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Preliminary Evaluation of the By-products of Quinoa as Alternative Source of Usable Biomass

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Quinoa is a little-known andean pseudocereal of ancestral use, easily cultivated by small, medium and large producers, thus being a cost-effective alternative and obtaining biomass at low cost from its by-products; among these are the stems, the brushwood, the perigonium and the leaves. Moreover, they are raw materials easy to acquire and even without economic value in the national market; however, they offer an alternative for agro-industrial use as a source of biomass. In this sense, the goal of the present investigation was the realization of the preliminary evaluation of the characteristics of the by-products of the quinoa production chain to obtain usable biomass. The by-products of the quinoa: stem, leaf, husk or perigonium and bushes were collected in two farms located in the city of Duitama, in the department of Boyacá, Colombia. To obtain relevant information, 1500 g of the product was gather up within 100 days after sowing; stems, straw and husk 6 months after sowing. The byproducts were stored in hermetic bag until the analysis was carried out; these processes were developed in the laboratory of Natural Ingredients of the Agricultural University Foundation of Colombia - UNIAGRARIA. To carry out the physicochemical analyzes (humidity, ash, fat and crude fiber), as well as for each by-product (leaves, stem and perigonium), samples of approximately 200 g were taken from each raw material. The results of the physicochemical characterization were analyzed by means of descriptive statistics through the determination of the average and standard deviation. In the meantime, the possible differences between the physicochemical results were analyzed by means of a Variance Analysis with the Statgraphics 5.1 PLUS statistical package with a confidence level of 95 %. From the physicochemical characterization, it was inferred that the leaf has a higher percentage of moisture and fat, 15.06 % and 13.70 % respectively, which is contrary to the amount of dry mass available, presenting in this vegetable organ the lowest content; the husk has a percentage of 13.21 % in ash and the brushwood contains 18.61% fiber, this shows the highest bromatological value in each by-product used.

1. Introduction

At present, there is an increasing trend towards the energy extraction of biomass waste generated in the primary sector (Abdelazim, 2018); in this line, Directive 2001/77 / EC (2001) of the European Parliament considers that this is a fraction a biodegradable of products, scraps and residues from agricultural, forestry and processing industries (including substances of animal origin). Likewise, Elsohaimya et. al. (2015) point out that due to its physico-chemical and calorific characteristics, agricultural biomass is shown as a high-value raw material for the production of energy (heat and electricity), of biofuels and alternative chemical products to those produced from resources non-renewable (oil, gas and coal). In the particular case of Quinoa, there has been a growing interest in its cultivation in recent years, due to its nutritional and medicinal value, considering it an almost perfect food due to its high protein and caloric content, leaving aside the potential of the vegetal residues of this crop, which reach to surpass 60 % of the total biomass produced in its productive cycle.

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Similarly, it is a crop with the capacity to adapt to diverse climatic conditions (Szilagyi, L. and Jørnsgård B., 2014), it presents high resistance to abiotic factors, which positions it as a promising crop in the production of biomass, together with the generation of high added value waste. In this same sense, despite its benefits and goodness, its products and by-products are being underutilized and there is still no joint or coordinated work between producers, processors and marketers to generate added value to the productive chain (Suárez-Rivero, 2018a).

2. Materials and methods

2.1. Generalities of the raw material

Quinoa is a food plant of annual development, dicotyledonous that usually reaches a height of 1 to 3 m, its leaves are broad and polymorphic (with different forms in the same plant), the central stem includes lobed and brittle leaves, in addition, it can have branches, depending on the variety or density of the sown, the flowers are small and lack petals. Additionally, they are hermaphroditic and are generally self-fertilizing, their fruit is dry and measures approximately 2 mm in diameter (from 250 to 500 seeds / g), surrounding the calyx, which is the same color as the plant, also has an extraordinary adaptability to different agro-ecological floors.

It adapts to climates from the desert to hot and dry climates, can grow with relative humidity from 40% to 88%, and withstands temperatures from -4 ° C to 38 ° C. It is an efficient plant for the use of water; it is tolerant and resistant to the lack of soil moisture and allows acceptable productions with rainfall of 100 to 200 mm (Villacres, 2011). Regarding the yields in subproducts, they vary according to the fertilization, obtaining on average 5000 kg / ha formed by perigonium (husk) and other parts of the plant such as leaves and stems. These components have the highest nutritional value for non-human use than many fruits of cultivated varieties (Pando, 2016).

2.2. Study Overview

The by-products of the Quinoa: stem, leaf, husk or perigonium and brushwood were collected in two farms located in the city of Duitama in the department of Boyacá. For each raw material, 1500 g of product were collected, in a green state. Upon arrival at the laboratory, it was supervised that these were free of impurities, as well as other elements that could hinder the quality of the study. Subsequently, the by-products were stored in hermetic bags (17 ° C for 7 days) until analysis was carried out (moisture content, ash, fat and crude fiber). These analyzes were developed in the laboratories of the Agricultural University Foundation of Colombia - UNIAGRARIA.

2.3. Physical-chemical characteristics of the by-products

To perform the respective physicochemical analyzes, three samples of each byproduct were taken of approximately 200 g each. These samples were taken to hermetic bag until the physical-chemical analysis mentioned in Table 1.

T*able 1: Methods de analysis*

Analysis	Unidad	Method
Humidity	%	AOAC 945.15
Ashes	%	AOAC 945.38
Grease	%	AOAC 945.38 920.09.E
Fiber	%	AOAC 945.38 962.09.E

Source: Adapted from Suárez et al., 2018.

2.4. Mixtures of by-products and pelletized

From the results of the physicochemical characterization of the byproducts of Quinoa (table 1), 4 mixtures with the different by-products were elaborated. Each of the mixtures in triplicate with the purpose of looking for if the elements of the previous analysis were strengthened in the combinatorial processes.

Table 2: Mixtures of by-products

Mixtures	Stem	Sheet	Broza	Husk
1	0,25	0,25	0,25	0,25
2	0,20	0,20	0,25	0,35
3	0,15	0,30	0,45	0,10
4	0,15	0,30	0,35	0,20

2.5. Preparation of pellets

This process was divided at different times, thus:

- Reduction of the size of the raw material with a mill of IKA brand blades and sieving (2 mm sieve).
- Manual mixing of the raw materials, according to the formulations described in Table 2 (1kg per mixture).
- Moistening to ensure pellet compaction (the amount of water is not important since it is removed during drying and is only a vehicle to form the pellet).
- Pelletization obtaining a compact product of approximately 4 mm in diameter and between 1.50 cm - 1.60 cm in length (SKLN-E200 brand pelletizer).
- Drying at 60 ° C in semi-industrial (LabTech brand) forced conversion furnace for 16 h.

2.6. Physicochemical and mechanical characterization of the processed pellets

For each product elaborated, a characterization was made by the physicochemical tests described in Table 1; In addition, mechanical stress tests were carried out to determine the degree of compaction of the pellets. For the mechanical stress analyzes, three samples of the pellets of each mixture were taken for a total of twelve samples; using a universal machine with the use of software (MATHLAB), an effort was made at a speed of 2mm / min at a scale of 0.5 kN, which yielded approximately 2500 data for each sample placed on the disk; also, from the data obtained, it was possible to obtain the maximum data (peak) equivalent to the maximum compression force necessary for the deformation of the pellet.

2.7. Statistical analysis

The physicochemical characterization results, both of the raw material and of the elaborated formulations, were analyzed by means of descriptive statistics through the determination of the average and standard deviation. In the meantime, the possible differences between the physicochemical and mechanical stress results of the four formulations were studied by means of a Variance Analysis and subsequent Tukey test for each variable, with a confidence index of 95%. In the figures that are shown in the results from the statistical analysis, the same letters do not differ statistically and different letters show significant statistical differences.

3. Results and discussion

3.1. Analysis of raw material

According to the results obtained in the physicochemical characterization of the different raw materials, it was found that the highest percentage of humidity (Figure 1) is found in the stem with 58.56%, differing significantly from the rest of the treatments. This, possibly, due to the fact that in its internal structure it has a soft medulla (parenchyma) that with the development becomes spongy which stores moisture (Suárez-Rivero, D. et al., 2018b; Gómez, 2016). Different results were presented for the other three parts of the plant used as raw material, in which, although it is true, statistical differences are observed, they are few from the mathematical point of view. Additionally, Gómez (2016) states that when the reduction of moisture in the waste is not sufficient with natural drying techniques, forced drying or combination systems of both are resorted to by means of equipment that, through a thermal flow, allows drying up to the desired values.

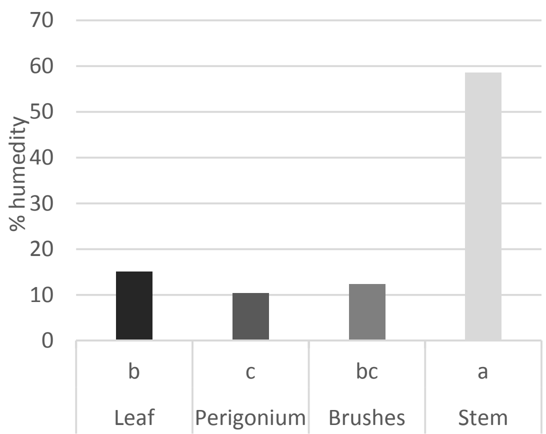

Figure 1. Moisture behavior.

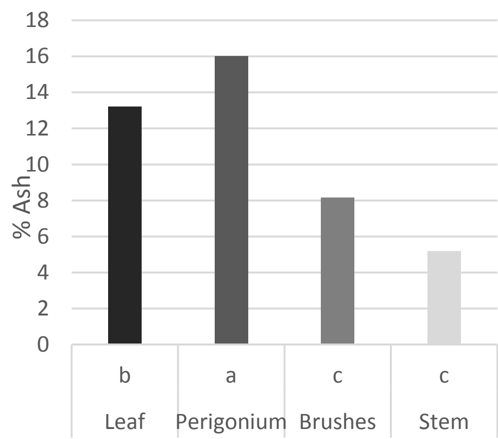

Figure 2. Ashes behavior.

For its part, figure 2 shows a different behavior to figure 1, with the ash behavior being inversely proportional according to the method used. In this sense, it is appreciated that the highest values of ash are presented in the Perigonium, differing significantly from the rest of treatments, reaching 16% of these. Likewise, the Perigonium, as established by Suárez-Rivero, D. (2018b), is mainly made up of fibers with a high content of peptic substances and almost no content of parenchymal tissues.
It is noteworthy that the determination of humidity can be the most important dissection carried out in a by-product and, however, it can be the analysis from which it is more difficult to obtain accurate and accurate results. Likewise, the determination of ashes is referred to as the study of inorganic residues that remain after the ignition or complete oxidation of organic matter. The remaining ash is the inorganic waste and the measurement of the total ash is useful in the analysis of food, since various minerals contained in the sample can be determined (Rozalino-Santos, 2016; Gómez, 2016).
On the other hand, figure 3 reflects the fat contents according to the source, highlighting the highest values in the leaves. This raw material presented values very close to 14% of fat, differing significantly from the rest of treatments, which may be favored by the development of metabolic processes *in situ* and by the succulence of the tissues that comprise it. Another element to highlight in the research is that the stem had the lowest values in fat, apparently determined by the structure-function relationship of this plant organ.

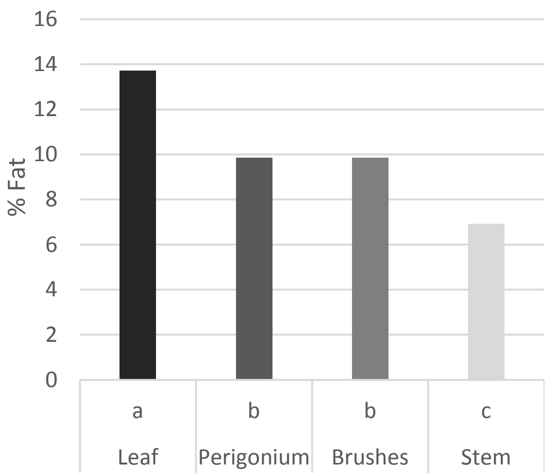

Figure 3. Fat behavior.

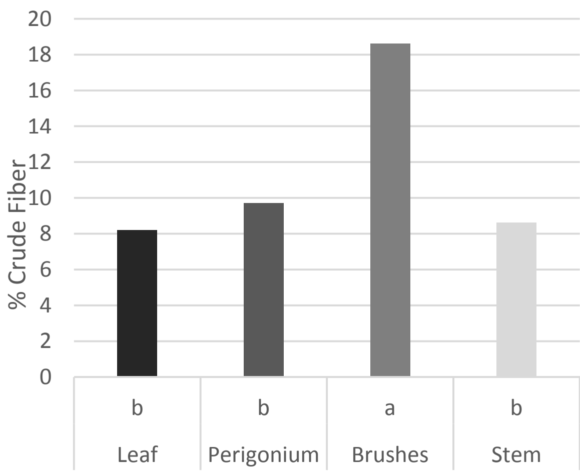

Figure 4. Raw fiber behavior.

From another point of view, in the results it was observed that Brushes has a large amount of fiber (18.61%) which means that it has a large non-digestible portion, therefore, the higher its concentration in a given product, the nutritional value will be lower, while the leaf contains 8.21%; indicating that the nutritional value is greater than the other raw materials. Likewise, significant differences were observed between the raw material Brushes with respect to the rest.
Authors such as Rozalino-Santos (2016) and Gómez (2016), point out that the Quinoa stem has a high content of proteins, vitamins, minerals and water, among others, which allow that after a process of protein enrichment can be incorporated into the animal feed (cattle, pigs, poultry), thus obtaining concentrates of high nutritional value; additionally, they note that the stems of this crop turn out to be a source of natural fiber for the production of cellulose, an element of great value from the point of view of biomass; which could be used as a raw material for the manufacture of paper, cardboard and ethanol.
It´s noteworthy that figures 1 to 4 show very low % error between the replicas of the different analyzes. In this sense, the following % error can be indicated for the leaf, the perigonium, the brush and the stem:

- Moisture behavior presented a 0.27, 0.16, 0.92 and 0.31 % error respectively.
- Ashes behavior presented a 1.03, 2.8, 1.25 and 3.4 % error respectively.
- Fat behavior presented a 7.1, 5.8, 5.4 and 6.9 % error respectively.
- Raw fiber behavior presented a 6.9, 7.4, 4.6 and 8.5 % error respectively.

3.2. Physicochemical and mechanical analysis of pellets

The physical transformation processes of the residual biomass represent a technical and economic challenge for the energy use of these materials, which, due to their heterogeneity, present high management costs and difficulty in the development of the technology making expensive and conditioning the projects potentially feasible in the renewable energy sector.

Therefore, after manufacturing the pellets under the described methodology, when performing a detailed analysis of Table 3, it was noted that the physicochemical characteristics, for the four formulations, show that the variables analyzed (% moisture and Fiber) are those showed some degree of statistically significant differences between treatments, with mixtures 1 and 2 having the lowest moisture content and 4 having the highest fiber content.

Table 3: Physicochemical characterization of each mixture

Mixtures	Humidity	Ashes	Grease	Fiber
1	5,63 ± 0,37 [a]	15,80 ± 1,51 [a]	1,80 ± 0,85 [a]	28,14 ± 7,73 [a]
2	5,92 ± 0,13 [a]	13,06 ± 3,76 [a]	1,45 ± 0,26 [a]	32,08 ± 8,98 [ab]
3	8,73 ± 1,00 [b]	27,64 ± 8,71 [a]	1,51 ± 0,46 [a]	33,34 ± 7,74 [ab]
4	**8,40 ± 0,05 [b]**	**18,43 ± 5,79 [a]**	**2,71 ± 1,67 [a]**	**56,86 ± 10,92 [b]**

* Different letters for the same column indicate significant differences, with a confidence level of 95%.

Accordingly, when performing the mechanical stress tests on the processed pellets, considering the results of the four formulations processed in the universal machine, very close values were presented in compatibility, as shown in table 4.

Table 4: Mechanical stress tests for each formulation (KN)

Mixture	Average
1	0,0112 ± 0,0027 [a]
2	0,0113 ± 0,0075 [a]
3	0,0272 ± 0,0164 [b]
4	0,0100 ± 0,0003 [a]

* Different letters for the same column indicate significant differences, with a confidence level of 95%.

It is evident then, that the initial raw material transfers its characteristics to the final product; this is how the third formulation presented a higher strength support (0.0272 kN), which means that the pellets do not disintegrate easily and have a greater degree of compactness than the other formulations. The pellets need a sufficient mechanical durability to avoid their disintegration in dust and to avoid the consequences of these, like problems in combustion, transport, loading, unloading and storage. Likewise, the fines to which disintegration can lead to a greater amount of dust in storage, possible damage to boilers, lower efficiency, greater amount of fly ash and higher emissions of aerosols.

Regarding the results, it can be affirmed that biomass is a renewable energy source obtained through the process of photosynthesis and its sustainable use does not entail risks for future generations and allows to reduce the consumption of energy whose reserves are limited (oil, gas, coal and uranium) and are distributed irregularly on the planet. Therefore, the development of biomass does not limit its benefits to energy production, having these important positive effects in environmental and socioeconomic spheres.

Although, the most important barriers to the implementation of biomass are the costs of production, supply and the difficulty of having a reasonable periodic supply over time, the by-products of Quinoa promise, by their volume of production, adaptability and quality, become a source of biomass alternative. Likewise, it is noteworthy that pelletizing is the process of manufacturing pellets that, among others, converts the raw material into a solid biofuel standardized internationally. They are shaped like cylinders of small dimensions coming from the biomass of different origins without chemical agents intervening in the process, but rather, by means of pressure, temperature and humidity, the lignocellulose present in the waste, acts as binder.

4. Conclusions

According to the results obtained in the physicochemical characterization of the different raw materials, it was found that the highest percentage of humidity is found in the stem, the husk has a high percentage of ash, the fiber is found in greater quantity in the brush and last the sheet is the byproduct that contains the fattest percentage.

The physicochemical and mechanical analyzes performed on the four formulations showed that the initial raw material transfers its characteristics to the final product, which, separately or jointly, can generate value for the Quinoa production chain, either as a nutritional supplement animal, as a source of cellulose for the paper industry or as a source of biomass for the biofuel industry (the latter subject to future investigations).

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