

Physicochemical and Techno-Functional Characterization of Native Corn Reintroduced in the Andean Zone of Jujuy, Argentina [†]

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Abstract: The chemical and techno-functional properties of nine maize races from the Andean zone of Jujuy, Argentina, in the process of reintroduction, were determined. Principal component analysis (PCA) was applied to establish the differences between them. The breeds studied showed high variability in their chemical and techno-functional properties, which would indicate that their applications in the food industry will also be differentiated. The PCA analysis allowed us to group them into four groups, and the Capia Marron and Culli races showed unique properties, mainly in the formation of gels.

Keywords: Andean; native corn; physicochemical; race; techno-functional

1. Introduction

The native corn of the province of Jujuy, Argentina, has been the foundation of the alimentary culture of the Andean region for centuries. However, the way of feeding has changed with the progression into modernity, and this has led to the loss of numerous maize races, affecting the biodiversity of this crop. Currently, there are very few communities that are suppliers of corn seeds that were cultivated in the past [1]. However, the Puna, Quebrada and Valles regions are considered amongst the most important in situ Andean maize germplasm banks in the country.

The functional properties of corn flours indicate their possible uses in the food industry [2]. For example, the soft endosperm hydrates much better because starches are easily reached by water, as they have fewer bodies of zein surrounding the endosperm [3]. Likewise, the amylose–amylopectin ratio in starches explains the differences in the granular structure, the physico-chemical properties, the swelling power, the viscosity, and the gelatinization temperature, the firmness of the gel, the retrogradation and the susceptibility to enzymatic attack [4]. The incorporation of starches with high amylopectin content into flour has a beneficial effect in bakeries, as higher moisture delays retrogradation and extends shelf life [5]. The same does not occur in pasta, since it produces less firmness and greater stickiness [6]. There are also certain characteristics of the corn that make it suitable for producing specific foods, and for their use in beverages, as they are 85% grain and 15% cob [7].

The re-insertion of native breeds is of great importance for biodiversity, and the knowledge of their technological aptitudes is fundamental in determining their possible industrial applications. The objective of this work was to analyze the nutritional composition and the techno-functional

properties of the integral flours of nine Andean maize races, and to group them by applying principal components analysis (PCA).

2. Materials and Methods

2.1. Raw Materials, Sowing, Pollination and Harvest

The genetic material was provided by the INTA-Pergamino germplasm bank. The identification and origin of the genetic material is described in Table 1.

The sowing, pollination and harvesting was carried out in the experimental field of the Research Institute for Family Farming (IPAF INTA, Tilcara, Jujuy, Argentina) for two consecutive years (2017 and 2018). The ear corn were dried in the sun on metal sheets for 7 days (average temperatures: daytime 26 °C and nighttime 10 °C), then they were transported to the laboratory for analysis.

2.2. Chemical Composition, Amylose Content and Endosperm Hardness

The macronutrients of the different races were determined by Official Methods of Analysis [8]: humidity at 105 °C (AOAC 930.15), lipids by acid hydrolysis (AOAC 922.06), total nitrogen and proteins (AOAC 984.13), and ash by carbonization at 550 °C (AOAC 925.10). The amylose content was determined via the colorimetric method [9]. The hardness of the endosperm was determined by the hectoliter weight technique [3].

2.3. Properties of Hydration, Absorption of Oil and Thermal

The water holding capacity (WHC) at 30 °C and the oil holding capacity (OHC) at 70 °C were determined by the method of Ahmed et al. (2016). Both properties are expressed as g/g flour.

The thermal properties of the flours were analyzed by differential scanning calorimetry (DSC Q2000). The samples were prepared directly in capsules, with a final solids concentration of 25%, and they were heated from 20 to 130 °C at a rate of 10 °C/min in the presence of nitrogen. The initial temperature (T_0), peak temperature (T_p), final temperature (T_f) and enthalpy ($\Delta H/g$) were determined from the area corresponding to each peak.

Table 1. Origin and identification of plant material.

Identifier	Race	Province	Department	Location
ARZM 09342	Capia blanco	Jujuy	Tumbaya	La Ciénaga
ARZM 09411	Capia Garrapata	Jujuy	Tilcara	Huacalera
ARZM 09417	Capia Marrón	Jujuy	Tilcara	Huacalera
ARZM 09332	Cristalino Amarillo	Jujuy	Tumbaya	Huachi Chocana
ARZM 09154	Culli	Jujuy	Tilcara	Potrerrillos
ARZM 09435	Cuzco	Jujuy	Tumbaya	Huajra
ARZM 09144	Rojo	Jujuy	Tilcara	Pampa Grande
ARZM 09424	Morocho	Jujuy	Tilcara	Quebrada de la Huerta
ARZM 09418	Perlita	Jujuy	Tilcara	Huacalera

2.4. Firmness of Gels and Stability in Refrigeration

The gels were prepared from a flour/distilled water dispersion (3.5 ± 0.01 g flour in 25 ± 0.01 g water). The dispersion was heated to boiling with constant stirring for 3 min with a consistent heating plate temperature (temperature about 93 °C). They were then poured into cylindrical containers (3.5 m internal diameter, 4 cm high), allowed to stand for 25 min at room temperature and stored at 4 °C for 24 h for stabilization of the gel. The texture analysis was performed at room temperature on a texture analyzer TA.XT plus (Stable Micro Systems Ltd., Surrey, UK) equipped with Texture Exponent Lite software for Windows. A compression cycle was performed at a constant speed of 0.5 mms^{-1} to a depth of 8 mm of the sample, followed by a return to the original

position. The force-time curve was obtained, and was used for the determination of firmness (the maximum force observed before the fracture). The stability of the gels was determined at 4 °C by measuring the syneresis for 96 h [10].

2.5. Statistical Analysis

All measurements were in triplicate. Data were analyzed using XLSTAT software (V2008.1.50162). Linear correlations between any two samples were estimated by Pearson correlation analysis. Principal component analysis (PCA) was carried out to reduce the dimensions of variables and to visualize the similarities among different samples.

3. Results and Discussion

3.1. Raw Materials

The nine races of corn planted were identified as Capia, Culli, Morocho, Garrapata, Perlita, Brown Capia, Red, Crystalline Yellow and Cuzco (Figure 1). For the identification of the different breeds, the manuals provided by the germplasm bank INTA-Pergamino were used.

3.2. Chemical Composition, Amylose Percentage and Endosperm Hardness

Table 2 presents the chemical composition and hardness of the endosperms of the different races. According to the endosperm hardness, the races were ordered from the hardest to the softest, as follows: Perlita, Morocho, Rojo, Cristalino amarillo, Culli, Capiamarrón, Capia, Garrapata and Cuzco. The moisture varied between 9.01% and 10%. The protein content varied between 7% and 12%. The Morocho and Capia Marron breeds had the highest and lowest protein contents, respectively. Culli and Perlita maize had the lowest (3.8%) and highest (5.7%) lipid content respectively. No correlation was observed between the hardness of the endosperm and the protein or ash content. However, a positive correlation was observed between lipid content and hectolitre weight. The amylose content varied between 15 and 29 mg/100 g. A tendency to increase the content of amylose was observed with the increase in hardness of the endosperm [11].



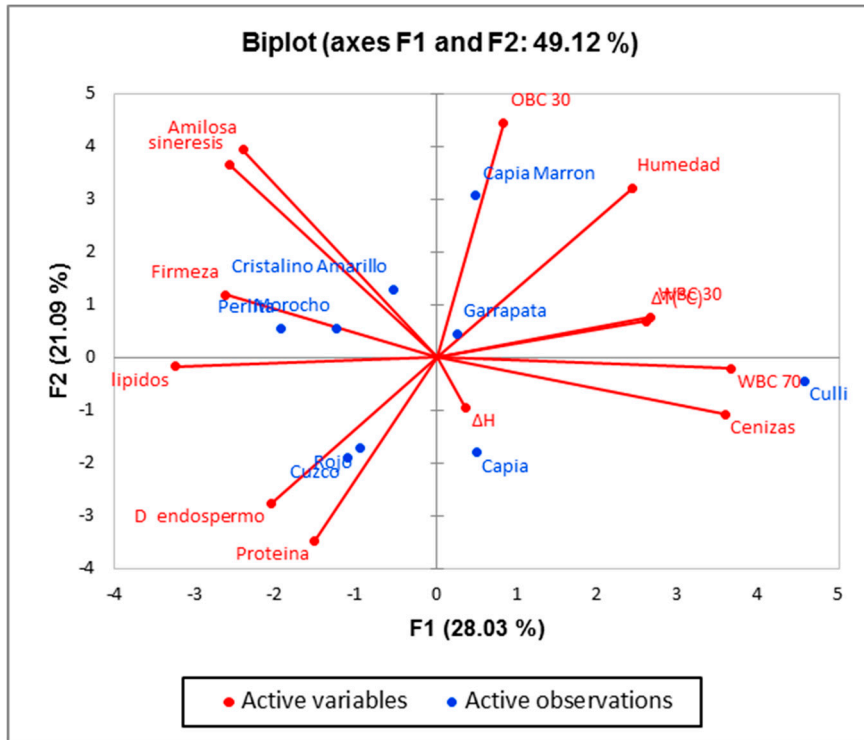
Figure 1. Races identified during the harvest.

3.3. Technological and Thermal Properties of Whole Meal Flours

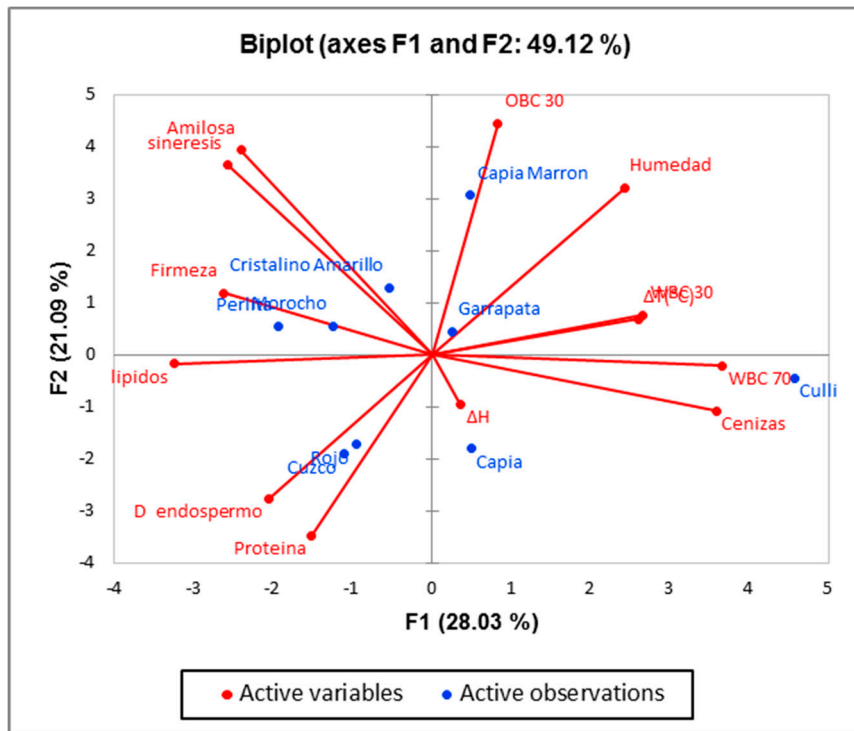
The values of WHC were between 2.3 at 30 °C and 3.6 at 70 °C (Table 2). The Perlita race showed the lowest values, which could be attributed to the low fiber, starch and protein contents. WHC values, in general, increased at 70 °C due to the swelling of the starch associated with the gelatinization process. The Perlita race had the lowest OHC, which was significantly different from the rest of the samples, possibly due to the higher lipid content and lower protein content [12]. The peak gelatinization temperature for the different corn races varied between 67 and 69 °C. There were no significant differences in enthalpy of gelatinization between the starches of the different maize races, indicating that similar energies are required for gelatinization. The temperature range of gelatinization (ΔT) varied between 13 °C (Cuzco) and 25 °C (Culli), which suggests a wide diversity in gelatinization properties. The wholemeal flours are a very complex matrix; the presence of proteins and fibers hinders the access to water of the starch, increasing the T_f and ΔT . The gels presented a wide variation in firmness (16–81 Kp), and the lowest firmness corresponds to the gels of Cuzco (very soft endosperm) and the greatest to the Perlita (hard endosperm). However, no correlation was observed with endosperm hardness. The stability of the gels over 96 h in refrigeration was represented by syneresis between 4% and 32%; the greater stability was found for the Culli, and the least for Capia Marron. The percentage of syneresis correlated positively with the amylose content.

3.4. Principal Component Analysis (PCA)

Figure 2a shows the PCA applied to the chemical composition and techno-functional properties. The F1 factor explains 28.3% of the variability of the chemical composition, attributed mainly to the contents of ash and lipids, while F2 (21.09%) is attributed to the amylose content. The sample with the highest positive F1 score was the Culli race, and the highest F2 was Perlita. The main techno-functional properties that contributed to F1 were WHC and firmness. In F2, the variability was contributed by the OHC and syneresis. Only the variable ΔH is close to the crossing of the axes, which suggests its low contributions to the variability of the properties. It corresponds for F1 to the race Culli, and for F2 to Perlita. In Figure 2b, two groups of races with similar characteristics are distinguished: one composed of the Capia, Cuzco and Rojo races, with high endosperm hardness and protein content; and the other composed of the Perlita, Cristalino Amarillo and Morocho races, which formed firm gels. The Capia Marron and Culli breeds showed distance from the other two groups, suggesting that their properties are unique.



(a)



(b)

Figure 2. PCA of properties of maize races; (a) Chemical composition and techno-functional properties; (b) Grouping of maize races.

Table 2. Physicochemical and techno-functional properties of Andean corns.

Razas	Moisture	Protein	Lipids	Ash	Amilylose	WHC 30 °C	WHC 70 °C	OHC 30 °C	Firmeza Kp	S (%)	Hardness	T _p (°C)	ΔT (°C)	ΔH J/g
Capia Marron	9.78 ^c	7.04 ^a	4.20 ^c	1.31 ^d	29.81 ^f	3.43 ^{c,d}	6.83 ^b	3.37 ^c	23.48 ^{b,c}	32.00 ^f	61.94 ^d	68.55 ^c	18.70 ^b	9.27 ^c
Cristalino Amarillo	9.88 ^{d,e}	11.28 ^{c,d}	4.31 ^{c,d}	1.23 ^c	26.08 ^{c,d}	3.19 ^b	6.51 ^a	3.26 ^{b,c}	37.30 ^d	29.65 ^{e,f}	73.07.09 ^f	67.62 ^{c,d}	18.32 ^b	9.31 ^c
Perlita	9.93 ^e	9.49 ^b	6.14 ^g	1.17 ^b	28.43 ^{d,e}	2.31 ^a	7.41 ^c	2.87 ^a	81.20 ^f	19.99 ^c	80.94 ⁱ	61.89 ^b	20.38 ^c	9.01 ^c
Cuzco	9.35 ^b	11.08 ^c	4.00 ^b	1.18 ^b	23.68 ^{b,c}	2.37 ^a	6.89 ^b	2.87 ^a	16.04 ^a	11.68 ^b	55.03 ^a	65.96 ^{b,c}	13.26 ^a	9.57 ^c
Garrapata	9.79 ^{c,d}	10.87 ^c	4.41 ^{d,e}	1.35 ^d	25.31 ^c	3.59 ^d	7.85 ^d	3.15 ^{a,b,c}	17.87 ^{a,b}	26.44 ^{d,e}	57.99 ^b	63.34 ^{c,d}	16.9 ^b	7.820 ^a
Capia	9.29 ^b	10.98 ^c	4.48 ^{d,e}	1.67 ^f	21.68 ^b	3.36 ^{b,c}	7.03 ^b	3.01 ^{a,b}	29.38 ^{b,c}	11.68 ^b	64.03 ^d	69.28 ^d	18.34 ^b	8.97 ^b
Morocho	9.74 ^c	11.99 ^e	4.55 ^e	1.13 ^a	28.74 ^{d,e}	3.35 ^{b,c}	7.36 ^c	3.22 ^{b,c}	59.95 ^e	27.20 ^{d,e}	78.45 ^h	61.59 ^a	20.55 ^c	9.17 ^c
Rojo	9.08 ^a	11.70 ^{d,e}	5.33 ^f	1.15 ^{a,b}	15.82 ^a	3.58 ^d	6.57 ^a	2.94 ^{a,b}	29.12 ^c	25.60 ^d	73.52 ^g	61.84 ^{a,b}	20.81 ^c	9.45 ^c
Culli	10.29 ^f	9.64 ^b	3.54 ^a	1.57 ^e	16.57 ^a	3.62 ^d	9.19 ^d	3.05 ^{a,b,c}	18.11 ^{a,b}	4.13 ^a	66.09 ^e	60.54 ^a	24.91 ^d	9.49 ^c

WHC: Water holding capacity; OHC: Oil holding capacity; S: Percentage of syneresis; T_p: Peak temperature; and ΔH: enthalpy (Joule/g batter). Different letters in the same column mean significantly different ($p < 0.05$).

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4. Conclusions

A great variability in the chemical composition and technical-functional properties has been observed among the nine integral flours of the Andean corn races. According to their broad techno-functional behaviors, they could be used in different technological processes to produce integral foods. The analysis of the main components revealed that Culli and Capia Marron differ from the other races, mainly due to the formation of gels of intermediate hardness, and the high stability of Culli. The recovery of these races through the reevaluation of their technological properties will contribute to the maintenance of biodiversity and the food security of rural families in the Andean region of Jujuy, Argentina.

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