Study of quinoa plant residues as a way to produce energy through thermogravimetric analysis and indexes estimation.

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ABSTRACT.

Quinoa is a pseudo-cereal employed to provide nutrition and sustenance for a long time. Currently, the consumption of seeds of this plant is increasing. The seed are the only nutritionally part, which implies that both the husks like the rest of biomass represent a residue vaguely studied. Authors had studied the thermal behavior of these quinoa inedible parts. Fuel properties, biomass composition and DTG profiles were done for an oxidative atmosphere under different heating rates in the same way that several characteristic combustion indexes were estimated. Also, DTG profiles for a non-oxidative environment together with the characterization of the char obtained were showed. Results denoted that quinoa biomass presented a more suitable nature for combustion process compared with the husks. Furthermore, combustion DTG profiles showed two different stages: devolatilization and ignition. The maximum combustion weight loss value (20.63 %/min) was achieved for biomass under a 40 K/min rate. DTG profiles under inert atmosphere evidenced two weight loss stages clearly influenced by the cellulose and lignin content. Once again, biomass was the one with the better behavior instead of the husk for this pyrolysis process. Biomass which had good values in terms of yield (26.02 %) and heating value (15.41 MJ/kg).

KEWWORDS.

Biomass; char; husk; thermal indexes; thermogravimetry; quinoa.

1. INTRODUCTION.

Quinoa or quinua (*Chenopodium quinoa* Willd.) is a pseudo-cereal or pseudo-grain employed to provide nutrition and sustenance to Andean indigenous for a long time. Botanically, it is a gynomonoecious annual plant of about 1.5 m height with an erect stem and bears alternate leaves that are variously coloured [1]. It presents hermaphrodite and unisexual female flowers [2] and the seed size and colour are variable [3].

Although quinoa does not have an exceptionally high protein content compared with other grains (Table 1) [4,5], this protein is of good quality [6]. Therefore, it has a great potential to popularize in several countries not yet achieved, by introducing crops in human's food diet and providing new products [7].

The principal problem associated with quinoa grains consumption is their high saponin content (0.1 – 5 %)[8]. The saponins are glucosides that, upon hydrolysis, liberate one or more sugar units and free aglycon sugar, or sapogenins. Saponin content depended on the growing stage for all treatments and cultivars [9]. Such is the importance of the saponin content in quinoa, that most of the quinoa classifications are made according this component [10]. Hence, removal of saponin is a key factor when consuming it. These methods are divided into moist and dry ones [11], being, a combination of both, the considered as the most appropriate [12]. Once saponins are eliminated, quinoa can be consumed or processed.

Native from South American countries, this species has been introduced in Europe, North America, and Africa with high yields [13]. Quinoa seeds are the most valued part of the plant. Its annual production for the year 2013 was 2000 tons, more than double the quantity produced in the late 1990s [8]. Although quinoa consumption in high-income countries is increasing , it is still low compared with the main producer countries [14]. In the particular case of European countries, it is believed that it will continue to increase in the coming years [15]. Apart from its

value for human consumption, quinoa has also attracted attention as a forage crop [16] as well as a feed additive for pigs and poultry [17–19].

With the knowledge of the increase in the quinoa cultivated area, the authors of this article have realized that there is no any use for quinoa inedible parts (husk and aerial parts) that allows guarantees. Hence, the novelty of this work was related to the study of the thermal properties of these quinoa unusable parts under oxidative and non-oxidative atmospheres. It was done using thermogravimetric analysis (TGA). This technique has been extensively used by several researchers for investigation on basic combustion property of solid fuels [20]. This analysis is also very useful from a fundamental viewpoint, and for comparison between samples [21,22].

Barely studied, this new biomass source could become a new low-cost energy for countries with quinoa crops or an income for them. This statement can be made, among other reasons, due to the boom and evolution of biomass boilers. Utilizing biomass in boilers offers many economical, social and environmental benefits such as financial net saving, conservation of fossil fuel resources, job opportunities creation and CO_2 and NO_x emissions reduction [23]. Among the different combustion technologies, fluidized bed combustion has emerged as a viable alternative with significant advantages and a wide capacity range 0.5 T/h to over 100 T/h [24]. With all, this study may involve a first industrial approach to the use of quinoa in biomass boilers using this species directly or through blends with fossil fuels as other authors have already considered [25].

Main results here obtained denoted the good energy performance of the samples analyzed. Combustion profiles denoted two weight loss stages with the better results for quinoa biomass instead of the husk for a heating rate of 20 K/min. Inert atmosphere profiles showed again two release stages clearly influenced by the content in the cellulose and lignin.

2. MATHERIALS AND METHODS.

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2.1. Plants, soil and fertilization.

This study was carried out employing fertile seeds of short cycle real quinoa (without previous saponin washing process). Seeds were germinated for ten days (until the seedlings had 5-10 cm) under conditions of 24 °C temperature and 60% humidity through a 16/8 light cycle (16 hours of light and 8 hours of darkness). Once the plants had the above height, they were transplanted to pots of 8 l capacity. Experiment pots were located in a greenhouse from July to October with a temperature of 26 °C and 45% humidity.

The substrate employed was a conventional one whose characteristics can be seen in Table 2. Sampling was done according UNE-ISO 10381-1:2007. Once dried, samples were milled using a knife mill. UNE rules were employed for the substrate parameters estimation, moisture (UNE-EN ISO 17892-1:2015), pH (UNE-ISO 10390:2012), nitrogen (UNE 77306:1999) and electrical conductivity (UNE 77308:2001). The total organic matter was determined by calcination, calculating the difference in weight after ignition for 8 h at 400 °C. In the same way, heavy metals (except mercury) were estimated (UNE 77309:2001). The mercury content, as well as the phosphorus and potassium, was determined by digestion at atmospheric pressure with reflux and analysis by ICP Optic.

2.2. Quinoa fuel analysis.

The residues encompassed in this work were two: the biomass aerial parts (denoted as biomass) and the seed husks (called husk). Their fuel properties were approached by elemental and proximate analyses as well as by the determination of the calorific value. A series of rules were followed to carry out the analysis. Moisture (UNE-EN ISO18134-1:2016), volatiles (UNE-EN ISO18123:2016), ash content (UNE-EN ISO 18122:2016), higher heating value, HHV (UNE-EN ISO 18125:2018) carbon, hydrogen and nitrogen (UNE-EN ISO16948:2015).

Additionally, quinoa composition in terms of hemicellulose, cellulose, was also estimated by atomic balance of the components elemental formula following the method of Ranzi et al. [26]. This method assumes that elemental formulas for cellulose and hemicellulose are $C_6H_{10}O_5$ and $C_5H_{10}O_5$, respectively. However, lignin is a product of polymerization of three types of monolignols incorporated into lignin in the form of p-hydroxyphenyl (H type lignin), guaiacyl (G type lignin), and syringyl (S type lignin) [27]. The elemental formulas of H, G and S type lignin are $C_9H_{10}O_2$, $C_{10}H_{12}O_3$ and $C_{11}H_{14}O_4$, respectively. Straw contains about 45 % of H, 46 % of G and 9 % of S type lignin [27]. Hence, the representing elemental formula of lignin in both straws is $C_{10.4}H_{12.7}O_{3.4}$, given by their proportions of each lignin type [28,29].

2.3. Thermogravimetric analysis (TGA) and chars yield.

Before thermogravimetric analysis, quinoa biomass samples were dried by air-drying for a minimum of 72 hours. Then, samples were milled on a Fritsch mill Model P-19 to a 1 millimeter particle size. Afterwards, by using a Retch ball mill model MM200, particle sizes around about 0.2 mm were obtained. Thermogravimetric analysis was carried employing a TGA Instrument SDT2960. This instrument supplies a continuous measurement of sample weight as a function of time or temperature. Milled samples weighing around 7 mg were placed in a pottery crucible and heated under different atmospheres. For combustion, heating was carried out under a flow of 100 mL/min of air (at a gauge pressure of 1 atmosphere) to achieve the oxidative process that takes place during combustion. In the same way, three different heating rates (10, 20 and 40 K/min) were done from ambient to 1000 K. With these three rates, authors try to analyse the temperature dependence in the process. In the particular case of pyrolysis, a non-oxidative atmosphere was done employing a 100 mL/min N_2 flow with a 10 K/min heating rate from ambient to 1000 K. Likewise, once the pyrolysis of the samples was carried out, the yield of the obtained chars as well as the characterization of them was determined. Chars can be produced

by various thermal processes with restricted oxygen supply [30]. Yield was calculated using the following equation [31]:

$$Yield\ (\%) = \frac{W_f}{W_0} \cdot 100$$

Eq. (1)

where W_f is the mass (g) of the chars and W_o is the mass (g) of the precursors.

In the same sense, thermogravimetric profiles of the samples (TG) were obtained. To identify the different stages, it is advisable to derive these TG profiles (DTG profiles). With them, important parameters, as the temperature at which occur each stage as well as the mass loss, could be identified.

2.3. Quinoa characteristic combustion indexes (CCI).

The estimation of these indexes complement the results obtained during TGA for combustion thermal process. They can be obtained quickly and provide reliable information about samples kinetic parameters. Authors determined them for each of the two mainly stages identified in the DTG profiles. Doing so, a comparison of the different weight loss stages for the two residues (husk and biomass) was done.

2.3.1. Ignition temperature (T_e) and ignition index (D_i).

Considering a typical DTG curve for the combustion of quinoa (Fig. 1), the ignition temperature (T_e), which definition appears in [32], can be estimated thought the protocol defined by [33]. Firstly, through the DTG peak point a, a vertical line was made upward to meet the TG oblique line at point b. Secondly, a tangent line to TG curve was made at point b, which met the extended TG initial level line at point c. Thirdly, another vertical line was made downwards through point c, which met the cross axle at point d.

Meanwhile, the ignition index (D_i) represents the ignition capacity of a fuel so that, the higher D_i, the easier the fuel ignition occurs. This index was determined by the following equation [34]:

$$D_i = \frac{(\frac{dw}{dt})max}{t_p \cdot t_e}$$
Eq. (2)

where (dw/dt)$_{max}$ is the maximum combusiton rate (%/min), t_p is the time (min) at which the largest peak (at a temperature above 293 K) occurs and t_e is the ignition time (min).

2.3.2. Determination of burnout index (D_f).

The burnout index D_f denotes the combustion capacity of a fuel and was here determined to evaluate the burnout performance of quinoa. This index values were estimated according to:

$$D_f = \frac{(\frac{dw}{dt})max}{\Delta t_{1/2} \cdot t_p \cdot t_f}$$
Eq. (3)

$\Delta t_{1/2}$ is the time (min), in the first half of the DTG for the particular stage, since the half of the maximum DTG value is reached until achieve this DTGmax value (min), t_f is the time at which the end of the peak takes place (starting counting time zero to 293 Kelvin degrees and considering the final moment as that in which it reaches the 2% of DTG$_{max}$).

This index is very similar to the D_i but gives greater importance to the end of the peak and does not consider the ignition temperature.

2.3.3. Devolatilization index (D).

This parameter, which is related to the release of volatiles during combustion, was estimated as depicted in Eq. 4:

$$D = \frac{(\frac{dw}{dt})max}{T_{max} \cdot \Delta T}$$
Eq. (4)

T_{max} is the temperature at which DTG$_{max}$ is achieved (K), ΔT is the difference between T_{max} and T_e (K).

2.3.4. Combustion characteristic index (S).

This index can be used for a preliminary assessment of the quinoa combustion performance and represents the energy requiered to burn a fuel [35]. Also called combustion characteristic factor (CCF), it was calculated according Eq. 5:

$$S = \frac{(\frac{dw}{dt})max \cdot (\frac{dw}{dt})mean}{T_e{}^2 \cdot T_f}$$
Eq. (5)

where $(dw/dt)_{mean}$ is the average combustion rate considering the 1% of the DTG_{max} as the start and the end of the process (%/min), T_e is the igntion temperature (K) and T_f is the temperature value at which the end of the peak is achieved (1% of the DTG_{max}).

For all the values, a statistical analysis was done with the IBM SPSS Statistics v.24 software to identify significant differences. This analysis was based on a one-way ANOVA test with a 5% significance level

3. RESULTS AND DISCUSSION.

3.1. Fuel properties.

Results related to quinoa properties are shown in Table 3. Analyzing quinoa non-edible parts (husk and biomass), the biomass preseted better fuel properties than the husk: higher carbon content (43.80 %), lower nitrogen (0.58 %) and sulfur content (0.06 %), higher HHV (17.33 MJ/kg) and volatile matter (73.3 %) as well as a lower amount of ash (6.79 %).

There are practically no studies that analyze the thermal properties of quinoa. Because of that, results here obtained must be compared with biomass of other genera. Related to the elemental analysis, the reader can realize that the percentage content of the elements (C, N, H and S) are in concordance with the results obtained by other authors for herbaceous biomass like sawdust [36], corn stalks [37] or sugarcane [38]. Likewise, values obtained for these parameters are better than those reflected by one of the most used biomass sources, the rice straw [39].

However, these values are far from those obtained by other authors who have worked with biomass with a higher lignin content, such as pine [40] or poplar wood [41]. Sulfur and chlorine are also imporant. Whereas high content in sulfur can originates SO_x during the combustion, high chlorine values are probably related with fouling problems [42]. Hence, low values for these parameters will be advisable. According to sulfur content, quinoa husk values were higher (0.26 %) than the biomass ones (0.06 %), being, both, so similar to the values denoted by a comercial coal [43] and lower compared with the great majority of herbaceous biomass waste [44]. As refer as chlorine, as expected, its quinoa content (around 0.70 %) was quite lower than the obtained for rice straw [45] and higher than the literature values for other biomass herbaceous sources [44,46]. For this reason, quinoa waste combustion may have associated with fouling problems in boilers. A co-combustion with other energy sources without so much chlorine content would be advisable to solve this problem.

As far as the proximate analysis is concerned, the quinoa moisture content (around 7 %) was in line with cereal straw values [47]. On the other hand, as far as the ash content, the husks (14.08 %) had more than twice as much ash as the biomass (6.79 %). This ash content was obviously lower than coal values [47], higher than the densified biomass [48] and in agreement with the straw of common cereals (like wheat or barley) [47]. It is remarkable that the ash content of quinoa biomass was three times lower than that of rice straw [45]. Likewise, this species had a volatile content (73%) which clearly encourages the use of said material in combustion processes, since the obtained values were much closer to that of lignocellulosic biomass or a coal than to an herbaceous biomass [49].

One of the key parameters when talking about a material intended for thermal processes is the caloric power. With this parameter, higher calorific value (HHV), we are measuring the energy (heat) that gives us a material per unit mass, therefore high values of this parameter will be advisable. Again, quinoa biomass have higher HHV (17.33 MJ/kg) than quinoa husks (16.29

MJ/kg); biomass whose values closely resembled to the calorific value of certain herbaceous biomass sources widely used in combustions, such as the cotton stalk, sugar cane [50] or wheat straw [51]. Nevertheless, quinoa HHV values were far away from the calorific values of selected native woody shrub species from the same location as this paper [52].

Results related to hemicellulose, cellulose and lignin content (Table 4) are so important to characterize a fuel. Biomass from quinoa had more content in cellulose (38.70 %) and hemicellulose (35.86 %) compared with the husk. Nevertheless, lignin was higher in the case of husks (21.52 %). Similarly, results here obtained were so similar to the literature values for straw feedstocks [53–55].

Therefore, fuel analysis indicated that quinoa inedible parts can be used as a source of herbaceous biomass to produce energy.

3.2. Quinoa TGA.

3.2.1. Combustion profiles.

Thermal decomposition of *Chenopodium quinoa* during combustion for three different heating rates (10, 20 and 40 K/min) denoted two stages. These stages may be seen in the DTG profiles represented in Fig. 2 as most relevant data related to these peaks is shown in Table 4. In some cases and, depending on the raw material, different peaks appeared. Hence, in the particular case of quinoa biomass, only one peak was present in the first stage and two in the second one. However, when authors worked with quinoa husk, two peaks were notorious for both stages. These combustion DTG profiles were in the line with the obtained by other authors for herbaceous biomass like wheat, rice straw [56] or reed canary grass [57] and so different from coal [35] and woody biomass [58,59]. The following paragraphs describe, in detail, the behavior of each phase of material release.

Stage 1 was related to devolatilization. This stage started at temperatures around 510 K for biomass and 475 K for husk. The weight loss associated with it is due to the emission of volatile cellulose and hemicellulose [60]. In this stage, small amounts of volatile compounds can also be released from the lignin [61]. In our particular case, considering the herbaceous nature of quinoa, lignin did not play a leading role during this phase. Talking about biomass, only one peak was determined. In contrast, two emission peaks can be observed when the husk profiles were appreciated: the first one (at an approximate temperature of 475 K) may be due to the breaking of weaker carbon bonds and the second peak (at around 500 K) occurred due to the emission of biodegradable material (cellulose and hemicellulose) when the bonds break stronger fixed carbon and this peak occurring in the biggest loss of weight of the sample.

Stage 2 was the ignition phase itself. Here, the weight loss was linked to the devolatilization and the reaction between the char and the volatiles released in the previous phases [62]. In this stage two different peaks were appreciated for both materials, although it is true that in the particular case of biomass, under slow heating rates (10 and 20K/min) peak 2 was not appreciable; this may be due to the great overlap that exists between peaks 1-2 of this second stage, something that, as already stated in [63], two types of char reaction were possible. This fact could be related to the nature of the components of the biomass present in the original material. For biomass, the start of the stage was around 670 K, and the second peak was only clearly appreciated in the 40 K/min ramp starting at, approximately, 700 K. In the case of the husk, this second stage started over the 655 K and the second peak at 670 K. The highest DTG_{max} values occur in the first of the peaks for both materials.

Analyzing TGA results (Table 5) along with DTG profiles (Fig. 2), it can be observed how the devolatilization stage initiated earlier in the case of the husks (475 K) than in the biomass (510 K), this was due to the degradation temperature of hemicellulose and lignin is lower than that of cellulose, which indicates a higher cellulose content in the biomass [64]. During stage 1, when

the heating rate was increased, DTG_{max} value was higher and the temperature at which this DTG_{max} was achieved was smaller: the explanation to this fact could be related with an increase in the kinetic of the reaction (as we will analyze with the thermal indexes (3.3.- CCI results). Besides, in this phase, it can also be observed how DTG_{max} is higher for biomass (around 80 %/min for ramps of 20 and 40 K/min) than in husk (60 %/min for the same ramps), reaching the maximum value (82.65 %/min) for this stage with biomass at a 20K/min ramp. During the second stage, that is less representative than the first, it can be shown how the start temperature was very similar for both materials (around 670 K). The highest DTG_{max} values for this second stage were linked to biomass at the 40 K/min (20.63 %/min) and with the husk at 10 K/min (12.92 %/min).

3.2.2. Pyrolysis profiles and chars.

DTG quinoa pyrolysis profiles were closely related to the hemicellulose, cellulose and lignin content of the raw materials. Thus, and being consistent with that determined in other studies [65,66], the decomposition of the quinoa denoted (Fig. 3), apart from the release of moisture (which was not shown in the profiles because it was not relevant for this study), a stage clearly differentiated associated with the hemicellulose and cellulose was observed. The cellulose decomposition, as demonstrated by other authors [67], resulted in a much higher decomposition maximum compared to the hemicellulose (Table 6). When this stage finished, the lignin liberation started. Due to the low lignin content, this second stage was less appreciable. Analyzing the thermal profiles (Fig. 3) together with the samples composition (Table 4), cellulose peak was higher for the biomass due to the higher content of this compound (38.70 %). Also, a more pronounced weight loss was observed at 725 K in the case of husks due to the higher lignin content (21.52 %). These quinoa profiles differed considerably from those obtained for wood from trees [68], where the highest lignin content plays an important role, and from coal [69,70].

Related to the chars obtained, yield and nature of them were shown in Table 7. The large amount of parameters involved in the elaboration of them implies a wide range of chars that may have different applications [71]. Biochar yield decreases from 26.02 % to 22.36 % depending on the quinoa raw material employed. Biomass had the highest value. This better quinoa biomass behavior instead of the husks was also reflected in the rest of the properties. Biomass had higher calorific (15.41 MJ/kg) and volatile matter values (24.94 %) than the husks. These values can be important, since the high heating values of chars make them attractive sources for clean energy production instead of fossil-based solid fuels [72,73]. HHVs reported in literature for chars produced from biomass vary between 10 MJ/kg [74] and 33 MJ/kg [75]. Thus, results here obtained for quinoa (both for biomass and husk) HHV were in the lower limit of this range. Regards to the CHN content, quinoa inedible parts values were so close to other cereals, like wheat [76] or rice straw [77], but far from the char obtained from tree branches [78] or coal [79].

3.3. CCI results.

Values obtained for the indexes have been shown in Table 8. In the same way, statistical analyses related to them are shown in Table 9.

3.3.1. Ignition temperature (T_e) results.

The lower this value is, the easier is the thermal degradation of the substance with which one is working; then we will pursue small values of this parameter. For this parameter there were no significant differences for the variables analyzed.

3.3.2. Ignition index (D_i) results.

This index allows us to know the combustion facility. The higher this value, the easier is the combustion of a fuel. The highest values for the two materials were related to the highest heating ramp (40K/min). In addition, during the first weight loss (at above 550 K), D_i values were higher than those associated with those of the second stage. The plausible significant differences

between ramps, especially for stage 1 (Table 6), may be due to the fact that this index gives a great weight to the DTG_{max}; where the ramp of 40 K/min had higher values. This index clearly penalizes low heating rates. Hence, in case of having to opt for a material and a ramp according to this index, we would select quinoa biomass for 40 K/min (higher overall values for both stages).

3.3.3. Burnout index (D_f) results.

The interpretation of this index is analogous to D_i. The main difference is that, contrary to the previous one, D_f attributes greater importance to the final part of the peak and not to the ignition temperature.

Again, the low ramps were penalized with this index. The highest values (4.626 and 1.057 %/min⁴) were also manifested for biomass under 40 K/min ramp. The heating rate emphasis was even more remarkable when statistical analysis was done. For this index, significant differences for both phases (p=0.004 and p=0.015) were shown when the heating rate was the comparative variable; something that did not happen when the quinoa inedible part acquired this role.

3.3.4. Devolatilization index (D) and combustion characteristic index (S) results.

Authors decided to group the interpretation of both indexes since both have provided fairly homogeneous results. The reason of this homogeneity may be related with the fact that these two indexes did not penalize low heating ramps.

Again, it was appreciated how the biomass had higher values for both indexes practically in all the cases compared with the husks values. As it has been a trend throughout the interpretation of the indices, stage 1 was more noticeable than the second one (even significant differences, p=0.039, were seen in the S index, possibly due to the reduced value of the 10 K/min ramp). However, 20 K/min heating rate, showed acceptable values for both parameters, being these, in some cases, superior to those of the highest ramp (for example: $29.464 \cdot 10^{-6}$ (%/min)^2/K^3 was the S index biomass value).

Therefore, based on the thermal indices for quinoa, the authors recommend the use of the 40 K/min ramp with quinoa biomass due to indexed obtained values. It should also be remarkable that, in some cases, similar thermal properties can be obtained if a 20 K/min ramp of is chosen. This decision will depend on the needs and possibilities of the readers.

Quinoa indexes results were always higher than $2 \cdot 10^{-7}$, meaning that samples had a good general burning performance [80]. Practically there are no studies that have determined these indexes for each stage, something that made difficult the comparison with other materials results. However, if a partial comparison of the indices is made, those obtained for quinoa are superior to those obtained by other authors for herbaceous biomass as straw dust or wheat straw [35]. This trend continues when results were compared with emerging biomass sources, such as microalgae [81], or even, for certain values, when compared with coal [80].

The results here obtain were, at least, encouraging. This is so since, if data related to expansion of the cultivated area are true, in a short period of time, there will be large quantities of quinoa whose inedible part will be difficult to manage. In these sense, thermal valorization of these residues, in all their forms, can be a viable option.

4. CONCLUSIONS.

Quinoa inedible parts denoted a good performance for energy purposes. Biomass from this species had a better fuel compared with the husks due to, among others, the calorific value obtained (17.33 MJ/kg) and the volatile matter (73.3 %). Combustion profiles denoted two weight loss stages, devolatilization and ignition, for both quinoa raw materials. The first one was the most representative. The maximum combustion weight loss value (20.63 %/min) was achieved for biomass under a 40 K/min rate. This same behavior was also corroborated by the combustion thermal indexes (S values around $28 \cdot 10^{-6}$ $(\%/min)^2/K^3$ for quinoa biomass under 40 K/min) and the statistical analysis. On the other hand, DTG profiles under inert atmosphere were clearly influenced by the quinoa samples composition. Two weight loss stages were identified,

the first associated with the release of hemicellulose and cellulose and the second one was related to the release of lignin. Because of the higher cellulose content (38.70 %), biomass had a higher value for the first stage (8.957 %/min) whereas husk, with higher lignin content (21.52 %), was the one with a more pronounced value for the second one (1.203 %/min). Related to the char, the one derived from quinoa biomass was better than the husk char in terms of yield (26.02 %) and heating value (15.41 MJ/kg). These char were so similar to conventional straws widely studied in the literature.

5. AKNOWLEDGEMENTS.

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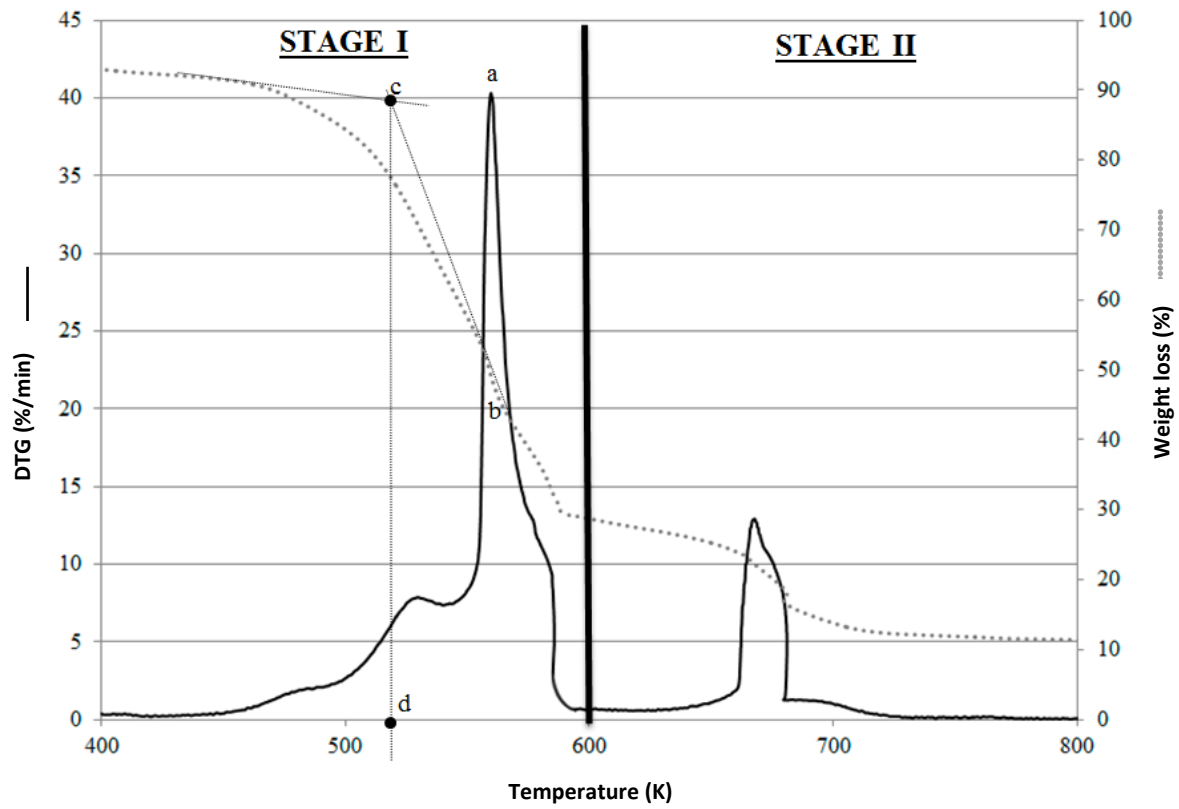
Fig. 1. Thermogravimetric curves for the combustion process of quinoa husk. Points a, b, c, and d are employed to calculate ignition temperature (T_e) index. DTG (%/min) is related to the black curve and weight loss (%) is represented by the gray dotted curve.
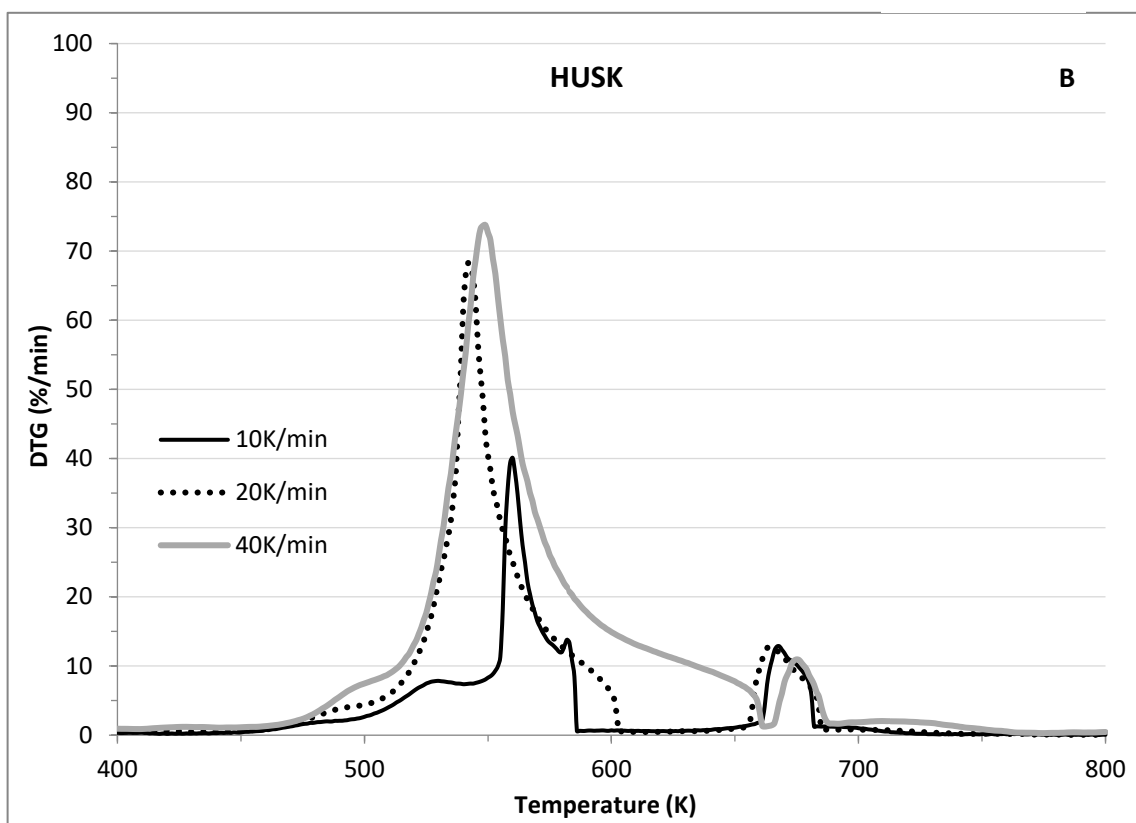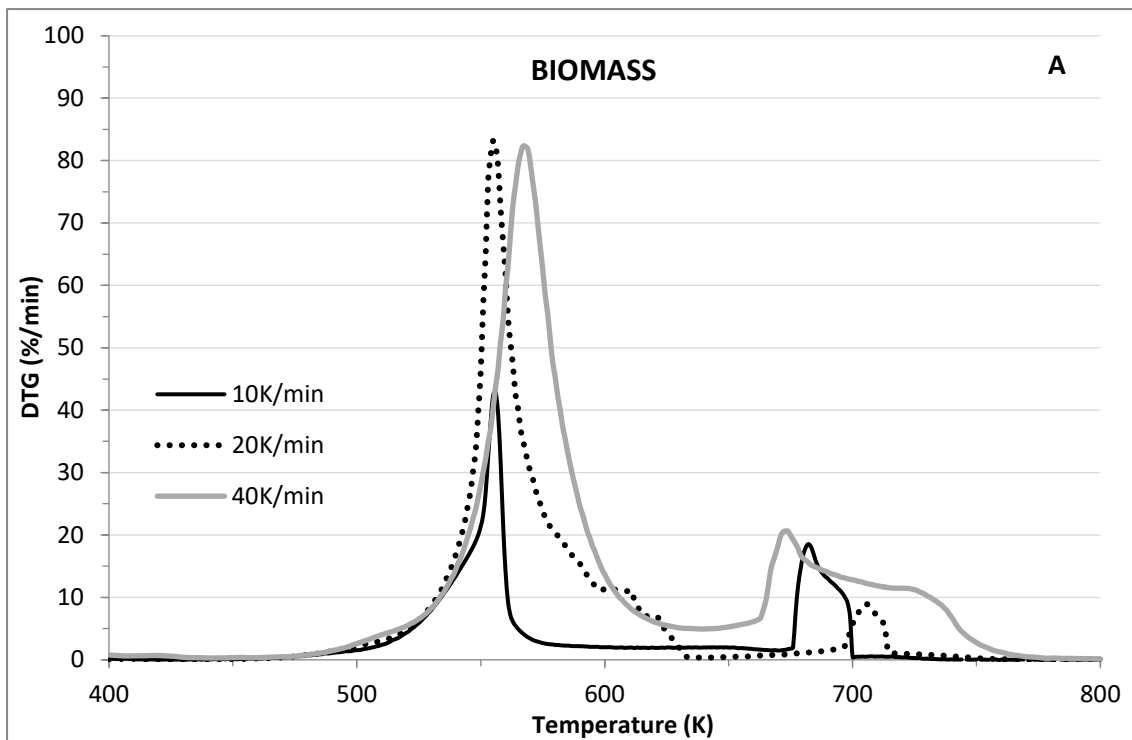
Fig. 2. Quinoa thermogravimetric combustion curves at different heating rates (10, 20 and 40 K/min) for biomass (A) and husk (B).
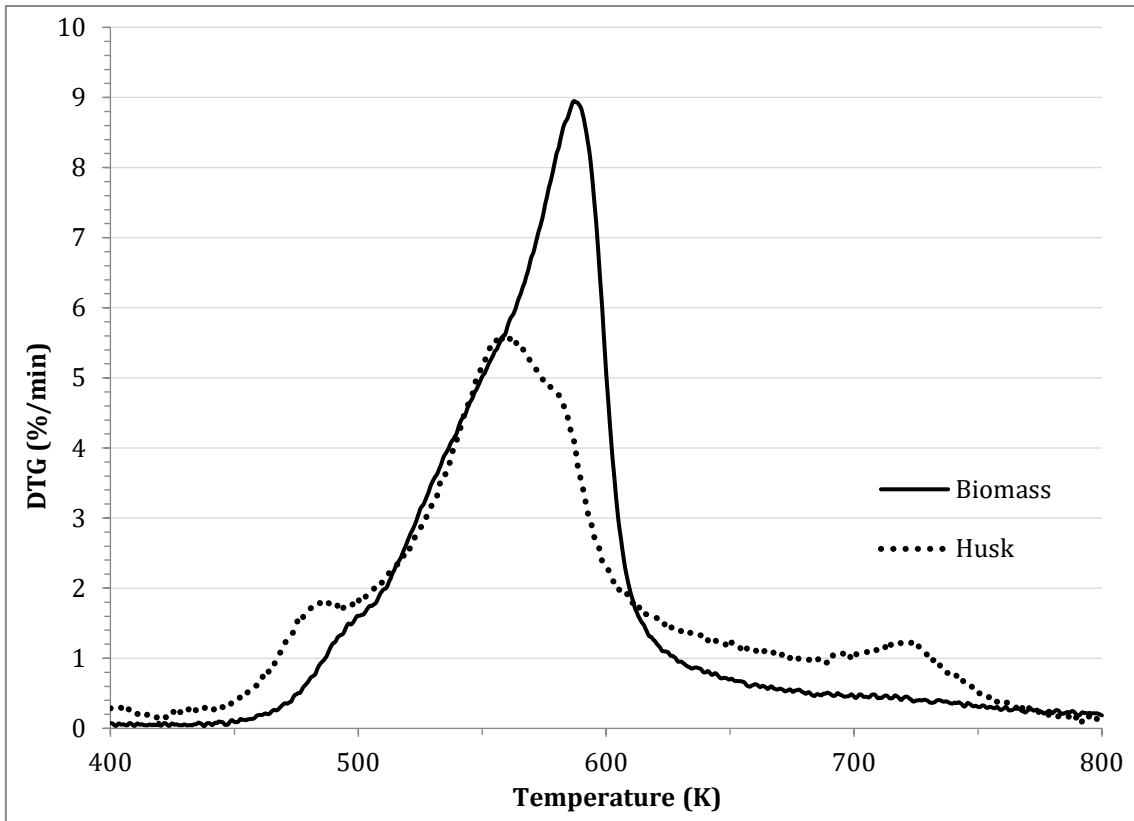
Fig. 3. Quinoa inedible parts thermogravimetric pyrolysis 10 K/min.

Table 1. Composition of several common cereals and grains (grams per 100 g of material dry matter) – [4,5].

	Protein	Fat	Raw fiber	Ash	Carbohydrate
Common rye	13.4	1.8	2.6	2.1	80.1
Corn	11.1	4.9	2.1	1.7	80.2
Oats	11.6	5.2	10.4	2.9	69.8
Rice	9.1	2.2	10.2	7.2	71.2
Sorghum	12.4	3.6	2.7	1.7	79.7
Triticale	15.0	1.7	2.6	2.0	78.7
Wheat	10.5	2.6	2.5	1.8	78.6
Quinoa	14.4	6.0	4.0	2.9	72.6

Table 2. Physicochemical characteristics of the substrate used. Except moisture, all values are expressed as dry basis.[a] Quantification limit. [b] All elements values as well as their associated SD are shown in mg/kg

	SUBSTRATE	
	Value	**SD**
Properties		
Moisture (%)	54.08	1.23
pH	7.47	0.57
Conductivity (mS/cm)	0.49	0.01
Total Nitrogen (%)	0.54	0.01
Organic matter (%)	51.52	0.41
Organic Nitrogen (%)	0.47	0.01
NH_4^+ - N (%)	0.07	< 0.01
NO_3^- - N (%)	< QL[a]	-
Heavy Metals[b]		
Cr	26.78	0.92
Ni	7.28	0.49
Cu	19.40	0.82
Zn	92.75	0.78
Cd	0.22	0.02
Hg	0.05	0.00
Pb	26.90	1.60
Macronutrients[c]		
P	395.26	7.43
K	2722.87	4.82

Table 3. Elemental and proximate analysis as well as calorific value of *Chenopodium quinoa* and other four energy sources for comparison purposes. [a] In percentage. All values are in dry basis except moisture. [b] Oxygen content was estimated by difference O (%) = 100 (C + H + N + ash). [c] HHV: high heating value

	Elemental analysis						Proximate analysis			Calorific value
	C[a]	H[a]	N[a]	O[b]	S[a]	Cl[a]	Moisture[a]	Ash[a]	Volatiles[a]	HHV[c] (MJ/kg)
Quinoa husk	41.10	5.39	2.16	39.43	0.26	0.62	7.2	14.08	71.8	16.29
Quinoa biomass	43.80	5.26	0.58	44.15	0.06	0.84	7.0	6.79	73.3	17.33
Bituminous coal [47]	73.10	5.50	0.40	13.40	1.70	0.01	11.2	8.00	35.0	26.20
Poplar [41]	49.50	5.80	0.56	41.42	0.11	0.01	7.9	3.28	79.9	19.78
Rice Straw [45]	37.87	4.61	0.63	38.45	0.14	1.01	7.4	19.07	68.0	14.71
Chlorella sorokiniana [81]	47.90	6.40	8.74	37.87	0.78	0.01	9.6	7.83	76.1	18.72

Table 4. Composition of quinoa inedible parts (wt.%) calculated by atomic balance. All values are in dry basis.

	Cellulose	Hemicellulose	Lignin
Biomass	38.70	35.86	18.51
Husk	31.69	32.60	21.52

Table 5. Characteristic parameters obtained from the DTG combustion curves obtained for quinoa husk and biomass under different heating rates. "-": This peak is not appreciable in the DTG profiles. T_o: temperature at which a certain peak starts. T_f: temperature at which a certain peak ends. T_{DTGmax} : temperature associated to DTG_{max}. DTG_{max}: largest value of DTG in the considered process.

	Husk			Biomass		
Heating rate (K/min)	10	20	40	10	20	40
Stage 1 - Devolatilization						
Peak 1						
T_0 (K)	506.77	470.47	476.14	-	-	-
T_f (K)	542.70	519.63	524.24	-	-	-
DTG_{max} (%/min)	7.825	3.057	7.322	-	-	-
T_{DTGmax} (K)	528.86	482.71	498.86	-	-	-
Peak 2						
T_0 (K)	535.78	491.94	503.48	511.31	514.71	493.16
T_f (K)	585.04	599.79	661.04	569.16	625.88	616.80
DTG_{max} (%/min)	48.69	57.16	73.57	43.13	82.65	82.19
T_{DTGmax} (K)	560.09	543.07	547.61	555.55	555.55	566.89
Stage 2 - Ignition						
Peak 1						
T_0 (K)	658.77	653.10	661.04	671.25	693.94	661.04
T_f (K)	676.54	674.24	685.77	688.08	715.49	685.77
DTG_{max} (%/min)	12.92	12.43	10.87	18.36	8.903	20.63
T_{DTGmax} (K)	667.85	662.7	674.24	681.46	705.28	672.39
Peak 2						
T_0 (K)	667.31	667.31	681.16	-	-	699.62
T_f (K)	727.31	752.69	761.92	-	-	755.19
DTG_{max} (%/min)	1.168	0.755	1.985	-	-	11.15
T_{DTGmax} (K)	695.01	704.24	718.08	-	-	725.70

Table 6. Quinoa DTG pyrolysis profiles characteristic parameters. T range: temperatures at which the release of the phases begins and ends. T: temperature in which maximum pyrolysis rate occurs. DTG_{max}: largest DTG. HCE: hemicellulose. CE: cellulose. LI: lignin.

	T range $_{HCE-CE}$ (K)	T_{HCE} (K)	$DTG_{max\ HCE}$ (%/min)	T_{CE} (K)	$DTG_{max\ CE}$ (%/min)	T range $_{LI}$ (K)	T_{LI} (K)	$DTG_{max\ LI}$ (%/min)
Biomass	465 - 653	501.32	1.169	587.40	8.957	660 - 795	710.36	0.4242
Husk	424 - 678	486.57	1.802	557.27	5.579	662 - 787	720.81	1.203

Table 7. **Char properties**. All values are in dry basis except moisture. T: temperature at which the char was obtained. MC: moisture content. Oxygen content was estimated by difference. VM: volatile matter. HHV: high heating value

	T (K)	Yield (%)	MC (%)	C (%)	H (%)	N (%)	O (%)	VM (%)	Ash (%)	HHV
Biomass	737.96	26.02	6.9	52.19	0.93	1.75	38.71	24.94	6.42	15.41
Husk	742.33	22.36	7.8	50.02	0.85	1.44	37.22	21.03	10.47	12.70

Table 8. **Combustion characteristic indexes (CCI) for quinoa inedible parts**. T_e: ignition temperature. D_i: ignition index. D_f: burnout index. D: devolatilization index. S: combustion characteristic index

Heating rate	10 K/min		20 K/min		40 K/min	
	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
T_e (K)						
Husk	520	660	530	655	520	660
Biomass	520	680	550	700	550	670
D_i (%/min^3)						
Husk	0.067	0.009	0.453	0.038	1.923	0.123
Biomass	0.069	0.013	0.484	0.021	1.784	0.227
D_f (%/min^4)						
Husk	0.135	0.016	1.162	0.115	3.691	0.714
Biomass	0.077	0.022	1.350	0.056	4.626	1.057
D ((%/min)/K^2) x 10^{-2}						
Husk	0.179	0.240	1.081	0.218	0.469	0.111
Biomass	0.200	1.751	2.955	0.223	0.835	0.993
S ((%/min)^2/K^3) x 10^{-6}						
Husk	8.117	0.444	19.700	0.427	24.571	0.354
Biomass	7.734	0.797	29.464	0.176	27.876	1.024

Table 9. Combustion characteristic indexes (CCI) statistical analysis (one-way ANOVA). α (signification level): 0.05. Bold results reflect the existence of significant differences (p < α)

	Heating rate (10, 20 and 40 K/min)				Material (Husk and biomass of quinoa)			
	Stage 1		*Stage 2*		*Stage 1*		*Stage 2*	
	F	p	F	p	F	p	F	p
T_e	1.000	0.465	0.188	0.838	2.500	0.189	7.759	0.050
D_i	519.238	**0.000**	8.706	0.056	0.002	0.965	0.151	0.717
D_f	57.331	**0.004**	23.030	**0.015**	0.043	0.846	0.057	0.822
D	2.975	0.194	0.593	0.607	0.743	0.437	3.257	0.145
S	11.559	**0.039**	0.806	0.525	0.246	0.646	1.019	0.370