Structural, thermal and energetic properties of Andean-pseudocereal flours with high nutritional values

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Abstract

Structural, thermal and energetic properties of quinoa, kiwicha and kañiwa native Andean-pseudocereal flours have been studied. Moisture, protein and fat contents and also metallic and semi-metallic levels were, in general, within of the range values reported in the literature. Empirical formulas of quinoa, kiwicha and kañiwa flours have been determined as $CH_{1.87}O_{0.81}N_{0.06}S_{0.0015}$, $CH_{1.90}O_{0.82}N_{0.05}S_{0.0019}$ and $CH_{1.76}O_{0.73}N_{0.06}S_{0.0017}$, respectively. The elemental carbon concentration (C_{flour}) in organic matter follows the trend, $C_{kañiwa}$ (45.6%) > $C_{kiwicha}$ (43.2%) ≈ C_{quinoa} (43.3%), which reflects the greater structural similarity between the quinoa and kiwicha flours, with respect to kañiwa flour. Regarding thermal and energetic properties: (i) in the temperature range of 261.15–343.15 K, we found no significant differences among the specific heat capacities of the three flours, which are ranged between 1.3 and 1.9 J g^{-1} K^{-1}; (ii) the organic matter decomposition temperature (T_{dec}) followed the trend, $T_{dec,kañiwa}$ (489.8 ± 1.6 K) > $T_{dec,kiwicha}$ (479.1 ± 1.5 K) ≥ $T_{dec,quinoa}$ (477.1 ± 1.5 K) indicating a greater thermal stability range of kañiwa flour; (iii) the gelatinization temperatures and also the gelatinization enthalpy of kañiwa flour (4.3 ± 1.6 J g^{-1}) were lower than corresponding thermal gelatinization parameters of quinoa and kiwicha flours; and (iv) the standard massic energy of combustion ($-\Delta_c u°$) or its associated net calorific value (q_{NCV}) of kañiwa flour (18.77 ± 0.15 kJ g^{-1} or 4487 ± 36 kcal kg^{-1}) was slightly greater than for kiwicha (18.47 ± 0.11 kJ g^{-1} or 4415 ± 26 kcal kg^{-1}) and quinoa (18.60 ± 0.16 kJ g^{-1} or 4445 ± 39 kcal kg^{-1}) flours. Taking into account the associated uncertainties, q_{NCV} trend is similar to the C_{flour} and T_{dec} trends. Accordingly, our results indicate a greater range thermal stability and greater net calorific value for kañiwa flour than for kiwicha and quinoa flours.

Keywords Pseudocereal flours · Quinoa · Kiwicha · Kañiwa · Net calorific values · Standard massic energy

Introduction

Quinoa (*Chenopodium quinoa* Willd.), achita or kiwicha/amaranth (*Amaranthus caudatus*) and kañiwa or cañihua (*Chenopodium pallidicaule* Allen) are native Andean-pseudocereals—starchy dicotyledonous seeds—with high nutritional contents, such as gluten-free sources of protein and fiber, rich in polyunsaturated fatty acids, balanced aminoacids, phenolic and other antioxidants, minerals and vitamins. These products are, the oldest crops, widely cultivated in Andean region, being Perú (in Huamanga−Ayacucho province, quinoa was produced before 5000 BC) [1, 2] and Bolivia the major producing countries [3]. All of them have been associates with health benefits (healthier foods) and are considered as potential healthy alternatives to gluten-containing cereals [4]. FAO (Food and Agriculture Organization of the United Nations) nominated quinoa as a crop most likely to significant contribute to global food security in the twenty-first century [4]. The United Nations has declared 2013 the International Year of Quinoa.

Pseudocereals, such as buckwheat, kiwicha and particularly quinoa have received a lot of attention in the last decades, and their crops and consumptions have been introduced practically throughout the world, mainly as seeds and flours [5, 6] and also as novel ingredients in food products,

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enhancing and improving the nutritional and functional properties (with antioxidant, antimicrobial and anti-inflammatory activities) and other characteristics [7–9]. Kañiwa, despite all these interesting properties, has been the least studied.

Quinoa, kiwicha and kañiwa flours are high in protein-quality content (9−24%, see Table 1), rich in, (i) dietary fibers (9−21%), e.g., several times higher than in rice [10–12], (ii) antioxidant and bioactive products (involving those with cytotoxic activities [9, 13] such as phenolic compounds (gallic-, dihydroxybenzoic-, vanillic-, ferulic- and caffeic-acids; sesamin, tyrosol or cardol) [14, 15], flavonoids (anthocyanins, flavones, flavanones, isoflavonoids and flavanols) [6, 15, 16], vitamin E [6]; (iii) minerals, including among other metals Ca, K, Mg, Fe or Zn that are related to the-called "ash content" (0.23 to 5%) [6, 8, 11, 17–20] which is higher than that of rice (0.5%), wheat (1.8%) and most other grains [21].

Starch is the major component of the pseudocereal flour, accounting for between 50 and 75% of its content [18, 22]. This carbohydrate has low amylose level, between 4 and 23.7% [10, 11, 21, 23–25], mainly kiwicha flour is considered as waxi variety. The amylose content is in general less than in well-known cereals such as corn (20−30%), wheat (28%) or rice (14−25%) [17]. On the other hand, kiwicha and quinoa flours have higher carbohydrate content than soya flour (34.1%) but lower than wheat (78.4%) and maize flours (81.1%) (Muchekeza et al. [26] and references therein).

Starch granules of the pseudocereals have usually polygonal shapes and are small in diameter (below 3.5 μm) [8, 24, 27, 28]. In quinoa and kiwicha, the starch granules have comparable particle size distributions, whereas kañiwa has a minor size distribution (below 2 μm) instead [3, 24]. The impact of particle size was evaluated by Ahmed et al. [29], who showed significant changes in composition (e.g., protein, dietary fiber and fat) and functionality with a reduction in particle size due to its increase in surface to volume ratio.

Thermal and energetic properties of pseudocereal flours, such as specific heat capacity, thermal diffusivity, total energy content, gelatinization enthalpy, or gelatinization temperatures, are important parameters that can be useful to the cereal processing industry related to treatments such as drying, storage, refrigeration or to characterize functional and nutritional qualities of both starch and flour cereals. The literature practically does not report consistent experimental values of some of these parameters. This is the case of caloric value or massic energy [30], usually obtained by empirical estimations of protein, carbohydrates, and fat contents. In this work, we have determined, using combustion calorimetry technique, the total massic energy content or net-calorific value q_{NCV} [31] of quinoa, kiwicha and kañiwa flours, which is the amount of energy (J, kJ or kcal) released by each unit of biomass (g, 100 g or kg). q_{NCV} is related to the complete combustion of biomass (basically constituting C, H, O, N) at constant volume in an oxygen atmosphere, implying the absence of C and CO in the final combustion products.

In this work, we have summarized, grouping into ranges, the data available in the literature (abundant for quinoa and rather scarce for kañiwa) on both, structural (organic and inorganic composition) and thermal-energetic properties of the quinoa, kiwicha and kañiwa flours. This information has allowed us to guarantee the reliability and consistency

Table 1 Elemental analysis, moisture, protein and fat contents of Andean-pseudocereal flours

| | Elemental analysis/m%[a] | | | | |
	C	H	N	S	O + others
Quinoa	43.33 ± 0.17	6.81 ± 0.03	2.79 ± 0.13	0.17 ± 0.05, (0.14)[b]	46.90 ± 0.22
Kiwicha	43.17 ± 0.17	6.87 ± 0.06	2.53 ± 0.11	0.21 ± 0.07	47.21 ± 0.22
Kañiwa	45.57 ± 0.43	6.72 ± 0.04	2.97 ± 0.07	0.21 ± 0.03	44.54 ± 0.44
Estimated moisture/m%					
Quinoa		Kiwicha		Kañiwa	
8.4 ± 0.9[c] **[3.91–11.64]**		6.1 ± 0.7[c] **[4.38–12.07]**		7.0 ± 1.1[c] **[6.26–11.79]**	
Estimated protein content / m%					
17.4 ± 1.7[d] **[9.1–23.94]**		15.8 ± 1.3[d] **[10.3–21.5]**		18.6 ± 0.9[d] **[11.69–18.8]**	
Estimated fat content / m%					
7.9 ± 0.8[e] **[3.95–8.7]**		7.2 ± 0.6[e] **[5.52–10.9]**		8.4 ± 0.4[e] **[4.46–11.67]**	

In bolt and between brackets, range of the values reported in the literature (See Table S1)

[a]This work, [b]Contreras-Jiménez et al. [17], [c]Percent mass loss of the flour, due to the drying process, [d]Estimated using conversion factor 6.25 and uncertainties taken as twice of the standard deviation, [d]Estimated taking into account the protein/fat ratio of 2.2:1

of our data, particularly those that have not been previously reported. In this way, we highlight the differences and similarities of the structural and thermo-energetic properties among the flours of the three most important Andean-pseudocereals.

Materials and methods

Materials

Quinoa (*C. quinoa* Willd.), achita/kiwicha/amaranth (*A. caudatus*), cereal grains were supplied by Tambillo (Ayacucho-Perú) farmers, while kañiwa/cañihua (*C. pallidicaule* Allen, Cupi-Puno variety) red-grains were bought in the market. All the grains were studied once processed (scarified and de-saponified, particularly for quinoa) and manufactured as food products. The flours were obtained by milling the cereals in a hammer mill and then drying under vacuum, using rotatory pump, at room temperature for 2 h. The flours were passed through a 100-mesh (0.147 mm) screen for gelatinization experiments.

Combustion calorimetry

The combustion experiments were performed in an isoperibol calorimeter, built in our laboratory and equipped with a static bomb (0.38 dm^3) and an isothermal water jacket. The calorimetric temperatures were measured to within $\pm 10^{-4}$ K by means 100 Ω platinum resistance thermometer, using a calibrated resistance bridge (Model F300, Automatic System Laboratories Ltd.). The flour samples (between 0.49 and 0.521 g) were pressed in pellet forms and ignited in oxygen at 3.04 MPa with 1 cm^3 of water added to the bomb, following a procedure similar to that described in reference [30]. The combustion bomb was flushed with oxygen before to combustion experiment. In order to obtain complete reactions of combustion, benzoic acid was used as auxiliary substance. The initial temperature of the combustion experiments was approximately 296.65 K, and the energy of reaction was always referred to the final temperature of 298.15 K. Previously, the pellet sample was connected to the ignition system (0.84 J, energy discharge of a capacitor) by means of a cotton thread fuse, which the empirical formula ($CH_{1.740}O_{0.871}$) and massic energy of combustion ($- 17,410 \pm 37$) J g^{-1} were determined in our laboratory. The mass of the samples, platinum crucible and cotton thread were all measured on a Mettler H33AR balance (sensitivity $\pm 10^{-4}$ g). The energy equivalent of the calorimeter, ε, was determined from the combustion of benzoic acid, NIST standard reference sample 39j, having a massic energy of combustion under the conditions specified on the certificate of $- 26\,434 \pm 3$ J g^{-1}. We obtained a value of

$\varepsilon = 14\,249.6 \pm 5.2$ J K^{-1} from five calibration experiments, where the uncertainty quoted is the standard uncertainty of the mean. To verify complete combustion, at the end of each experiment, the total quantity of gas in the bomb was slowly released through Dräger tubes. No traces of CO were detected. Finally, the liquid phase in the bomb was transferred to a flask with rinsing water. To determine the total acid, this solution was titrated with standard alkali, 0.1N NaOH(aq).

Differential scanning calorimetry (DSC)

The thermal properties of the samples were determined by differential scanning calorimetry, using a DSC PerkinElmer Pyris 1 calorimeter equipped with an intra-cooler unit. Temperature and power scales were calibrated by measuring the melting parameters of the recommended high-purity indium, gallium and tin as reference materials [32]. Curves of samples hermetically sealed in aluminum or stainless steel capsules were recorded in a nitrogen atmosphere at 10 K min^{-1}. The mass of the encapsulated samples were measured on a Mettler AT21 microbalance, with a detection limit of $\pm 10^{-6}$ g. Specific heat capacities *c.e.* were determined by the "scanning method" following the experimental methodology previously described [33] with synthetic sapphire (α-aluminum oxide) as reference material. For gelatinization studies, stainless steel high-pressure capsules of 3×10^{-5} dcm^3 of internal volume were used. These capsules are practically a mini-autoclave; they include a base and cover of stainless steel and gold plated as a gasket. The flour samples, between 6 and 8 mg, were introduced into base-pans. Water, between 2.0 and 2.2×10^{-5} dcm^3, was added from a microsyringe and the capsules were then hermetically sealed and placed on a rotatory agitator at room temperature (~ 298.15 K) for at least 12 h before measurements were made.

Metallic and semi-metallic analysis

The content of metallic and semi-metallic elements in the samples was analyzed by inductively coupled plasma-atomic emission spectrometer (ICP-OES PerkinElmer Optima 4300 DV). The samples were previously digested in hot solution of nitric and perchloric acids.

Results and discussion

Elemental analysis: proximate composition of flours

The elemental analysis (m%, on dry matter) of the pseudocereals studied is given in Table 1. The percentage of oxygen and other elements non-detected in the analysis

amounts up to 44% of the total content. The elemental carbon concentration (C_{flour}) in kañiwa flour ($C_{kañiwa}$) was higher than in kiwicha ($C_{kiwicha}$) and quinoa (C_{quinoa}) flours. These values followed the trend, $C_{kañiwa}$ (45.6%) > $C_{kiwicha}$ (43.2%) ≈ C_{quinoa} (43.3%). Taking into account the presence of most significant elements (C, H, O, N, S), the empirical formula of quinoa, kiwicha and kañiwa flours would be $CH_{1.87}O_{0.81}N_{0.06}S_{0.0015}$, $CH_{1.90}O_{0.82}N_{0.05}S_{0.0019}$ and $CH_{1.76}O_{0.73}N_{0.06}S_{0.0017}$, respectively. We can appreciate the similarity between these formulas, barely distinguishable—within the uncertainties of measurements—for those of quinoa and kiwicha. It is important to mention that the literature report scarce information on the elemental quantification of S, particularly in the kañiwa case, despite the fact that all these pseudocereals contain compounds with S, such as sulfured amino acids.

The concentration of crude protein (mass % respect to dry flour) was determined as % nitrogen content (%N) × 6.25 [34], and the fat concentration was estimated taking into account the protein/fat ratio of 2.2:1, which was updated and taken as average value from literature data consigned in Table S1 of Supporting Information.

The moisture, protein and fat contents of quinoa, kiwicha and kañiwa flours are reported in Table 1. The obtained results in this work are within of the range values reported in the literature (See Table S1). The wide range in moisture, protein and fat data would be explained by varietal difference, agronomic and environmental factors such as soil condition, fertilizer among other conditions used in the cultivation, harvesting and treatment of grains.

The literature shows that pseudocereal flours studied have an excellent nutritional profile with a good source of high-quality protein, fat and other nutritious constituents. Although the protein content, in the range of 9 to 24%, is lower than that of legumes, it is in general comparable or higher than other cereals such as rice (< 7%), corn (< 9.5%), barley (< 10%), rye (< 10.5%), sorghum (10.7%) and wheat (< 13.7%) [35, 36]. The high protein content is related to the presence of essential and sulfured amino acids such as of lysine, methionine, histidine, isoleucine or cysteine. Our results, in good accordance with the literature, showed no significant difference between protein content in quinoa (17.4 ± 1.7%) and kañiwa (18.6 ± 0.9%) flours and a slightly lower for kiwicha flour (15.8 ± 1.3%). On the other hand, fat content of kañiwa flour (8.4 ± 0.4%) was comparable to the quinoa (7.9 ± 0.8%) and slightly higher than for kiwicha (7.2 ± 0.6%). Shotts et al. [37] reported that the highest percentage of fatty acids in these flours is Omega 6 (linoleic acid), being 50% for quinoa, ranging from 33 to 44% for kiwicha [38] and 43% for kañiwa. Huamani et al. [39] reported linoleic acid values between 45.8 and 49.6% for three kañihua ecotypes.

Metallic and semi-metallic composition (Table 2)

Pseudocereal flours are an excellent alternative to other known flours, such as wheat, since they not only by the content of vitamins, phytochemicals (saponins, polyphenols, phytosterols, etc.) and other interesting health-benefit compounds, but also they are important source of minerals (based on Ca, Fe, Zn, Cu, Mg, P etc. metallic and metalloid elements). Their Ca, Mg, Zn and Fe contents are comparable or even higher than in common grains, such as rice [11, 22]. It is important to mention that the literature does not report K, Mg, Na, Mn and Cu contents in kañiwa flour.

Taking into account the uncertainty values, S, Na, Zn and Cu levels were comparable among the three flours (See Tables 1 and 2). The literature reports scarce information on the quantification of S in these pseudocereals, despite the fact that all of them include important sulfur compounds.

It is interesting to mention that Ca content was almost twice in kiwicha (1000 mg kg^{-1}) that in quinoa and kañiwa flours, and these values are within the reported ranges by the literature (See Table 2). Compared to other gluten-free flours, such as rice, maize, oat, millet, buckwheat, chickpea, tiger nut, or plantain, the Ca level in kiwicha is the highest [25]. About the metallic and metalloid levels in kañiwa (the least studied pseudocereal) flour: (i) Fe content (125 mg kg^{-1}) was close to the value reported by Repo-Carrasco et al. [22] and higher than in kiwicha and quinoa flours. The Fe levels in kañiwa and kiwicha flours were higher than in several gluten-free flours analyzed by Coletu et al. [25]; (ii) Zn content (26 mg kg^{-1}) was consistent with the value reported by Repo-Carrasco et al. [40] and comparable to the contents in kiwicha and quinoa flours; (iii) Mg, P and Mn contents were comparable to the corresponding levels in quinoa flour; and (iv) K content (4653 mg kg^{-1})

Table 2 Metallic and semi-metallic composition (mg of metal by kg of dry-matter) of Andean-pseudocereals

mg kg^{-1}	Quinoa	Kiwicha	Kañiwa
Ca	510, **[268–1487]**	1000, **[995–2976]**	600, 1100[a], 279[b]
K	6608, **[6274–14550]**	4665, **[2900–5630]**	4653
Mg	1597, **[1541–5020]**	1895, **[2310–3480]**	1670
Na	41, **[19–930]**	32, **[6–310]**	46
P	3953, **[220–5300]**	5078, **[4410–7960]**	3912, 3750[a]
Fe	40, **[11–334]**	75, **[50–530]**	125, **[49–150]**
Mn	28, **[19.5–28]**	8, **[15–35]**	28
Zn	31, **[8–48]**	26, **[12.5–56]**	26, 21.5[b]
Cu	9, **[5.9–95]**	10, **[4–24]**	6

In bolt and between brackets, range of the values reported in the literature (See Table S2)

[a,b]Reported by Repo-Carrasco et al. [22, 40]

was comparable to the level in kiwicha but lower than in quinoa (6608 mg kg^{-1}).

Thermal and energetic properties

Specific heat capacities, $c.e$, of quinoa, kiwicha and kañiwa flours were determined (by DSC) in the temperature range of 261.15–343.15 K (See Fig. 1). For this range, we found no significant differences among the heat capacities of the flours, which are ranged between 1.3 and 1.9 J g^{-1} K^{-1}. The similarity of the $c.e.$ (T) trend of the three flours, would be related to the similarity among their corresponding empirical formulas (Table 1).$c.e.$/J g^{-1} K^{-1} ranged from 261.15 to 313.15 K was fitted to quadratic polynomial function with R^2 higher than 0.9:

Quinoa:$c.e(T/K) = 5.1 \cdot 10^{-5} \cdot (T - T_o)^2 + 4.89 \cdot 10^{-3} \cdot (T - T_o) + 1.367$

Kiwicha:$c.e(T/K) = 3.5 \cdot 10^{-5} \cdot (T - T_o)^2 + 5.09 \cdot 10^{-3} \cdot (T - T_o) + 1.387$

Kañiwa:$c.e(T/K) = 5.6 \cdot 10^{-5} \cdot (T - T_o)^2 + 4.55 \cdot 10^{-3} \cdot (T - T_o) + 1.360$where $T_o = 273.15$ K. At room temperature (298.15 K), $c.e.$/J g^{-1} K^{-1} of quinoa (1.54), kiwicha (1.52) and kañiwa (1.51) values were (i) lower than for corn-starch (2.07) and for the pseudocereal flours estimated by Muchekeza el al. [26]; (ii) comparable to millet grains and flours determined (using mixture method) by Subramanian and Viswanathan [41].

Figure 2 shows the thermal stability ranges, between 323.15 and 503.15 K, of the studied flours. We can define as up limit of the thermal-stability range to the decomposition temperature T_{dec}, which is associated with the typical decomposition thermal peak of organic matter (protein, lipids and fibers). For kiwicha flour, Bet et al. [27] found, using TG/TDG techniques, a stability range up to close 499 K. Their results indicate that at temperatures above 428.15–430.15 K, the lipids began to oxidase, leading the progressive decomposition of the sample.

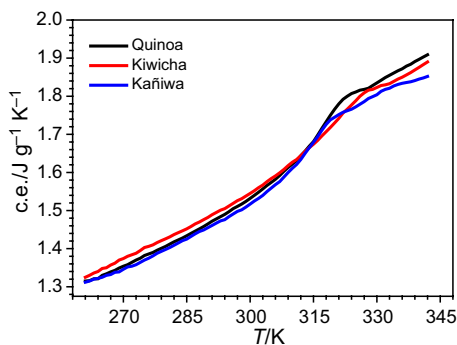T_{dec} followed the trend: $T_{dec, kañiwa}$ (489.8 ± 1.6 K) > $T_{dec,kiwicha}$ (479.1 ± 1.5 K) ≥ $T_{dec,quinoa}$
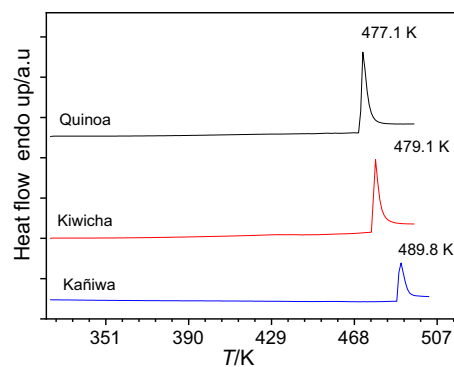

Fig. 2 DSC curves showing decomposition peaks

(477.1 ± 1.5 K). This result indicates that thermal stability range of kañiwa flour is greater than of kiwicha and quinoa flours. The T_{dec} trend is the same as that of C_{flour}, which would be a consequence of the structural similarity among the three studied flours, where the empirical formulas of quinoa and kiwicha are barely distinguishable.

Gelatinization properties of the quinoa, kiwicha and kañiwa flours have been determined, using the DSC technique (See Fig. 3). Taking in account the uncertainty values, both temperature and enthalpy gelatinization parameters determined in this work are within of the range values reported in the literature (See Table 3). It is interesting to note for kañiwa flour, (i) the gelatinization-temperatures (onset T_i, final T_f and gelatinization-peak T_{max}) were lower, between 1 and 4 K, than corresponding temperatures of quinoa and kiwicha flours; (ii) the gelatinization enthalpy ΔH_{gel} (= 4.3 ± 1.6 J g^{-1}) was very close to the reported by Luna-Mercado and Repo-Carrasco [23] (Illpa Inia variety) and Salas-Valero et al. [18] (Illpa Inia and Cupi varieties); and (iii) ΔH_{gel} was lower than for kiwicha (5.7 J g^{-1}) and quinoa flour (7.9 J g^{-1}). This last trend is maintained for the corresponding starches, although ΔH_{gel} of the flours are between 3 and 8 J g^{-1} less than for the starches [3, 28].
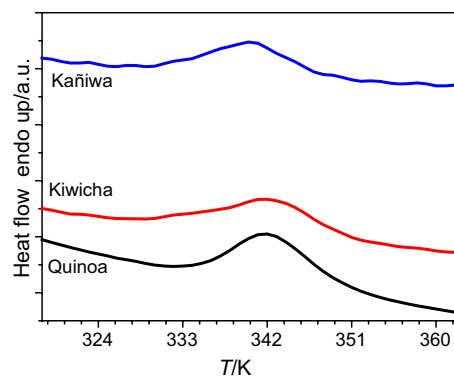

Fig. 1 Specific heat capacity, $c.e.$, of Andean-pseudocereal flours

Fig. 3 Typical DSC curves of gelatinization processes

Table 3 DSC data[a] for gelatinization thermal parameters of Andean-pseudocereal flours

	T_i/K[b]	T_{max}/K[c]	T_f/K[d]	$\Delta H_{gel}/J\ g^{-1}$[e]
Quinoa	334.1 ± 1.3 **[323.0–340.1]**	341.3 ± 1.6 **[336.0–346.2]**	349.7 ± 2.3 **[344.0–360.1]**	7.9 ± 0.6 **[4.3–10.9]**
Kiwicha	335.3 ± 2.1 **[328.5–339.2]**	342.0 ± 2.0 **[336.5–352.1]**	351.4 ± 2.0 **[345.6–361.4]**	5.7 ± 1.0 **[3.9–10.4]**
kañiwa	332.1 ± 2.2 **[326.5–331.9]**	340.3 ± 2.2 **[334.0–337.8]**	347.8 ± 2.0 **[341.8–345.9]**	4.3 ± 1.6 **[3.5–4.8]**

In bolt and between brackets, range of values reported in the literature (See Table S3)

[a]Presented as the mean value ± standard deviation of four experiments. [b]T_i = Gelatinization onset temperature or temperature at which gelatinization began. [c]T_{max} = Gelatinization peak temperature. [d]T_f = Gelatinization conclusion temperature or temperature at which gelatinization halted. [e]ΔH_{gel} = The heat absorbed for flour gelatinization per gram dry sample

The variation in the thermal gelatinization properties of the different flours is related to characteristics of the starch granules (morphology, composition and molecular structure), presence and structure of compounds, such as amylopectins, proteins, dietary fibers and water contents, among other factors [25, 42]. In this context, the lower values of thermal gelatinization parameters of kañiwa flour would be due the presence of very small starch granules (> 2 µm), compared those of kiwicha and quinoa (both > 3.5 µm) [3, 43], which require less time to reach low gelatinization temperatures and to stabilize emulsions investing less energy to break their molecular interactions.

The combustion of the studied pseudocereal flours was complete, without the presence of residual biomass, traces of CO (checked by Dräger tubes) and neither C soot. The results are given in Table 4 (for more details, see Table S4). The absolute value of average standard massic energy of combustion ($\langle \Delta_c u^o \rangle$, for four experiments) has been associated with the total energy content or net calorific value of the sample q_{NCV}.

Table 4 Results of combustion experiments

	Quinoa	Kiwicha	Kañiwa
Typical experimental results			
m (compound)/g	0.4994	0.4987	0.5137
m′(benzoic acid)/g[a]	0.2546	0.2379	0.2616
m″(fuse)/g[b]	0.0030	0.0026	0.0028
$\Delta T_{ad}/K$[c]	1.1194	1.0820	1.1550
ε(calor)($-\Delta T_{ad}$)/kJ[d]	− 15.951	− 15.418	− 16.458
ε(cont.)($-\Delta T_{ad}$)/kJ[e]	− 0.018	− 0.017	− 0.019
$\Delta U(HNO_3)$/kJ[f]	0.002	0.002	0.002
ΔU(corr. to std. states)/kJ[g]	0.011	0.011	0.012
$- m' \Delta_c u^o$(benzoic)/kJ[h]	6.730	6.287	6.916
$- m'' \Delta_c u^o$(fuse)/kJ[i]	0.052	0.046	0.049
$\Delta_c u^o$(compound)/kJ g^{-1}[j]	− 18.37	− 18.22	− 18.49
$\langle \Delta_c u^o(298.15\ K) \rangle$/kJ g^{-1}[k]	− 18.60 ± 0.16	− 18.47 ± 0.11	− 18.77 ± 0.15
q_{NCV}/kJ g^{-1}[l]	18.60 ± 0.16	18.47 ± 0.11	18.77 ± 0.15
q_{NCV}/kcal kg^{-1}	4445 ± 39	4415 ± 26	4487 ± 36
q_{NCV}/kcal $(100\ g)^{-1}$[m]	444.5 ± 3.9	441.5 ± 2.6	448.7 ± 3.6
Massic energy values reported in the literature/kcal kg^{-1}			
	3570[n], 2827[o], 3680[p], 4530[t], (4200–4240)[u]	2623.4[q], 4610[s]	(3866.7, 3823.6)[r], 4640[s], (3443, 3381)[t]

More details in Table S4. The symbols were defined according to Hubbard et al. [49]

[a]Mass of benzoic acid used as combustion auxiliary. [b]Mass of fuse (cotton). [c]Corrected temperature rise. [d]Total energy released in the heat form. ε(calor) is the energy equivalent of the whole system excluding the heat capacity of the bomb. [e]ε(cont.) energy equivalent of the contents of the bomb. [f]Energy of formation of nitric acid. [g]Standard state correction. [h]Energy released by benzoic acid combustion. [i]Energy released by fuse combustion. [j]Standard massic energy of combustion, $\Delta_c u^o$(compound) = Σ[(e) to (j)]. [k]Average value of $\Delta_c u^o$ and its standard uncertainty for four experiments. It includes mass correction according to the metal content analysis. [l]Net calorific value associated to the absolute value of standard massic energy of combustion. [m]q_{NCV} in kcal by 100 g of dry sample. [n]Nowak et al. [47], [o]Ayseli et al. [36], [p]Navruz-Varli et al. [21], [q]Burgos and Armada [45] (raw grains), [r]Luna-Mercado and Repo-Carrasco [23], [s]Ortiz-Chura et al. [19], [t]Moscoso-Mujica et al. [46] and [u]Pereira et al. [44]

Within of the uncertainty values, q_{NCV} of kiwicha flour (18.47 ± 0.11 kJ g^{-1} or 4415 ± 26 kcal kg^{-1}) was comparable to the quinoa flour (18.60 ± 0.16 kJ g^{-1} or 4445 ± 39 kcal kg^{-1}) and both slightly less than for kañiwa (18.77 ± 0.15 kJ g^{-1} or 4433 ± 35 kcal kg^{-1}). These values are between, (i) 85 and 195 kcal kg^{-1} lower than those reported by Ortiz-Chura et al. [19] as "gross energy" and performed by combustion technique; (ii) 205 and 1822 kcal kg^{-1} higher than those reported by Pereira et al. [44], Luna-Mercado and Repo-Carrasco [23], Ayseli et al. [36], Navruz-Varli et al. [21], Burgos and Armada [45], Moscoso-Mujica et al. [46] and Nowak et al. [47] as "energy content" estimations considering protein + carbohydrates + fat contents. The closest value (less than 245 kcal kg^{-1}) corresponds to the quinoa flour, estimated by Pereira et al. [44] applying the relation $4\times$(g protein)+$4\times$(g carbohydrates)+$9\times$(g fat). It is important to mention that Huang et al. [48] also estimated for quinoa flour, using the content protein/carbohydrates/fat relation of 9:4:4, a very high "energy" value (6879.4 kcal kg^{-1}) which is not been considered in Table 4.

It is interesting to note that the net calorific value q_{NCV} of kañiwa is slightly higher than the comparable values of kiwicha and quinoa flours. This result, supported by the combustion experiments, is consistent with the elemental analysis, given that the empirical formulas of quinoa and kiwicha flours are, within uncertainty of measurements, barely distinguishable. So, the q_{NCV} trend is similar to the C_{flour} (elemental carbon concentration) and also to T_{dec} (decomposition temperature) trends. These results can be explained in terms of flour composition: a slightly higher C_{flour} concentration in kañiwa flour that in quinoa and kiwicha flours (which are rather similar). C_{flour} would be present in organic structures including, among others, C–C strong bonds.

Conclusions

In this work, we have been studied structural, thermal and energetic properties of quinoa (*C. quinoa* Willd.), kiwicha (*A. caudatus*) and particularly kañiwa (*C. pallidicaule* Allen) pseudocereal flours.

Taking into account the presence of most significant elements (C, H, O, N, S), we have determined the empirical formula of quinoa, kiwicha and kañiwa flours: $CH_{1.87}O_{0.81}N_{0.06}S_{0.0015}$, $CH_{1.90}O_{0.82}N_{0.05}S_{0.0019}$ and $CH_{1.76}O_{0.73}N_{0.06}S_{0.0017}$, respectively. The empirical formulas of quinoa and kiwicha flours are, within uncertainty of measurements, barely distinguishable and it is reflected on the elemental-carbon concentration (C_{flour}, mass %) which follows the trend, $C_{kañiwa}$ (45.6%) > $C_{kiwicha}$ (43.2%) ≈ C_{quinoa} (43.3%).

Our results showed no significant difference between protein content in kañiwa ($18.6 \pm 0.9\%$) and quinoa ($17.4 \pm 1.7\%$) flours and a slightly lower for kiwicha flour ($15.8 \pm 1.3\%$). This trend was also maintained for moisture and fat contents among the three flours. To estimate the fat concentration, we have proposed a new protein/fat ratio, 2.2:1.

With respect to metallic and semi-metallic contents, S, Na, Zn and Cu levels were comparable among the three flours. Fe content in kañiwa flour (125 mg kg^{-1}) was higher than in kiwicha and quinoa flours, while K in quinoa (6608 mg kg^{-1}) was the highest.

Our thermal and energetic results, using DSC technique, showed no significant differences of specific heat capacities *c.e.* among the three flours. This result would be a consequence of the similarity among the corresponding empirical formulas. Although, the decomposition temperature T_{dec} associates with the organic matter (protein, lipids and fibers) decomposition, followed the trend, 489.8 ± 1.6 K (kañiwa) > 479.1 ± 1.5 K (kiwicha) ≥ 477.1 ± 1.5 K (quinoa), which is the same as that of C_{flour}. About thermal gelatinization parameters of kañiwa flour, onset T_i (332.1 ± 2.2 K), final T_f (347.8 ± 2.0 K) and gelatinization peak T_{max} (340.3 ± 2.2 K) temperatures were between 1 and 4 K, lower than the corresponding temperatures in quinoa and kiwicha flours. Its gelatinization enthalpy ΔH_{gel} ($= 4.3 \pm 1.6$ J g^{-1}) was also lower than in quinoa (7.9 ± 0.6 J g^{-1}) and kiwicha flour (5.7 ± 1.0 J g^{-1}).

The total energy content or net calorific value q_{NCV}, performed with combustion calorimetry, of kañiwa (4487 ± 36 kcal kg^{-1}) was slightly greater than for the comparable values of kiwicha and quinoa flours, 4415 ± 26 and 4445 ± 39 kcal kg^{-1}, respectively. Within corresponding uncertainty values, the q_{NCV} trend is the same to the T_{dec} (decomposition temperature) and C_{flour} (elemental carbon concentration) trends. These results would indicate that kañiwa has a greater thermal stability range and also a greater energetic content than kiwicha and quinoa flours.

Author contributions JZDP involved in data analysis and writing—original draft. ATR involved in data combustion and review. VRC involved in DSC experiments and review. GCS involved in elemental analysis and review. FGG involved in data analysis, metallic analysis and review. All authors commented on previous versions of the manuscript, read, and approved the final version.

Declarations

Conflict of interest The authors of this paper declare no conflict of interest.

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