

RESEARCH ARTICLE

Physical–chemical, thermal, and functional properties of achira (*Canna indica* L.) flour and starch from different geographical origin

Margarita M. Andrade-Mahecha¹, Delia R. Tapia-Blácido² and Florencia C. Menegalli¹

¹ Food Engineering Department, State University of Campinas – UNICAMP, SP, Brazil

² Departamento de Química, Faculdade de Filosofia, Ciências e Letras, Universidade de São Paulo, Ribeirão Preto, SP, Brazil

Achira (*Canna indica* L.) is a plant native to the Andes in South America, a starchy source, and its cultivation has expanded to different tropical countries, like Brazil. In order to evaluate the potential of this species, starch and flours with different particle size were obtained from Brazilian achira rhizomes. Proximal analyses, size distribution, SEM, swelling power, solubility, DSC, XRD analysis, and FTIR were performed for characterization of these materials. Flours showed high dietary fiber content (16.5–32.2% db) and high concentration of starch in the case of the smaller particle size fraction. Significant differences in protein and starch content, swelling power, solubility, and thermal properties were observed between the Brazilian and the Colombian starch. All the studied materials displayed the B-type XRD pattern with relative crystallinity of 20.1% for the flour and between 27.0 and 28.0% for the starches. Results showed that the starch and flour produced from achira rhizomes have great technological potential for use as functional ingredient in the food industry.

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1 Introduction

Achira (*Canna indica* L.) is a perennial plant native of the Andes in South America, but which is also distributed in tropical regions of America. Achira has received different names; e.g., “sagú”, “arawac”, “imocoma”, “chisgua”, “maraca”, and “capacho”, depending on the indigenous culture of each place. Achira is part of the 25 consumer starchy sources in the tropics. Its cultivation has expanded to Asia, especially China, Vietnam, Taiwan, and Thailand, where its starch is used in the food industry for the pro-

duction of “noodles” and employed as a thickening agent for sauces, condiments, and soups. Moreover, it is also utilized in the pharmaceutical industry [1–3]. Some authors have indicated that this plant has great potential for application in food because its roots are an interesting raw material for the extraction of starch and the development of edible films [4, 5].

Some reports have documented that the canna starch is characterized by very large granules, high AM content, clear paste, high viscosity, high retrogradation, and high resistance to hydrolysis by α -amylase [4, 6, 7]. The high viscosity and clear paste of the canna starch makes it potentially interesting for use as a thickening agent.

In Brazil, achira has been cultivated as an ornamental plant only. However, over the last decade some research studies developed by Centro de Raízes e Amidos Tropicais CERAT/UNESP (São Paulo) using varieties adapted to the soil and local weather have demonstrated the large poten-

Correspondence: Dr. Florencia C. Menegalli, Food Engineering Department, State University of Campinas – UNICAMP, Rua Monteiro Lobato no 80, Barão Geraldo, Zip Code 13083-862, Campinas, SP, Brazil
E-mail: fcm@fea.unicamp.br
Fax: +55-19-3521-4027

Abbreviations: BS, Brazilian starch; CS, Colombian starch

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tial of this plant for starch production [8]. Nevertheless, complete characterization of this starch and its comparison with commercial achira starch have not yet been accomplished.

Because the yield of achira starch production is low (about 12 g starch/100 g fresh rhizomes) [8], one way to increase the commercial potential of achira rhizomes would be to produce the flour, which may be an interesting material if dietary fiber content is considered. In this context, the objective of this work was to produce flour and starch from achira rhizomes cultivated in Southeast Brazil and characterize their physical and chemical properties. Concerning the achira flour, the properties were analyzed for various sieving fractions. The Brazilian achira starch was also compared with the commercial native achira starch produced on a large industrial scale in Colombia. This information could be useful to motivate farmers to cultivate this species, which represents a potential economic source due to its possible industrial utilization.

2 Materials and methods

2.1 Materials

Commercial native achira starch (Colombian starch (CS)) was purchased in a local market in Gutierrez, Cundinamarca, Colombia (4° 15' 00" N, 74° 00' 00" W, 2291 m above sea level). This region is localized on the eastern range of the Andes Mountains in Colombia and has tropical climate with precipitation along all the year. This starch was obtained from 12 month old rhizomes (15 kg of the *Canna indica* L. *Verde* variety), and its extraction was immediate.

The achira flour and starch were obtained from rhizomes cultivated in humid subtropical climate (Köppen *Cwa*) in the city of Conchal, SP, Brazil (22° 19' 48" S, 47° 10' 22" W, 591 m above sea level). No synthetic fertilizers or pesticides were employed in this crop. Seven-month-old rhizomes (40 kg of *Canna indica* L.) were harvested and supplied by Corn Products Brazil, washed with water, dried at ambient temperature, and kept at 8°C for one week prior to starch extraction and flour preparation. $K_2S_2O_5$ was purchased from Synth (Sao Paulo, Brazil).

2.2 Flour and starch extraction

The clean rhizomes were immersed in $K_2S_2O_5$ solution (0.5% w/v) at 3°C for 15 min. Then, the rhizomes were peeled manually, cut into 3 mm slices, and immersed again in $K_2S_2O_5$ solution (0.8% w/v) for 15 min, to prevent oxidation of the slices. To obtain the flour (Fig. 1), the

slices were placed in trays and dried at 40°C for 45 h in a temperature-controlled oven (model MA 415UR, Marconi, Piracicaba, Brazil). The dried slices were finely ground on a Brabender Quadromat Senior Mill (Duisburg, Germany) and sequentially passed through a sieve set (32, 42, 80, 115, and 400 mesh). Next, three flour fractions, namely FA (>32 mesh), FB (42–80 mesh), and FC (115–400 mesh), were selected and stored at 8°C in sealed polyethylene containers.

The Brazilian starch (BS) was obtained according to a procedure described by Leonel et al. [8] with slight modifications (Fig. 1). The rhizomes were peeled manually and disintegrated in a blender with $K_2S_2O_5$ solution (0.5 w/v) at a 1:2 ratio. The slurry was filtered through a 60-mesh sieve, to separate the bagasse (fibrous material). The starch-containing supernatant was passed through a 200-mesh sieve, and then the starch was recovered after natural sedimentation for 3 h. The starch was washed with distilled water twice, placed in Teflon trays, dried, and stored under the same conditions employed for flour production.

2.3 Chemical composition analysis

The moisture content of the flour and the starch were determined by the vacuum oven drying method (AOAC 925.09), in which pre-weighed samples were placed over silica gel overnight and then vacuum oven-dried at 70°C for 24 h. The moisture content was taken to be the loss in weight, expressed as a percentage of the weight of the original sample [9]. The crude protein content was determined by means of the Micro-Kjeldahl method (AOAC, 926.86), where “protein” is measured as total organic nitrogen multiplied by a specific factor ($N \times 6.25$) [9]. The ash content was calculated by high temperature incineration in an electric muffle furnace (550°C) and expressed as a percentage of the initial sample weight (AOAC, method 923.03) [9]. The total dietary fiber content was obtained by following a combination of enzymatic and gravimetric methods (AOAC, 991.43), using α -amylase (A 3306, Sigma–Aldrich Corp.), protease (P 3910, Sigma–Aldrich Corp.), and amyloglucosidase (A 9913, Sigma–Aldrich Corp.) to remove the protein and starch present in the sample. Ethanol was added to precipitate the soluble dietary fiber; the residue was then filtered and washed with ethanol (Synth, Brasil) and acetone (Synth, Brasil). After drying, the residue was weighed, and half of the samples were analyzed for protein and the others were ashed, so that the total dietary fiber content was, the weight of the residue minus the weight of the protein and ash [9]. The starch content was determined according to the method of Diemair [10], based on the partial acid hydrolysis of starch followed by measurement of the optical rotation of the resulting solution. This was based on the controlled acid degradation of the starch, in which

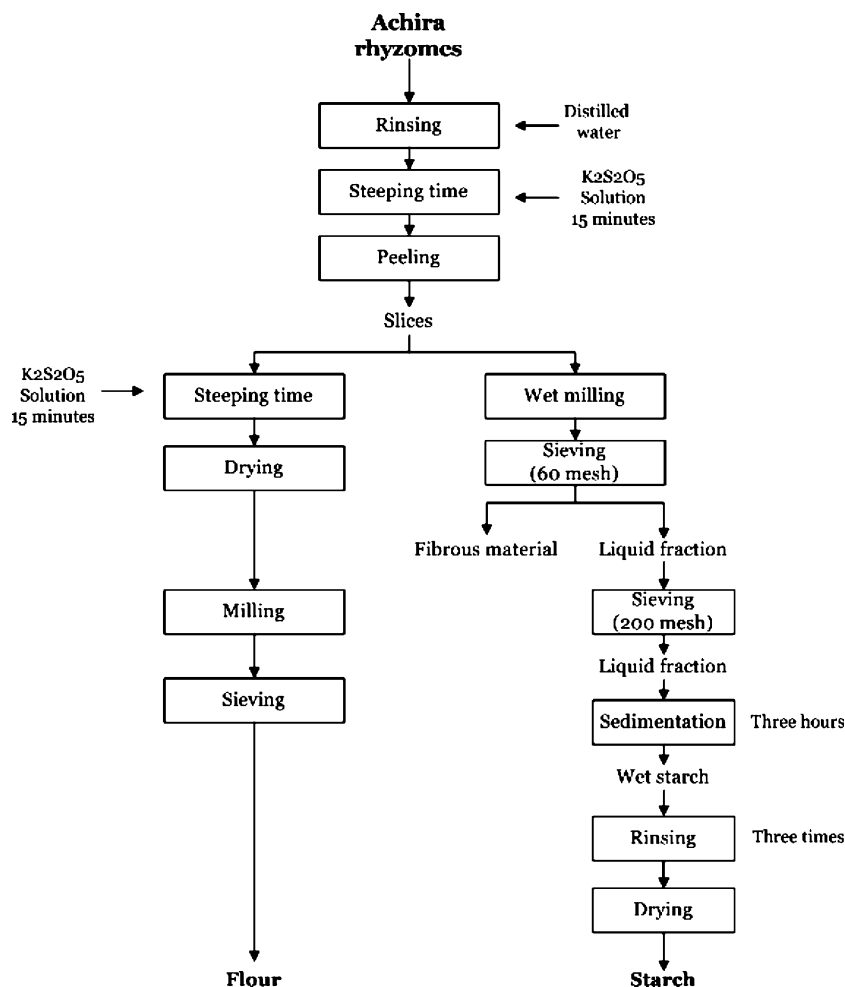


Figure 1. Procedure used for the production of the achira flour and starch.

the granules are firstly fully gelatinized, followed by the solubilized starch hydrolysis. Total lipid content was extracted in a one phase solvent system chloroform/methanol/water and quantified according to Bligh and Dyer method [11]. The AM contents were measured following the ISO 6647 method [12], which determines the affinity of AM for iodine at 720 nm, to minimize interfering effects of AP. All analyses were performed in triplicate.

2.4 Starch granules size distribution

Starch granules size distribution was analyzed as described by Da canal and Menegalli [13]. The samples were deposited and dispersed on a Petri dish with a black background and observed under a stereomicroscope (Citoval 2, Zeiss, Germany) at 40× magnification. The images were obtained with a digital camera (Kodak EasyShare DX4530). Fifty slides per sample were necessary for acquisition of images of a sufficient number of particles (about 20.000). The 2D surface area (S) of the starch granules was extracted from images using the soft-

ware IMAGEJ v1.37 (National Institutes of Health, USA). The equivalent diameters (dp_{eq}) were calculated using Eq. (1):

$$dp_{eq} = 2\sqrt{S/\pi} \quad (1)$$

In order to analyze the starch granules portion present in the three flour fractions. Only, particles with equivalent diameter (dp_{eq}) lying between 5 and 200 μm were assumed as starch. Size distribution and mean particle diameter (dp_m) were obtained from the fraction of particles (X_i) with equivalent diameter ($dp_{eq\ i}$), as represented in Eq. (2):

$$dp_m = \sum X_i dp_{eq\ i} \quad (2)$$

2.5 Scanning electron microscopy (SEM)

Flour and starch samples were attached to circular stubs by means of double-sided copper tape, coated with gold in a sputter coater (VG Microtech model SC 7620,

Cambridge, UK) and finally observed under a scanning electron microscope JEOL JSM-5800LV (Tokyo, Japan) at an accelerated voltage of 10 kV.

2.6 Swelling power and solubility

The swelling power and solubility were determined in triplicate, following the method described by Yu et al. [14]. To this end, about 0.5 g (db) of flour and starch samples (W) were weighed into a centrifuge tube, followed by addition of 20 mL distilled water. The tubes were heated at 55, 65, 75, 85, and 95°C in a shaking water bath for 30 min. Each tube was cooled to room temperature and centrifuged at $2600 \times g$ for 15 min. The supernatant was placed in a glass dish (of known weight) and dried at 105°C to constant weight (W_r). The material adhered to the wall of the tube was considered as sediment and weighed (W_t). The swelling power (SP) and the solubility (S) were computed according to Eqs. (3) and (4):

$$SP = \frac{W_t}{W - W_r} \quad (3)$$

$$S = \frac{W_r}{W} \times 100\% \quad (4)$$

2.7 Differential scanning calorimetry (DSC)

The thermal properties were measured using a Differential Scanning Calorimeter (DSC 2920, TA Instruments, New Castle, DE, USA). For this purpose, approximately 7 ± 0.1 mg of 30% (w/w db) flour and starch suspension were directly weighed into aluminum pans (TA Instruments, USA). The pan was then hermetically sealed and left to equilibrate for 1 h at room temperature, to allow for complete starch hydration. The scanning temperature range was 30–100°C, and the heating rate was 10°C/min using an empty pan as reference. The onset temperature (T_o), peak temperature (T_p), final temperature (T_f), and enthalpy of gelatinization (ΔH) were determined by using the Universal Analyzer software (TA Instruments, USA). The thermal properties determined for all the samples correspond to the average of three measurements. The enthalpy of gelatinization (ΔH) is expressed per gram of dry starch.

2.8 X-ray diffraction pattern (XRD)

XRD analysis was performed using an X-Ray Diffractometer D5005 (Siemens, Karlsruhe, Deutschland) equipped with a crystalline graphite monochromator. Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 0.154$ nm) was produced at 40 kV and 30 mA. XRD diffractograms were obtained at

room temperature (25°C) over a 2θ range of 5°–70° in steps of 0.02°/s, using Diffrac Plus Evaluation 11 Release 2005. Diffractograms were smoothed using a Savitsky–Golay method (polynome = 2, points = 15). The relative crystallinity index of the samples was quantitatively estimated following the method of Nara and Komiya [15] using the Origin software 8.5 (Northampton, MA, USA).

2.9 Fourier-transformed infrared spectroscopy (FTIR)

FTIR spectroscopy was carried out using a model Spectrum One Fourier transform infrared spectroscope (PerkinElmer, Waltham, MA, USA) equipped with a universal attenuator for total reflectance (UATR). Infrared spectra were collected for the wavenumber range 4000–650 cm^{-1} at a resolution of 4 cm^{-1} , and 20 scans were accomplished. Spectrum One B software (version 5.31) was employed, in order to process the results.

2.10 Statistical analysis

Statistical analyses on the means of triplicate experiments were performed using the STATISTIC 7.0 software (StatSoft, Inc., USA). The Tukey test was applied at a 5% significance level to determine differences between samples.

3 Results and discussion

3.1 Flour and starch extraction process

The yields for the Brazilian flour and starch were 13.2 and 6.3 g/100 g fresh rhizomes, respectively, which are considered low as compared to those reported by Leonel et al. [8] for 9-month-old achira rhizomes (11.4 g starch/100 g fresh rhizomes). Differences in the extraction yield could be associated with stage maturity, since achira rhizomes used in this study were harvested at 7 months of age. In addition, information from Colombian producers reports that the commercial achira starch used in this work was obtained from 12-month-old rhizomes with an extraction yield of 14 g/100 g fresh rhizomes without the peeling step.

3.2 Particle size distribution

The three fractions of the Brazilian achira flour display unimodal distribution with predominance of smaller sizes in the following order: $\text{FA} > \text{FB} > \text{FC}$, as shown in Fig. 2. In the case of the flour fractions, FA and FB, the size of the starch granules range between 13 and 128 μm , with

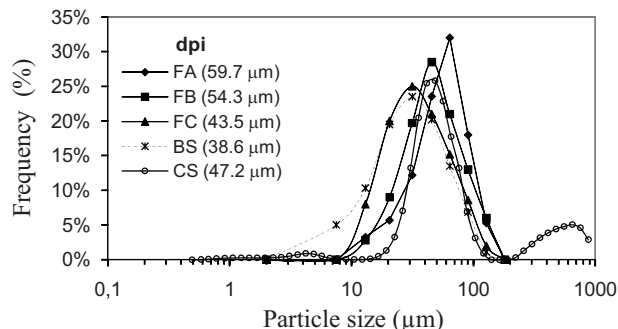


Figure 2. Particle size distribution of the achira flour fractions and the starches. FA, flour A; FB, flour B; FC, flour C; BS, starch from Brazil; and CS, commercial starch from Colombia.

an average size of 59.7 and 54.3 μm , respectively. Meanwhile, 97.8% of the granules from fraction FC present sizes ranging from 13 to 90.5 μm . There is a decrease in the granules fraction of larger size (90.5–128 μm), resulting in a mean size of 43.5 μm . The presence of larger sizes in fractions FA and FB as compared to FC can be associated with formation of agglomerates of particles that were retained in the 32 and 80-mesh sieves. The BS also exhibits a unimodal distribution, in which 98.9% of the granules have sizes lying between 7.5 and 90.5 μm , thus furnishing a mean size of 38.6 μm , while the CS has a bimodal distribution pattern with two distinct populations of granules: one with sizes ranging between 19 and 121 μm and a mean particle diameter of 48.3 μm , and another with sizes between 200 μm and 0.9 mm. The existence of large particle sizes (>200 μm) in the CS could be attributed to the presence of agglomerated starch granules. Punched-Arnon et al. [3] have studied the relationship between granule size and rhizomal development of edible canna grown in Thailand. These authors found a broad range of granule sizes, from 10 to 140 μm , and they reported that starches from immature, premature, and mature segments exhibit a similar profile, with a noticeable peak at a granule size of 50–60 μm . However, slight shifts

in the proportion of starch granules toward the larger size were found as the segments progressed from immature to premature, and mature segments. The mean granule sizes of starches from immature, premature, and mature segments were 54, 53, and 60 μm , respectively. In our study, a similar behavior has been observed, because the BS granules present smaller average size and are obtained from immature rhizomes (7 months old), as compared to those used for extraction of the CS (12 months old).

3.3 Chemical composition

Table 1 lists the chemical composition of the studied starches and flours. The methodology (Fig. 1) employed for the production of starch from achira rhizomes effectively leads to virtually pure starch (987.8 g/kg db). The fractions of flours consist mainly of starch, proteins, lipids, and fibers. All the flour fractions have a high fiber content, which is directly related to the granule size. Fractions with larger mean diameter (FA and FB flours) possess higher dietary fiber content ($p < 0.05$). It can also be verified that the achira flour has higher fiber, protein, and lipid content as compared to the cassava flour and more fiber content than the sweet potato flour [16, 17]. The protein content of the achira flour is lower in fraction FA and higher in fraction FB ($p < 0.05$). The lipid content of the flour samples has a narrow range (from 9.0 to 11.1 g/kg). The ash and starch contents of the achira flours are directly proportional to the granulometry of each flour fraction. Thus, the FA flour with the largest particle size presents the highest ash content (78.5 g/kg), while the highest starch content is found in the flour fraction with the smallest particle size; i.e., FC ($d_{p,m} = 43.5 \mu\text{m}$). So the higher amount of fiber removed from FC culminates in higher starch concentration and lower ash content in this fraction. Research on achira flour has not yet been reported in the literature. Here, the achira flour was produced by means of an easy method that allowed for more complete use of the rhizome. In this way, whole flour containing starch and also a high dietary fiber content (164.9–322.1 g/kg) was obtained. This fiber

Table 1. Approximate chemical composition of the flour and starch produced from achira rhizomes (*Canna indica* L.)

Products	Moisture (g/kg db)	Total dietary fiber (g/kg db)	Crude protein (g/kg db)	Lipid (g/kg db)	Ash (g/kg db)	Starch (g/kg db)	Amylose (g/kg db)
Flours	FA	47.0 \pm 0.3 a	322.1 \pm 7.1 a	40.6 \pm 0.6 a	11.1 \pm 0.8 a	78.5 \pm 2.7 a	506.6 \pm 2.2 a
	FB	47.0 \pm 0.8 a	229.5 \pm 5.1 b	45.4 \pm 0.1 b	9.0 \pm 0.5 a	68.2 \pm 0.8 b	602.3 \pm 2.9 b
	FC	45.6 \pm 0.8 a	164.9 \pm 16.0 c	42.9 \pm 0.7 c	10.8 \pm 2.4 a	51.1 \pm 0.4 c	684.0 \pm 7.8 c
Starches	BS	97.6 \pm 0.5 A	8.6 \pm 0.3 A	6.0 \pm 0.4 A	1.5 \pm 0.1 A	5.3 \pm 0.8 A	987.8 \pm 0.8 A
	CS	83.5 \pm 0.9 B	8.2 \pm 0.1 A	8.1 \pm 0.6 B	0.5 \pm 0.02 B	2.2 \pm 0.1 B	998.4 \pm 0.4 B

Different letters (small: amongst different fractions of flour; capital: amongst starches) indicate statistically significant differences ($p \leq 0.05$). FA, flour A; FB, flour B; FC, flour C; BS, Brazilian starch; and CS, Colombian starch.

is a kind of bioactive compound known to play beneficial physiological roles in human health such as decreases in the risk of obesity, metabolic syndrome, type II diabetes mellitus, gastrointestinal disorders, and development of cardiovascular disease [18]. High fiber content (54.84 g/100 g) can also be found in the by-product of the *Canna* starch extraction process, as described by Zhang et al. (2010) [19]. Some studies have reported that achira rhizomes exhibit a moderate antioxidant activity associated with the presence of phenolic compounds and soluble dietary fiber [18, 19]. Therefore, the achira flour produced in this study can be considered as a functional ingredient for use in the food industry.

The BS and CS are not significantly different in terms of total dietary fiber, but the protein, starch, and AM content of the BS is lower as compared to the CS. These differences could be explained by the lower purity (987.8 g/kg) and high lipid content (1.5 g/kg) of the BS as compared to the CS (998.4 g/kg). However, both starches present higher protein content as compared to starches obtained from different varieties of *Canna* cultivated in some regions of Thailand and Vietnam [2–4]. The AM values obtained in this work are close to those obtained by Cisneros et al. [7] for the starch of achira cultivated in the San Gabán region, in southeastern Peru. In this work, it has been shown that the BS has higher moisture content (97.6 g/kg) as compared to the Brazilian flour (45.6–47.0 g/kg). This result could be related to the high capacity of moisture retention by the starch, due to its hydrophilic character. This happened during the extraction process of this material, for which there were a higher number of steps in the presence of water (wet milling, sieving, sedimentation, and three successive washes). In the case of the achira flour production, there is less contact with water. Moreover, molecular interactions between the components present in the flour could have limited the hydrophilic character of this material as a result of its high lipid content as compared to achira starches (BS, CS).

3.4 Granule morphology

Scanning electron micrographs of the fresh rhizome (a), flour FA (b), flour FB (c), flour FC (d), BS (e), and CS (f) are depicted in Fig. 3. Figure 3a–d clearly show the presence of starch granules and fibers in the rhizoma and achira flour, while the starch granules remain intact. This demonstrates that the methodology used to obtain the achira flour was effective and did not alter the morphology of the granules. This can be attributed to the use of simple physical operations such as slicing, drying, grinding, and sieving, in which changes to the morphology of the granules may be minimal as compared to other methodologies that involve pH modification and/or extraction using chemical reagents or water. In the sequence of micrographs

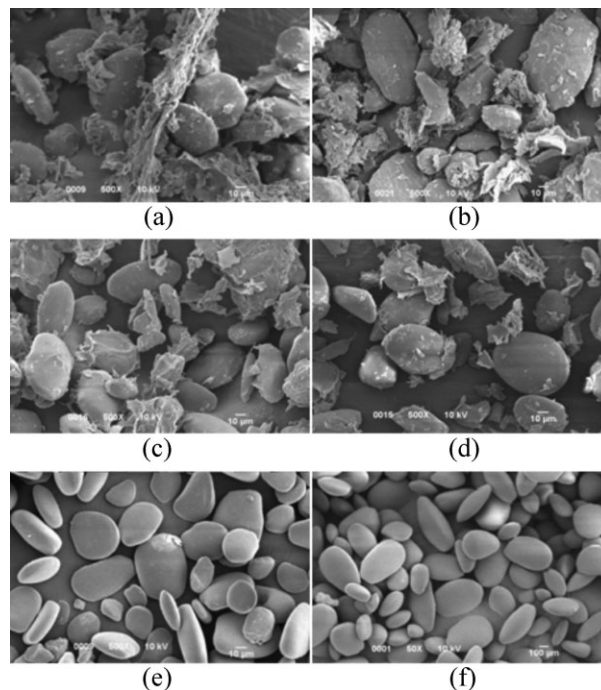


Figure 3. Scanning electron micrographs of the (a) rhizome, (b) flour FA, (c) flour FB, (d) flour FC, (e) BS starch, and (f) CS starch from achira (*Canna indica* L.).

(Fig. 3a–d), a decrease in the amount of cuticles surrounding the starch granules can be detected, which coincides with the reduction in the fiber content of the studied materials (Table 1). The majority of the achira starch granules in the Brazilian flour have oval and elliptical shapes for small and large sizes, characteristics that have also been found by different authors [2–4]. Fig. 3f evidences the same morphology for the CS. However, in this figure starch granules of greater size predominate, as compared to the BS (Fig. 3e), which is consistent with the differences in mean size found between the two starches (Fig. 2).

3.5 Swelling power and solubility

The swelling power of the flour fraction with smaller granule size (FC), the BS, and the CS at different temperatures are represented in Fig. 4. In the range of 55–65°C, the values of swelling power for the Brazilian flour are higher as compared to the BS, while at higher temperatures (75–95°C) this behavior is reversed; i.e., the swelling power of the BS is 1.3 times greater than that of the Brazilian flour. The higher water absorption capacity of the Brazilian flour may be due to the presence of a larger amount of polar amino acid residues from proteins, which have an affinity for water molecules [20], but the high hydrophilicity of the cellulose present in the fibers can also account for this fact. The main chemical compounds that enhance the water

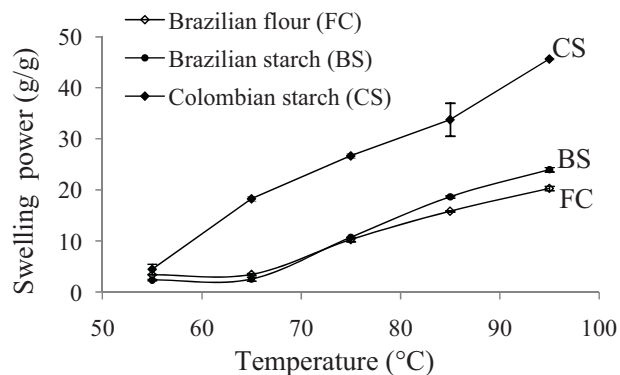


Figure 4. Swelling power of the achira flour and starch at different temperatures. FC, flour C; BS, starch from Brazil; and CS, commercial starch from Colombia.

absorption capacity of flours are proteins and fibers, since these constituents contain hydrophilic parts, such as polar or charged side chains [21]. The swelling power values obtained in this work for the Brazilian flour and starch are close to those reported for the canna starch extracted from varieties grown in Thailand and Vietnam [4, 6], but higher than those reported for the cassava flour (5.87–13.48%) [16]. The CS has higher swelling power (4.4–45.7 g/g) as compared to the Brazilian raw materials (2.4–24.0 g/g) in all the studied temperature range. In comparison with the starch extracted from other tuberous such as cassava, potato, and sweet potato, the Brazilian and Colombian achira starches display higher swelling power between the temperatures of 60 and 80 °C [22]. The higher swelling power exhibited by the achira starches would be explained by its large granule size and high AM content [23]. This

property is an indication of the water absorption index of the granules, so these achira flour and starches could be used to retard staling and control moisture as well as ice crystal formation, thereby increasing food stability [24]. Figure 5 displays the structure of the starch granules stained with iodine solution for all the studied raw materials. This figure reveals swelling of the starch granules with increasing temperature (from 65 to 85 °C), breakdown of granules, and AM release. The presence of AM can be observed by the blue regions surrounding the swollen granules in some micrographs. It can be clearly seen that granules of the CS lose their integrity at lower temperatures as compared to the Brazilian variety, reflecting the weaker structure of the former.

Some studies have reported that AM can form insoluble complexes that inhibit swelling in the presence of lipids [25]. This can be ascribed to the swelling power behavior obtained in this work, in which the sample with the lowest lipid content (CS) has the highest swelling power. Furthermore, differences in the swelling power of starchy materials can be attributed to the starch content, presence of impurities (e.g., proteins and lipids), and processing history [26].

Figure 6 shows the solubility of the flour fraction with smaller granule size (FC), the BS, and the CS as a function of temperature. At low temperature (55 °C), the solubility of FC is significantly greater than that of both starches. The high solubility values achieved for the flour FC may be due to its higher protein content and the presence of soluble fibers, while in the studied starches, the presence of AM-lipids complexes may contribute to their decreased solubility. The solubility of FC (8.1–16.8%) is higher than that of BS (1.5–13.7%) in the studied temperature range.

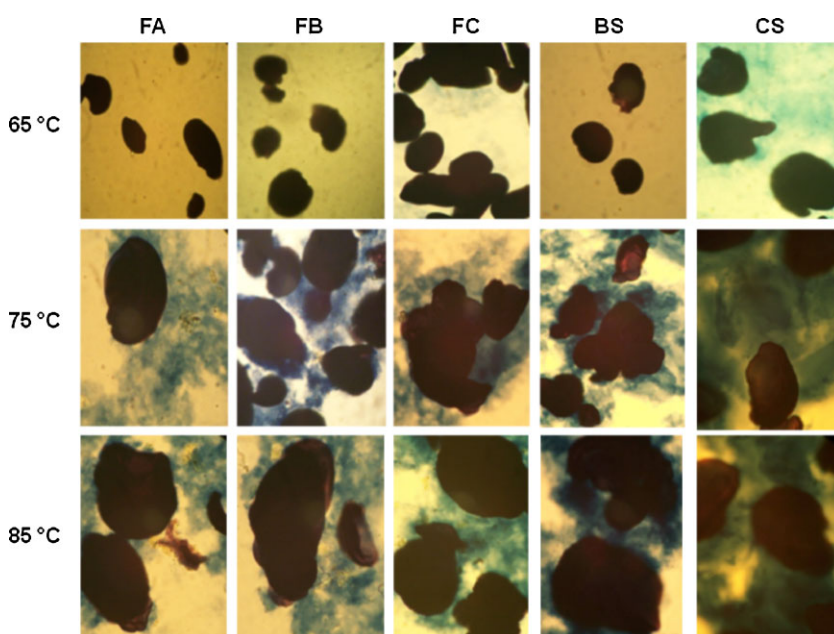


Figure 5. Achira starch granules stained with iodine solution and heated at different temperatures (40×). (FA) Flour A, (FB) flour B, (FC) flour C, (BS) Brazilian starch, and (CS) Colombian starch.

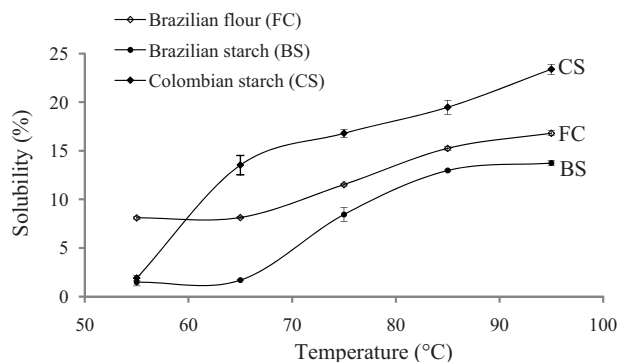


Figure 6. Solubility in water of the achira flour and starch at different temperatures. FC, flour C; BS, starch from Brazil; and CS, commercial starch from Colombia.

This result suggests that the solubility values for FC may also be influenced by the presence of some soluble components such as sugars and soluble fiber, as cited by some authors in the case of the sweet potato flour [27]. High solubility values have been reported for flours from different varieties of cassava ($65.3 \pm 4.5\%$) and sweet potato (18–23%), as compared to the respective starches [16, 17, 28]. On the other hand, the solubility values for the CS are higher than those of the BS in the 65–95°C temperature range. This result may be related to the composition of these materials, since the AM and protein contents ($40.8 \pm 0.3\%$ and 8.1 ± 0.6 g/kg db, respectively) of the CS are higher than those of the BS ($39.0 \pm 0.2\%$ and 6.0 ± 0.4 g/kg db, respectively). The starch solubility is largely due to the solubility of AM that is leached from the granules during gelatinization, which can be clearly observed in Fig. 5.

3.6 Thermal properties

The thermal properties of the three flour fractions and of the starches from achira are summarized in Table 2. Comparing the values of the initial and final temperature

of gelatinization (T_o and T_f) of the three flours (FA, FB, and FC), it can be seen that there are no significant differences ($p < 0.05$). In relation to the gelatinization peak temperature (T_p), there is a significant difference of 0.8°C between FA and the BS, and T_p is higher for FA. Therefore, the higher fiber, protein, and lipid content of FA increases the gelatinization peak temperature in this flour fraction, due to the protective action of these components through inhibition of hydration of the granules and subsequent gelatinization. This is confirmed by the lower values of gelatinization enthalpy. Some studies have also reported a rise in the gelatinization peak temperature for flours based on cereals and tubers, which is due to the higher fiber content and the presence of stable AM-lipids complexes [29] in the flour fractions (9.2 – 9.7 J/g of dry starch) as compared to the starches (14.0 – 14.5 J/g dry starch). Since this parameter represents the amount of energy required to break the molecular interactions within the starch granules during gelatinization, the lowest ΔH values obtained for flours may indicate partial melting of the AP crystals, which may also be related to a difference in the stability of the crystals associated with the size of starch granules [30]. Some authors have related the size of starch granules with their thermal properties. Thus, the flour with larger starch granules diameter has higher T_p values and lower ΔH values, as reported by Coral et al. [30]. According to the literature, the enthalpy values for the *Canna* starch vary in the 9.4 – 20.1 J/g range [3, 31]. In relation to achira starches, the differences between the chemical composition of the CS and BS are also correlated with their thermal properties, since the BS has higher gelatinization temperature. This could be attributed to its lower purity and higher lipid content as compared to the CS, and to the fact that the lipids may form stable complexes in the presence of AM.

3.7 Crystalline structure

The XRD patterns of the studied materials are displayed in Fig. 7. Both the BS and CS have peaks around 5.6° , 17° ,

Table 2. Thermal properties of the flour and starch produced from achira rhizomes (*Canna indica* L.)

Products		Onset T (T_o (°C))	Peak T (T_p (°C))	Final T (T_f (°C))	Enthalpy ^{a)} ΔH (J/g)
Flours	FA	66.9 ± 0.9 a	72.0 ± 0.2 a	77.4 ± 1.0 a	9.2 ± 0.3 a
	FB	66.8 ± 0.1 a	71.8 ± 0.5 ab	77.9 ± 1.9 a	9.7 ± 1.7 a
	FC	67.3 ± 0.3 a	71.6 ± 0.1 ab	77.0 ± 0.3 a	9.5 ± 0.2 a
Starches	BS	67.6 ± 0.1 A	71.2 ± 0.2 A	77.4 ± 0.2 A	14.5 ± 0.5 A
	CS	59.9 ± 0.1 B	63.7 ± 0.2 B	71.6 ± 0.9 B	14.0 ± 0.8 A

Different letters (small: amongst different fractions of flour; capital: amongst starches) indicate statistically significant differences ($p \leq 0.05$). FA, flour A; FB, flour B; FC, flour C; BS, Brazilian starch; and CS, Colombian starch.

a) Enthalpy values calculated per gram of dry starch.

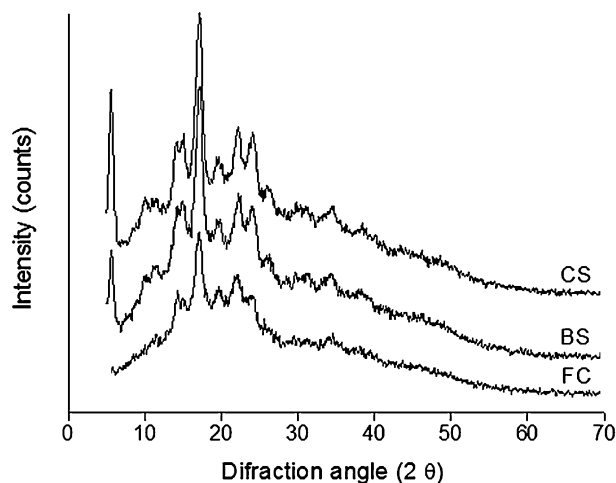


Figure 7. XRD patterns of the raw materials obtained from achira (*Canna indica* L.). FC, flour C; BS, starch from Brazil; and CS, commercial starch from Colombia.

22°, and 24°. These peaks are characteristic of a “B”-type crystalline structure, which is usually obtained from tuber and root starches, such as the potato starch and the *Canna* starch. The strongest diffraction peak in the XRD pattern appears at $2\theta = 17^\circ$, and there are also a few small peaks at 2θ values around 20°, 22°, and 24°. Similar results have been reported by different authors for the *Canna* starch [1–3, 6]. This material has been presumed to have a large proportion of long AP branch chains, as cited by Thitipraphunkul et al. [2]. In the case of the Brazilian flour, there is no peak at 5.6°, and the peaks at 17°, 22°, and 24° have diminished intensity. According to ref. 32, the type of crystalline polymorph has been shown to be influenced by the content of fatty acids due to the formation of AP-lipid complexes in the native starch. These complexes probably do not form crystallites of proper size to provide a proof indicating their existence at 5.6° in the achira flour (FC). This is because a minimum size of crystalline domains is required for detection of crystallinity by X-ray diffractometry [33]. In the present study, the calculated relative crystallinities are 20.1, 27.0, and 28.0% for FC, BS, and CS, respectively, which is in agreement with the results reported by Srichuwong et al. [31].

3.8 Fourier-transformed infrared spectroscopy (FTIR)

Figure 8 brings the spectra of the flours and starch from the Brazilian achira and the commercial starch from the Colombian achira. All the spectra exhibited a broad peak in the 3297–3280 cm^{-1} region, characteristic of the symmetrical and asymmetrical stretching of OH bonds. This region has a wide base and a round peak, which

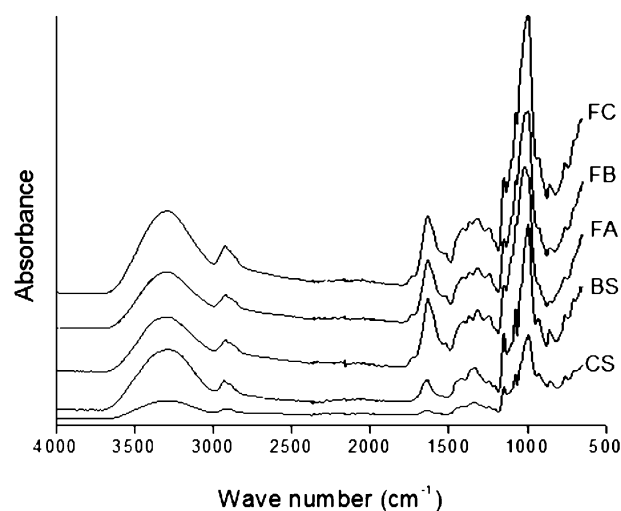


Figure 8. FTIR spectra of raw materials obtained from achira (*Canna indica* L.). FA, flour A; FB, flour B; FC, flour C; BS, starch from Brazil; and CS, commercial starch from Colombia.

indicates major contribution from water molecules. The second peak, observed in the 2921–2928 cm^{-1} region, is attributed to CH bond stretching (asymmetrical CH_2) [34]. This peak is displaced to higher wavenumbers (2926–2928 cm^{-1}) in raw materials with higher starch concentration (FC, BS, and CS), as compared to the flours FA and FB (2921 cm^{-1}). According to Kizil et al. [35], intensity changes in this range can be ascribed to the variations in the amount of AM and AP present in the starches.

All the studied materials display a peak in the 1633–1640 cm^{-1} region, which identifies the amide I band (primarily C=O stretching vibrations). This band provides information about the secondary structure of proteins. Contours of amide I band of proteins or polypeptides consist of overlapping component bands, representing α -helices, β -sheets, turns, and random structures. Bands in the 1640–1620 cm^{-1} region have been assigned to β -sheet [36]. In the achira flours (FA, FB, and FC), this peak occurs between 1633 and 1634 cm^{-1} , while in the case of the starches, it appears between 1639 and 1640 cm^{-1} , with highly attenuated intensity. The exact frequency of this vibration band depends on the nature of the hydrogen bonding involving the C=O and NH moieties [36]. It is important to consider that peaks detected in the region between 1642 and 1637 cm^{-1} may also be related to the starch crystallinity. Thus, variations in the crystallinity can potentially affect this band. In the present study, the raw materials with high crystallinity index present a weaker band in this region as compared to the three flour fractions. This behavior agrees with that reported by Kizil et al. [35].

Another important band concerning proteins is the one relative to amide III, which absorbs between 1200 and 1350 cm^{-1} and arises from the CN bond stretching and bending of the NH bond of the amide group of proteins. This band can be observed in all the studied raw materials. In the region between 1200 and 400 cm^{-1} , vibrations typical of carbohydrates can be identified. In this range, the bands at 1149 and 1148 cm^{-1} correspond to the CO bond stretching of carbohydrates, and they are seen in the spectra of all the tested materials. The bands at 1075 and 1076 cm^{-1} observed in the spectra of the flour and starch fractions, respectively, correspond to COH bending vibrations of the starch molecules [37]. The band at 1016 cm^{-1} , observed only in spectrum of FA, corresponds to COH vibrations or solvation. This band is displaced to lower wavenumbers in FB, FC, and BS (995 cm^{-1}), and appears at 993 cm^{-1} for the CS sample. According to Van Soest et al. [38], the band at 994 cm^{-1} , which is related to intramolecular hydrogen bonding of the hydroxyl group at C-6, is water sensitive. Thus, differences in the intensity of this band may be due to different water contents. The peaks identified in the region between 1700 and 1000 cm^{-1} for the raw materials employed in this work have also been reported by Tapia-Blácido et al. [34] for the flour and starch obtained from two different amaranth species. In general, the infrared spectra of the products under study are similar, with some variations in terms of peak intensity, as a consequence of the differences found in the composition of the products.

4 Conclusions

In this work, we have reported new information concerning the physical–chemical, thermal, and functional properties of the achira flour, for which there were no enough research in the field literature. Differences between the approximate composition of the flours and starches isolated from the *Canna* rhizomes demonstrate exert influence on their thermal and functional properties, which should encourage their production and use from a nutritional and technological viewpoint. For example, the achira flour could be used as a functional ingredient for the manufacture of value-added products in the bakery industry or in the preparation of low-fat, high-fiber dietetic products due to its starch properties and total dietary fiber content. Furthermore, the high AM content found in both achira starches (Brazilian and Colombian) is an important characteristic for the formation of strong polymeric matrices for the preparation of edible coatings and biodegradable films. Moreover, the high swelling power of these two achira starches as compared to other tuberous starches is a desirable characteristic that avoids syneresis and stabilizes products. Therefore,

the production of achira flour and starch are alternative approaches to addition of a value to this tropical crop.

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