water absorption index.

2010; Los et al., 2020). Therefore, the reduction of EC observed in most of the flours is related to the reduction of viscosity of these flours due to starch gelatinization.

The flours from cultivars No and Im presented the highest emulsion stability (ES) (60%) (Fig. 3). Pulses with excellent emulsifying properties allow the development of emulsion-based drinks and milk alternative drinks without emulsifiers (Alavi, Chen, & Emam-Djomeh, 2021; Vogelsang-O'Dwyer et al., 2021). The heat pretreatment reduced their ES with exception of the flours from cultivar Ma_C (Fig. 3). This reduction may be related to the protein denaturation which reduces the degree of the folded structure resulting in an unstable interfacial layer due to the low molecular interactions into the sub-surface. Another point that explains the reduction or even the increase in the ES is the protein profile of the flour. For example, globular proteins, like globulin (~ 70% of bean proteins), present more conformational limitations, therefore it adsorbs slowly and only partially unfold at the interface, hence exhibiting poor emulsification power (Lin & Fernández-Fraguas, 2020).

The cooked flours compared with the native material (raw flours) presented a reduction in the values of WSI, pasting properties (peak viscosity, final viscosity, breakdown, and seatback), hardness, emulsifying capacity, and emulsifying stability (Fig. 4). This happens because of starch pre-gelatinization and the denaturation of the proteins present in the flours during the cooking step. For instance, precooked flours may be suitable for biscuits development since the heat process contributes to the formation of complexes between amylose and lipids improving the functional properties of the flours, such as lowering the stickiness of biscuits and modifying viscosity profiles (reducing it). Moreover, the flours of pretreated beans may present more fragmentation of their components as a resulting of denaturation and gelatinization which has been related to a desirable smooth texture and also may be responsible for the stable suspensions in thin porridge (Kamau, Nkhata, & Ayua, 2020).

4. Conclusion

The carioca beans flour presented high content of protein, resistant starch, and dietary fiber, and the flour from cultivar Notavel presented the highest content of total dietary fiber and resistant starch for both cooked and raw flours. Additionally, the protein, resistant starch, and dietary fiber content of bean flour are higher than other pulses flours such as pea and lentil, which efforts the high nutritional value of bean flours. The bean flours made from cooked beans presented a reduction in the values of pasting properties (peak viscosity, final viscosity, breakdown, and setback), hardness, water-solubility, emulsifying capacity, and emulsification stability in all carioca bean flours. Hence, the proposed method (i.e., soaking the beans in water for 6 h followed by cooking it under the steam of autoclave for 5 min) was able to promote starch pre-gelatinization and the denaturation of the proteins of the flours (at least part of it). Pre-gelatinized bean flour processed from presoaked beans in the steam of autoclave may be useful for food development (such as snacks, soups, cakes, pasta, etc.) increasing their acceptability as a base ingredient since it might present appropriate functional properties. Therefore, the application of cooked flour in the preparation of new food products still needs more study. Also, there is a gap in information about the nutritional value of cooked carioca bean flour (e.g., the bioavailability of minerals and protein digestibility). So, both application and nutritional studies are needed for better use of this pulse flour.

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.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.afres.2021.100027.

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