Influence of the fertilizer type in the agronomic and energetic behaviour of the residues coming from oleander, cypress and quinoa.

AUTHORS: Sergio Paniagua[1], Laura Zanfaño[1], Luis Fernando Calvo[1*]

[1]University of León, Department of Chemistry and Applied Physics, Chemical Engineering Area, IMARENABIO, Avda. Portugal 41 (24071), León, Spain.

* Corresponding author email: lfcalp@unileon.es; Telephone: +34987291844

Abstract.

The use of biomass as an alternative energy source is a fact. Apart from the traditional ones, this work aims to carry out an energy and agronomic analysis of three new crops: oleander, cypress and quinoa. In the same sense, fertilizers of different nature (organic and inorganic) were applied to determine the influence on agronomic and thermal behaviour. TGA and characteristic indexes were employed for an oxidative atmosphere. All the crops here analysed had acceptable value as fuels. Organic fertilizer consisting of cow manure was the one that further increased the height and diameter of the plants. Likewise, oleander was the species with better fuel potential together with the lowest gases emission. Devolatilization and ignition weight loss stages were identified in DTG profiles being quinoa stems the raw material with higher DTGmax values (> 7 %/min). As kinetics concerned, fertilizer application decreased the activation energy values for almost all cases.

Keywords

Combustion; cypress; fertilizer; oleander; thermogravimetry; quinoa.

1. Introduction

Biomass is a renewable source of energy contains complex mix of carbon, nitrogen, hydrogen and oxygen. It is obtained from living or dead plants, by product of crop production, wood and agro based industry [1]. With a CO_2-neutral balance, energy derived from biomass appeared as a promising sustainable feedstock to partially replace fossil fuels by reducing CO_2 emissions and helping to mitigate anthropogenic contributions to a perceptible global warming [2]. It is the fourth largest source of primary energy in the world (meaning 12% of the total energy consumption) and rising to nearly 40% of it in some developing countries [3]. In order to select any biomass as a good fuel, there are several criteria to take into account. They compromise, among others, geographical conditions, availability of biomass feedstock, rate of combustion/emissions and calorific value [4].

Apart from the most common species [5], other lesser-known biomass species can be used to obtain energy. In this research work, three non-common species were evaluated from an agronomic and energy perspective as energy crops: *Nerium oleander*, *Cupressus macrocarpa* and *Chenopodium quinoa. N. oleander* is an ornamental shrub widely cultivated all over the world [6] admitting several pruning throughout the year [7]. Previous studies have determined the potential of this species as a renewable energy source being notorious the drastic reduction in HC, CO, NO_X and smoke compared with diesel [8]. Besides, and probably because the similarities between chemical between the polysaccharide content in this species and wood materials [9], *N. oleander* fibers have an excellent biosorption efficiency [10]. On the other hand, the genus *Cupressus* includes species spread throughout the temperate regions of the Northern hemisphere [11] reaching high heights and diameters [12]. In Europe, *C. macrocarpa* has been introduced as decorative element, something that has resulted in an increase in its pruning waste with considerable energy potential [13]. The last crop employed was qinoa or quinua (*Chenopodium quinoa)*. With Europe's increased in its consumption of it, the raise in the cultivation of this pseudo-cereal is also link with a high amount of biomass that, in most cases, is a waste to manage between 9 - 15 t/ha [14].

Fertilizer is another aspect that this paper has considered. Knowing that the nature of the fertilizer can affect the energy behaviour of biomass samples [15], authors analysed the energy response under both organic and inorganic fertilizer. Besides being, by themselves, an energy alternative [16], organic ones can be successfully used as fertilizer [17]; giving a utility to a material considered, in many occasions, as a waste. Cow manure was selected due to be an agricultural commonly available waste with low biogas yield potential [18].

Related to energy behaviour, samples combustion was done. Combustion of solid biomass is the most important sector for bioenergy, being the overall efficiency of the heat production process [19]. For its part, thermogravimetric analysis (TGA) has been commonly used to investigate the characteristic parameters associated with this thermal process [20] as well as their gas emission [21].

Hence, the novelty of this work lies on the use of biomass waste from new crops vaguely [22–26] or no studied in an integral way from an energy point of view. This study also considered the type of fertilizer used as well as the main gas emissions associated with the samples thermal combustion process.

2. Material and methods.

A summary of the methodology followed in this study is shown in the **Fig.1.** flowchart

2.1 Plants, soil and fertilization.

This study was carried out employing *Nerium oleander* (NO) and *Cupressus macrocarpa* (CM) seedlings as well as fertile seeds of real quinoa (Q). It was a greenhouse two-year trial (2016-2018). While oleander and cypress plants remained full time, a six months short cycle rotation quinoa was followed (annually from march to august). All seedlings had approximately the same height (50 cm for oleander and 20 cm for cypress) and the same growth period (18 months). Quinoa seeds were germinated for ten days (24°C, 60% humidity and 16/8 light cycle) in a Neurtek SGC 120© germination chamber. Once quinoa seedling achieved 5-10 cm high, they were transplanted to 8 l and 40 cm diameter pots to ensure a good root development and plant growth [27]. The same pots were used for the NO and CM and placed in a 50 m^2 greenhouse under controlled temperature (22°C) and humidity (45%) conditions. It was located in the School of Agricultural and Forestry Engineering (42°35'02.8"N 5°35'21.7"W) of León (Spain). In the same way, a drip irrigation system assured the correct and constant watering of the different specimens.

Literature indicates the optimal growth conditions for the selected crops in 20°C for NO (with higher growths in spring and summer) [28,29]. Between 0 – 32 °C for CM [30], thriving in a well-drained loamy or peaty soil and being very tolerant of hot dry conditions and poor sandy soils [31]. For its part, the optimum temperatures of growth and development of quinoa are between 15-25°C range in a wide range of soils preferably with good drainage and a high content of organic matter [32].

Soil properties can be seen in **Table 1**. Sampling was done according UNE-ISO 10381-1:2007 in triplicate. Dried samples were milled using a knife mill Pulverisette© 11 knife mill. UNE rules were employed for the soil 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 according EN 13039 standard. In the same way, heavy metals (except mercury) were estimated under the guidelines of the standard UNE 77309:2001. The mercury content was measured by cold-vapor atomic fluorescence employing an automatic mercury analyser AULA-254 GOLD®. Phosphorus and potassium were determined by digestion at atmospheric pressure with reflux and analysis by Optic ICP.

Greenhouse pots distribution followed a statistical design based on smaller blocks and blocks of several complete rows [33]. Related to fertilizers, three different treatments were applied. A first treatment, CONTROL, in which no fertilizer was added. A second, called MANURE, consisting of the application of sanitized cow manure (Table 1). The last fertilizer was an inorganic one, MINERAL, in which a mineral fertilizer, that varies depending on the species (25-20-10 NPK for quinoa and 25-20-10 NPK for both cypress and oleander), was applied. Six plants were used for each treatment. Thus, there was 18 plants of each species to bring a total number of 54 plants in the greenhouse.

Fertilization estimation was carried out based on fertilizers nitrogen composition as well as the needs of the plants showed in literature: cypress, 75 kg N/ha [34]; oleander, 70 g of (12-6-15) fertilizer per m^2 [35] and 80 kg N/ha for quinoa [36]. Both MANURE as MINERAL fertilizer was applied twice a year for cypress and oleander. Once in september as a basic dressing and a second in march as top dressing.

2.2 Agronomic variation.

To test fertilizer agronomic variations, height and diameter of the plants were measured once a month. Height was determined with a measuring tape considering the base of the stem as the lower reference and the highest apical point as the upper limit. Regarding the diameter, it was measured in all the plants at a height of 10 cm from the base of the stem employing a precision caliper.

Statistical analysis (ANOVA) was also done for the average height and diameter variation values considering each species and year. Then, Tukey's HSD test was used to compare treatment means, for which significant ($p < 0.05$) differences were determined by ANOVA.

2.3 Fuel properties.

At the end of the trial all plants were sampled (200 g approximately for each species and fertilization type). Different parts of the plant were selected. Leaves and stems for both cypress and oleander and stems and husk for quinoa (husk were separated from seeds by a TopHusk™ separator DRHC/DRSD). For quinoa, sampling was done after panicle formation and flowering. All the plants were cut to a height of 5 cm from the soil.

Samples fuel properties were determined by elemental and proximate analysis as well as the calorific value. A series of standardized rules were employed to estimate these properties.

Carbon, hydrogen and nitrogen (UNE-EN ISO 16948:2015), sulphur (UNE-EN ISO 16994:2017). Moisture content was determined by the stove drying method (UNE-EN ISO 18134-2:2017). The higher heating value (HHV), an important property of a fuel as a measure of energy content [37], was measured with UNE-EN 14918:2011 rule. Volatile matter (VM) was estimated according UNE-EN ISO 18123:2016 and ash with the UNE-EN ISO 18122:2016.

Biomass composition in terms of cellulose, hemicellulose and lignin was derived by atomic balance of the components elemental formula [38] and according to the [39] guidelines.

2.4 Thermogravimetric analysis (TGA) and gasses signals emissions (m/z).

Before TGA, samples were dried by air-drying for a minimum of 72 hours. Then, they were milled on a Fritsch™ mill Model P-19 to a 1 mm 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, which is able to supply a continuous measurement of sample weight as a function of time or temperature. Milled samples weighing around 7 mg were placed in an Al_2O_3 crucible and heated at a 10˚C/min heating rate from ambient to 1000˚C. This heating was carried out under a flow of 100 mL/min of air (at a gauge pressure of 1 atm) to achieve the oxidative process that takes place at combustion. This way, samples thermogravimetric profiles (TG) were obtained. To identify the different combustion stages, TG were derived to obtain DTG curves.

The gases emitted during the heating process were monitored by MS analysis using a Balzers™ GSD 300 equipment in line with the TG analysis system. The coupling of both systems was performed in series by connecting the mass spectrometer to the gas outlet of the thermal analysis equipment. This technique has been consolidated for a long time and it is still useful nowadays [40–42].

The evolution of gas species has been followed in situ by the coupled TG–MS system. The interpretation of the mass-spectra occurs on the basis of degassing profiles from the molecules of water (H_2O: *m/z* = 18), carbon monoxide (CO: *m/z* = 28), nitric oxide (NO: *m/z* = 30), carbon dioxide (CO_2: *m/z* = 44), nitrogen dioxide (NO_2: *m/z* = 46) and sulphur dioxide (SO_2: *m/z* = 64).

2.5 Kinetic values and characteristic combustion parameters.

Kinetic parameters (activation energy, E_a, and frequency factor, A or k_0) are very useful as a complement to the biomass samples analysis [43–45]. Activation energy (E_a) and frequency factor (k_0) values were estimated by approximate integral method, AIM [15].

In homogeneous reactions with gases, Arrhenius physical parameters can be interpreted in terms of molecular collision theory [46]. Hence, in gaseous conditions there would have a single emission peak and general values for kinetic parameters. However, solid samples thermal decomposition implies, due to their variable composition of cellulose, hemicellulose and lignin, different moments of emission and the presence of several peaks in DTG profiles. This fact would only limit the use of isoconversion methods as a tool to predict the reaction kinetics of solid-state processes when trying to apply to the whole process.

Characteristic combustion parameters are good indicators of the quality of a fuel. Ignition (T_i) and burnout (T_b) temperatures are two crucial properties of fuels [47,48]. The ignition temperature is defined as the minimum temperature at which a fuel ignites spontaneously in an environment without external source of ignition [49] and can be estimated thought the protocol defined by [50]. The burnout of a fuel is an indicator to stand for its reaction degree. The higher the burnout, the fewer the combustible components left in the fuel [51]. The burnout temperature refers to the temperature at which the fuel is almost completely consumed. Besides, a series of parameters were estimated to know the combustion performance of the fuels. The combustion characteristic factor (CCF, CCI or S) [52], the combustion stability index

(R_w) as well as the ignition combustion parameter (H_F) were the selected indices. The expresions proposed by [53–55] were the employed to estimate these parameters.

$$S = \frac{DTG_{max} \cdot DTG_{mean}}{{T_i}^2 \cdot T_b} \tag{1}$$

$$R_w = 8.5875 \cdot 10^7 \cdot \frac{DTG_{max}}{T_i \cdot T_p} \tag{2}$$

$$H_F = T_p \cdot \ln(\frac{\Delta T_{1/2}}{DTG_{max}}) \cdot 10^{-3} \tag{3}$$

where DTG_{max} is the maximum combustion rate (%/min), DTG_{mean} is the average combustion rate (%/min) considering as start and end the 1% of the DTG_{max}, T_i is the ignition temperature (°C), T_b is the burnout temperature (°C), T_p is the peak temperature (°C) and $\Delta T_{1/2}$ is the half peak width which is the temperature difference between two temperatures an the mass loss rate value equaling 0.5 times the DTG_{max}.

A higher S value means a better combustion property [56] and a higher value of R_w meant the sample had a better burning stability [57]. Related to H_F parameter, it describes the rate and the intensity of the combustion process. A smaller value reflects better combustion properties [55,58].

3. Results and discussion.

3.1 Agronomic variation.

Height and diameter plants variation appear in Fig. 2. Fertilizer application increased all the species values. Tukey's HSD statistical test corroborated these data except for oleander's diameter. Cypress was the species with the most notorious increase for both parameters. For both oleander and cypress, better values were observed for year 1 instead of year 2; a non-maintained trend for quinoa. Manure was the treatment with the best highest for both parameters. This fertilizer increased average height values (35 cm for oleander, 65cm for cypress and 30 cm for quinoa) and diameter (2, 7 and 5 mm for oleander, cypress and quinoa respectively). The mineral fertilizer was better than manure only when cypress diameter variation was considered (4.5 mm vs 3 mm). These results, in relation to what was obtained by other authors such as [59,60], suggest that the use of manure can improve both yield, height and diameter of the crops in better terms than inorganic fertilizers do. Moreover, this type of fertilizer can be used together with a mineral fertilizer or in an isolated way improving, this way, the yield and the growth of the species as well as the soil properties [61].

3.2 Fuel properties.

Biomass samples properties were shown in **Table 2.** Beginning with the moisture content, it adds unnecessary weight to biomass. Moisture high levels are not desirable in combustion processes [62,63]. The higher the moisture content of a sample, the lower its calorific value [64]. Cypress and oleander samples showed moisture values lower than quinoa. It should be taken into account that quinoa, unlike to oleander and cypress, has an herbaceous character. Within the quinoa samples, the husks had higher moisture than the stems. Quinoa moisture values are line with the obtained for typical herbaceous biomass [65]. Cypress and oleander data were even lesser than any woody species like pine, oak or eucalyptus [66].

Related to ultimate analysis, a similar trend was observed: quinoa samples vales were different from the rest of species. Carbon and hydrogen oxidations are exothermic. So, the higher the content of this element, the greater the energy will be released [67,68]. Oleander was the species with higher values for both elements. The fertilizer did not improve these parameters. This fact was maintained for the ultimate analysis of the rest of the species. Cypress and oleander C and H values were similar to woody biomass [69], whereas quinoa samples resembled with herbaceous feedstocks [70]. For its part, higher contents in S and Cl are not advisable. Sulfur can originates SO_x during the combustion and high chlorine values are probably related with fouling problems [71]. As an herbaceous biomass, quinoa had higher values for both parameters compared to the cypress and oleander, so this fact will have to take into account when designing the boilers with which they intend to work. The employ of manure fertilizer had that chlorine values were lower for practically all samples analyzed.

As the proximate analysis was concerned, samples showed an acceptable volatile matter values, being higher for oleander (80-81 %). Oleander was again the species with higher VM content. Values were much higher than the typical ones for charcoal [72] and so similar to woody sources [73]. For its part, biomass samples presented lower contents in ashes were those of the stems of oleander (around 4%). Both leaves and stems oleander ash values were lower than the obtained by other authors for the same species [74].

Considering the values of FC/VM ratio, having a low FC/VM ratio could be considered to be more reactive to combustion because they were characterized by having high oxygen content helping ignition and improving both combustion and flame stability, which depends on volatile matter content [75]. Quinoa husk (between 0.14 and 0.17) and oleander leaves (0.16 – 0.17) had the lowest values for this ratio. All the new crops FC/VM values here obtained were lower than the obtained by other authors for both bituminous coals and chars [76]. However, results for this ratio here obtained were in line with other biomass sources like almond shell, pine pellets, olive stone, rice husk [77] or poplar sawdust [78] among others.

HHV results were in the line with the trend for the rest of parameters. Quinoa values (15-17 MJ/kg) were lower in comparison with cypress (18-19 MJ/kg) or oleander (18-20 MJ/kg). Oleander leaves samples were the ones with an overall HHV results. Besides, although values were lower than commercially available fuels or biodiesel [79], they were so close to the HHV average for wood chips (tree species) [80] as well as wood and alternative residual biomass pellets [81]. Once again, fertilizer did not improve the values for this parameter.

The calculated cellulose, hemicellulose and lignin mass fractions (**Table 3**) greatly influence TGA profiles. Thus the trends obtained here are in line with literature [39]. As predictable, woody biomass parts had higher lignin values (34-41%) when compared to leaves (~30%). The nature of the biomass is clearly reflected in the disparity of the results obtained. Thus, the cypress and oleander stems had very similar values to those reflected in the literature for wood bark while the rest of the samples analysed obtained results in line with herbaceous straws [82,83].

3.3 TGA and gasses signals emissions results.

Fig. 3 showed DTG profiles. Three stages were identified. The first one (325 K) was linked to the loss of moisture. Due to its non-relevance for this study, it did not appear in the characterization table (**Table 4**). The second stage (400 – 650 K) was associated with the emission of volatiles derived from cellulose and hemicellulose as well as small amounts from volatile lignin compounds [84,85]. At this phase, approximately 60% of the weight was lost, being, therefore, the most representative weight loss. The last phase (700 – 950 K) was linked to the char and volatile compounds ignition [84]. In this third phase, two different peaks can be observed due to the diverse nature of the biomass [86]. These phases were in line with the obtained results by other authors for biomass DTG profiles under air atmosphere [87–90].

Related to the most representative stage, the second one, quinoa stems had higher DTG_{max} values (above 7 %/min). Apart from that, **Fig. 3** shows that the application of fertilizer did not have influence in the weight loss stages under air atmosphere (many of the curves were practically superimposed). Besides, while in the ignition phase the two peaks were clear for all cases, the devolatilization phase presented more differences. Only the quinoa stems showed a homogenous volatiles release. For the rest of the samples, the release of volatiles occurred in a phased manner.

Some of the emitted gaseous species appeared in the **Fig. 4.** This figure shows the maximum gases emissions during the 400 – 650K (temperate interval at which the highest gas release came out). The maximum emission values were very different depending on the gaseous species. Water vapour (m/z=18) was the one emitted to a greater extent. It is an important gas in the planet boundary layer (PBL) from the perspective of greenhouse gas effects [91]. Quinoa husks had the highest emission values for it. In particular, the application of mineral fertilizer increased them (18.32nA). The fact that applying inorganic fertilizer increased emissions was also maintained for the rest of gases and biomasses. CO (m/z = 28) is an important precursor of tropospheric ozone and a primary control on the oxidizing power of the atmosphere [92,93]. Higher emissions were observed again **(Fig.4.B)** for quinoa husks under mineral fertilization (0.001nA). The low CO emission scale indicated that combustions carried out were complete combustions. CO values were lower than the emitted during the combustion of chars derived from agricultural residues (shells) [94]. These type of combustions release CO_2 with the same trend than CO but in a greater order. Hence, the maximum value was also related to quinoa husk under mineral fertilization (4.916nA). Considering nitrogen oxides, NO (m/z = 30) and NO_2 (m/z = 46), due to the problems they cause on humans and the environment [95], low emission values for both gases will be advisable. Its constituents act as one of the primary precursors to acidic precipitation, especially in industrialized regions. NO values (**Fig.4.C**) were higher than NO_2 **(Fig.4.E**). These NO values were also higher than those obtained for pine chip and peanut hull at low temperatures than those obtained for [96]. Finally, authors also analysed SO_2 (m/z = 64) emissions (**Fig.4.F**). As happened with NO_2, Oleander leaves SO_2 emissions during inorganic fertilizer stood out (0.114nA) above the rest. Approximately 70% of the annual emissions of SO_2 are associated with the combustion of fossil fuels [97]. So, methods to capture SO_2 as well as CO_2 are being sought [98]. Readers should also take into consideration that the NO and SO_2 emission levels (**Fig. 4**) were so close to the N and S values of raw materials (**Table 2**).

To sum up, it can be stated that mineral fertilizer increased emission values for all samples in the same way as the lowest emissions were associated with oleander stems. With the exception of organically fertilized samples, the emission results were very similar to those of herbaceous biomass [99].

3.4 Kinetic and combustion parameters results.

The kinetic results appear in **Table 5**. Oleander and cypress had higher activation energy values in the case of ignition than in devolatilization. It may be because ignition reactions start at higher temperatures requiring higher activation energy. This aspect was also maintained for quinoa but only in the samples with fertilizer. These tend, higher E_a values for stager with higher DTG_{max}, was also identified by other authors for olive trees [100], hazelnut shells or wheat straw [101]. The application of fertilizer, for practically all cases, decreased the activation energy of the more representative weight loss stage (devolatilization). This decrease was greater with the use of manure.

Regarding the frequency factor, once again cypress and oleander presented a different behaviour from quinoa. During devolatilization, cypress and oleander had lower k_0 values than during ignition. For quinoa, however, devolatilization peaks were narrower (**Fig. 3. D-E**) indicating a higher reaction rate and therefore higher values of this parameter. The fertilizer application did not change the values of k_0 with a fixed pattern. It is worth noting that, for the most representative phase, manure fertilizer increased the value of k_o (2049.383 1/s) by almost twice as much as the control (1281.436 1/s) for the quinoa stems. Values here obtained during devolatilization phase for both both E_a and k_0 were lower than the obtained by other authors for coal [102] and higher than the compared ones with palm biomass pyrolysis [103].

Besides, and, despite not having a great list of publications with the species here employed (this is one of the main novelty of this paper), there are publications that can be used to compare our kinetic results. So, in the case of oleander and in spite of having using another methodology, [74] analysed both oleander leaves and stems. The values of E_a for the leaves of oleander were similar during the devolatilization phase for the two works ($\sim 40\ kj/mol$), however, those of the ignition phase were higher to those obtained here. Another important aspect is that quinoa stems had higher values of E_a and K_0 than husks, something maintained for all phases and fertilizers.

3.5. Combustion characteristic parameters.

Table 6 shows the combustion characteristic parameters. Related to the combustion characteristic factor (S), all values were higher $2 \cdot 10^{-7}$, what meant that all the new crops here analysed had a good burning performance [104]. Quinoa residues (especially stems) were the ones with higher values for both S (~ 5 $\%^2/(\text{min}\cdot°\text{C}^3)$) and R_w(~ 8 $\%/(\text{min}\cdot°\text{C}^2)$). Likewise, and with the only exception of cypress, MANURE fertilizer increased the S values for all samples. In the same way, S values obtained were also higher than the obtained in the literature for herbaceous biomass [43,105], certain fossil fuels [104,106] or mixtures of the above [43]. These quinoa stems were also the biomass with lower H_f values (~0.65). H_f values were in line with the obtained by other authors [107] for coal gangue samples in the same way that R_w were lower than hydrochar values [108].

4. Conclusions.

Biomass fuel properties showed that oleander was the species with better fuel potential. In the same way, fertilizer did not modify the biomass samples properties either the mass release. Manure fertilizer was the one that further increased the height and diameter of the plants (especially the cypress). Related to the weight loss, devolatilization and ignition stages were identified; being the stems of quinoa the raw material with higher DTG_{max} values (> 7 %/min). According to gas emission results, oleander stems was the biomass with less maximum values. Besides, fertilizer application (especially manure) decreased the activation energy values for almost all cases. Thereby, it can be stated that all the new crops here analysed had acceptable burning performance, being the best one associated with the quinoa stems according the combustion characteristic parameters estimated.

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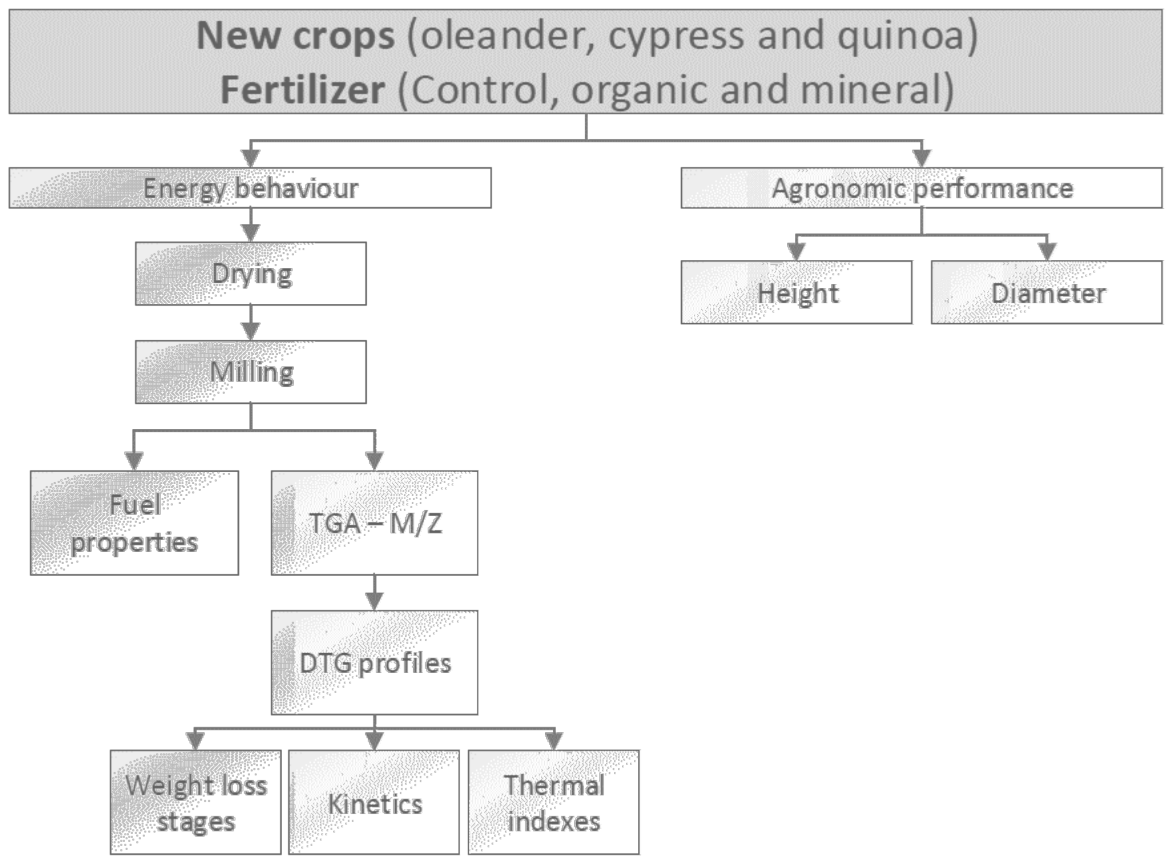

Fig.1. Methodology flow chart.

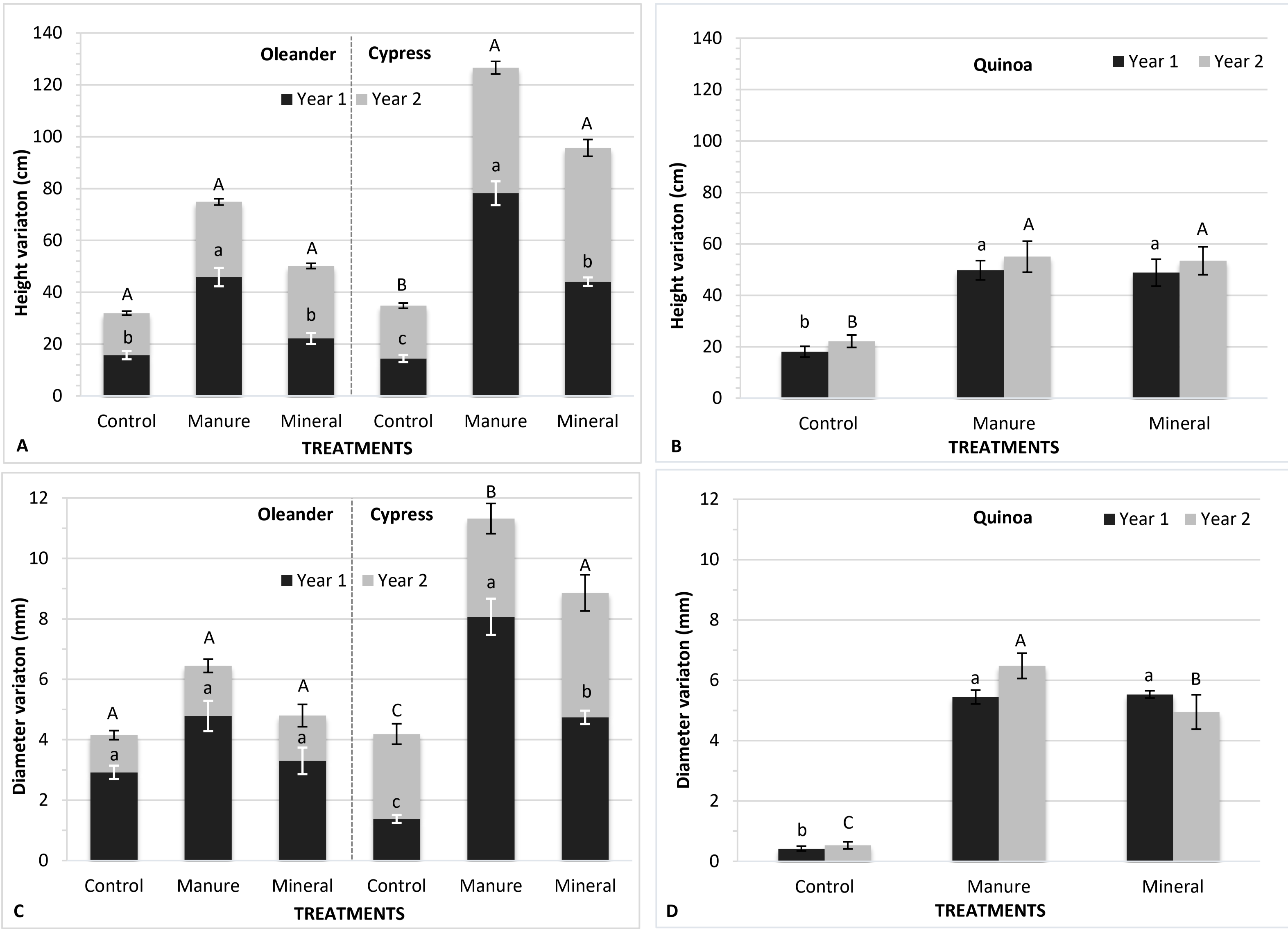

Fig. 2. Samples agronomic variation. This figure shows the fertilizer influence on the variation to the height (A and B) and diameter (C and D) of the new crops. Statistical analysis (Tukey's HSD test) was also done for each species and year. Lowercase letters for the first year and capitals for the second one.

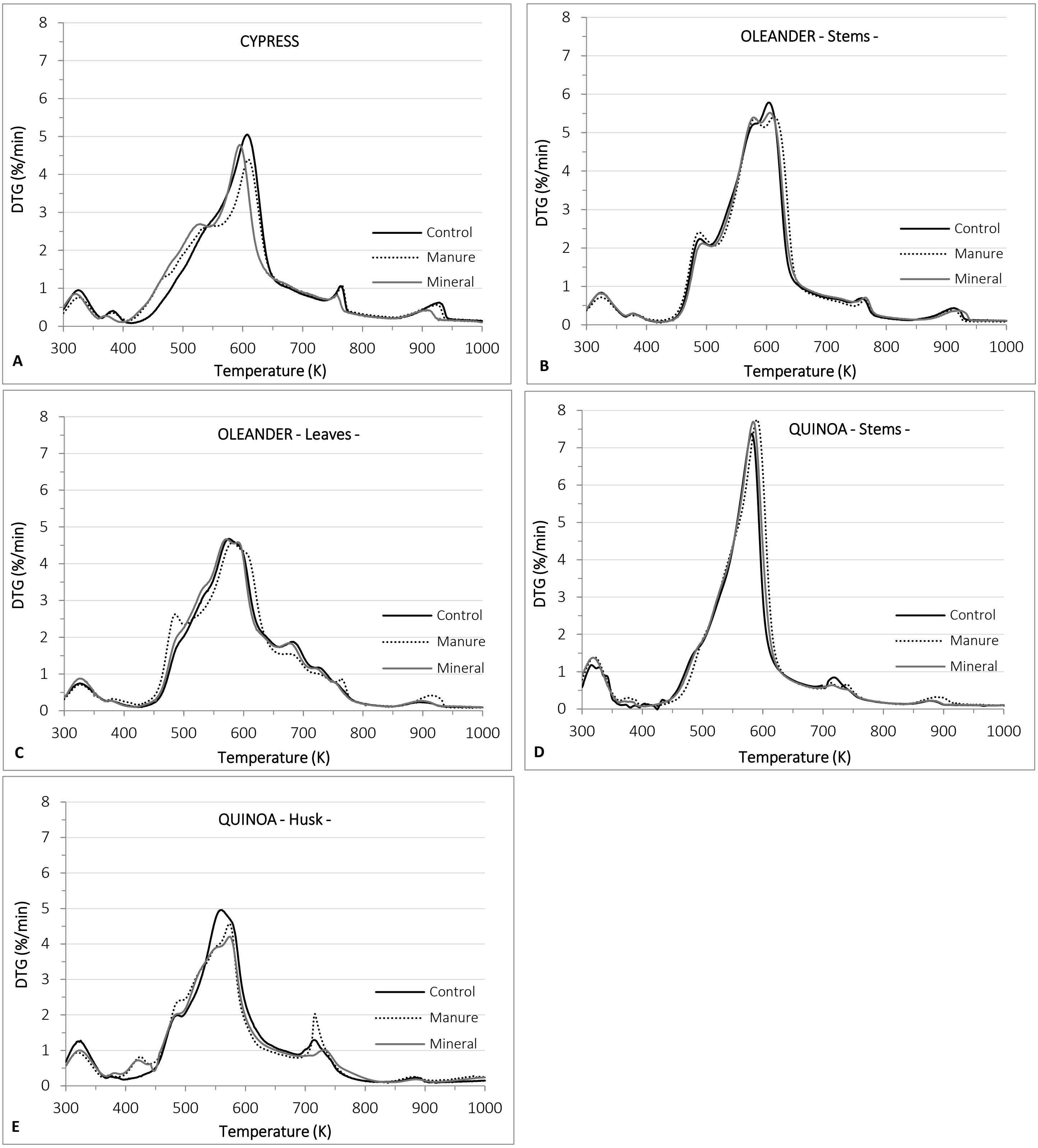

Fig.3. DTG profiles. Cypress (A), oleander stems (B) and leaves (C), quinoa stems (D) and husk (E).

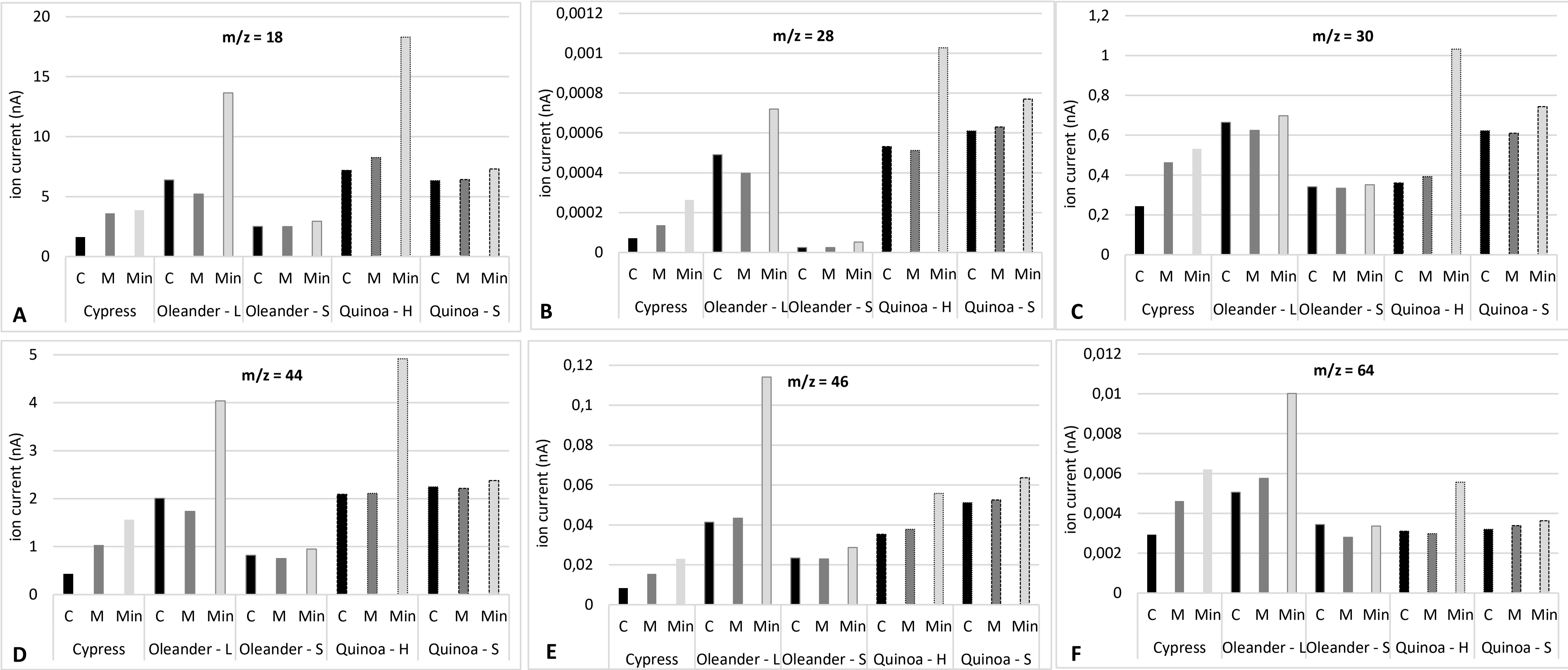

Fig. 4. Biomass maximum gasses emissions. C, M and Min are the fertilizer type (Control, Manure and Mineral respectively). Signals associated with the following gases species: H_2O (**A**), CO (**B**), NO (**C**), CO_2 (**D**), NO_2 (**E**) and SO_2 (**F**)

Table 1. Soil and manure physicochemical properties.

	SUBSTRATE		MANURE	
	Value	**SD**	**Value**	**SD**
Properties				
Moisture (%)	54.08	1.23	7.65	0.12
pH	7.47	0.57	6.75	0.17
Conductivity (dS/m)	0.49	0.01	4.17	0.31
Total Nitrogen (%)	0.54	0.01	6.45	0.44
Organic matter (%)	51.52	0.41	63.98	1.02
Organic Nitrogen (%)	0.47	0.01	5.51	0.26
NH_4^+ - N (%)	0.07	< 0.01	0.94	0.05
Heavy metals (mg/kg)				
Cr	26.78	0.92	95.03	3.57
Ni	7.28	0.49	25.32	2.11
Cu	19.40	0.82	1.18	0.05
Zn	92.75	0.78	1.37	0.05
Cd	0.22	0.02	8.31	0.53
Hg	0.05	< 0.01	121.79	17.55
Pb	26.90	1.60	172.94	20.18
Macronutrients (mg/kg)				
P	395.26	7.43	220.08	9.21
K	2722.87	4.82	2901.99	66.37

Except moisture, all values are expressed as dry basis.

Table 2. Biomass fuel properties.

PLANT	PART	FERTILIZER	Moisture (%)	Ultimate analysis (%)						Proximate analysis (%)			FC/VM ratio	HHV (MJ/kg)
				C	H	N	S	Cl	O	VM	FC	Ash		
Cypress	*Biomass*	Control	4.7	48.38	5.64	0.44	0.05	0.048	39.69	73.9	19.8	6.29	0.27	18.65
		Manure	3.0	48.70	5.74	1.04	0.05	0.038	40.12	73.6	21.0	5.44	0.29	18.73
		Mineral	3.0	49.29	5.89	1.15	0.10	0.100	39.78	73.7	21.3	5.04	0.29	19.21
Oleander	*Leaves*	Control	4.4	49.28	6.52	0.69	0.07	0.052	37.93	80.0	13.7	6.27	0.17	20.10
		Manure	1.9	48.04	6.85	1.14	0.08	0.043	39.26	81.1	13.1	5.85	0.16	19.58
		Mineral	4.2	49.56	6.36	0.81	0.07	0.049	39.04	81.5	13.5	5.04	0.17	20.11
	Stems	Control	3.1	49.35	6.47	0.26	0.04	0.130	39.84	81.2	14.5	4.34	0.18	19.74
		Manure	2.9	49.09	6.54	0.53	0.03	0.079	40.32	80.9	15.1	4.05	0.19	18.80
		Mineral	2.6	47.33	6.43	0.41	0.04	0.073	41.68	80.1	15.3	4.56	0.19	18.62
Quinoa	*Husk*	Control	7.3	45.60	5.75	0.74	0.06	0.621	37.80	78.2	11.0	10.85	0.14	15.53
		Manure	8.5	45.77	5.75	0.87	0.06	0.378	35.96	75.3	12.2	12.52	0.16	16.72
		Mineral	7.8	41.75	5.42	3.34	0.11	0.374	36.34	74.6	12.4	13.01	0.17	16.92
	Stems	Control	4.8	45.60	5.75	0.74	0.06	0.546	40.77	76.9	15.2	7.88	0.20	17.36
		Manure	6.0	45.77	5.75	0.87	0.06	0.381	43.39	78.4	16.5	5.09	0.21	17.92
		Mineral	5.6	45.02	5.63	1.28	0.06	0.523	43.19	77.4	16.4	6.16	0.21	17.54

All values are in dry basis except moisture. Oxygen and fixed carbon values were estimated by difference.

Table 3. Composition of dry biomass by wt.% calculated by atomic balance.

PLANT	PART	FERTILIZER	Hemicellulose	SD	Cellulose	SD	Lignin	SD
Cypress	*Biomass*	Control	26.3	0.2	29.3	0.2	39.2	0.3
		Manure	26.2	0.3	31.1	0.1	38.3	0.3
		Mineral	24.1	0.2	35.4	0.3	36.1	0.1
Oleander	*Leaves*	Control	32.4	0.3	33.2	0.2	29.0	0.3
		Manure	31.5	0.1	34.2	0.1	30.3	0.4
		Mineral	33.2	0.2	32.6	0.3	30.2	0.3
	Stems	Control	29.1	0.3	25.7	0.1	41.3	0.2
		Manure	30.2	0.4	26.9	0.2	40.1	0.2
		Mineral	29.1	0.2	26.4	0.2	41.3	0.3
Quinoa	*Husk*	Control	32.6	0.3	22.1	0.1	36.6	0.1
		Manure	35.8	0.3	15.3	0.2	38.3	0.3
		Mineral	33.4	0.1	15.4	0.3	36.8	0.1
	Stems	Control	26.2	0.3	32.1	0.2	34.6	0.3
		Manure	25.2	0.1	35.6	0.3	35.8	0.4
		Mineral	25.4	0.1	35.4	0.3	34.4	0.3

Table 4. Characteristic parameters for the different weight loss stages.

	CYPRESS	OLEANDER		QUINOA	
		Stems	Leaves	Stems	Husk
CONTROL					
Devolatilization					
T range (K)	430 - 730	450 - 735	435 - 710	460 - 690	440 - 685
DTG_{max} (%/min)	5.052	5.782	4.677	7.436	4.958
T_{DTGmax} (K)	606.74	603.09	574.82	581.43	558.38
Ignition - Peak I					
T range (K)	735 - 865	735 - 845	710 - 850	690 - 850	685 - 850
DTG_{max} (%/min)	1.058	0.693	1.171	0.851	1.289
T_{DTGmax} (K)	763.03	758.47	726.77	717.52	716.38
Ignition - Peak II					
T range (K)	865 - 940	845 - 930	850 - 930	850 - 900	850 - 905
DTG_{max} (%/min)	0.625	0.434	0.228	0.216	0.244
T_{DTGmax} (K)	927.99	912.06	899.55	879.07	882.48
MANURE					
Devolatilization					
T range (K)	415 - 740	445 - 735	425 - 750	470 - 690	450 - 685
DTG_{max} (%/min)	4.393	5.412	4.575	7.753	4.577
T_{DTGmax} (K)	609.15	614.18	581.00	590.09	573.46
Ignition - Peak I					
T range (K)	740 - 860	735 - 840	750 - 860	690 - 845	685 - 840
DTG_{max} (%/min)	1.073	0.670	0.854	0.701	2.015
T_{DTGmax} (K)	764.16	764.18	764.17	712.97	715.24
Ignition - Peak II					
T range (K)	860 - 940	840 - 930	860 - 935	845 - 910	840 - 905
DTG_{max} (%/min)	0.555	0.372	0.412	0.321	0.252
T_{DTGmax} (K)	927.99	910.92	916.61	893.86	880.21
MINERAL					
Devolatilization					
T range (K)	420 - 740	445 - 740	420 - 710	455 - 690	460 - 690
DTG_{max} (%/min)	4.783	5.519	4.671	7.698	4.272
T_{DTGmax} (K)	601.99	605.84	570.84	583.94	583.94
Ignition - Peak I					
T range (K)	740 - 865	740 - 860	710 - 850	690 - 840	690 - 850
DTG_{max} (%/min)	0.805	0.706	1.147	0.630	1.019
T_{DTGmax} (K)	765.3	764.16	723.56	717.52	730.03
Ignition - Peak II					
T range (K)	865 - 930	860 - 940	850 - 930	840 - 900	850 - 910
DTG_{max} (%/min)	0.417	0.364	0.266	0.222	0.180
T_{DTGmax} (K)	917.75	922.30	896.69	882.48	887.03

T range: temperature interval in which the phase occurs, DTG_{max}: largest value of DTG, T_{DTGmax} : temperature associated to DTG_{max}.

Table 5. Kinetic parameters obtained for the biomass samples combustion by the application of the approximate integral method (AIM) -

	CYPRESS	OLEANDER		QUINOA	
		Stems	Leaves	Stems	Husk
CONTROL					
Devolatilization					
E_a (kJ/mol)	46.487	44.398	40.703	61.214	58.974
k_0 (1/s)	28.355	21.154	8.612	1281.436	715.310
R^2	0.990	0.983	0.981	0.993	0.983
Ignition					
E_a (kJ/mol)	66.913	79.814	60.99	52.626	40.911
k_0 (1/s)	73.957	800.687	50.514	11.932	2.011
R^2	0.999	0.994	0.988	0.991	0.991
MANURE					
Devolatilization					
E_a (kJ/mol)	36.495	41.609	33.048	64.169	42.872
k_0 (1/s)	3.368	10.801	1.490	2049.383	25.292
R^2	0.988	0.986	0.987	0.983	0.983
Ignition					
E_a (kJ/mol)	84.907	90.071	76.318	64.531	47.942
k_0 (1/s)	1272.697	4232.298	365.930	75.204	7.584
R^2	0.988	0.994	0.996	0.984	0.984
MINERAL					
Devolatilization					
E_a (kJ/mol)	36.398	45.202	40.12	58.974	45.299
k_0 (1/s)	3.179	23.793	8.135	716.375	41.190
R^2	0.983	0.983	0.984	0.983	0.984
Ignition					
E_a (kJ/mol)	90.071	76.593	60.416	67.607	63.924
k_0 (1/s)	2593.468	391.651	45.737	1146.958	88.976
R^2	0.993	0.996	0.985	0.989	0.992

E_a: activation energy, *k_0:* frequency factor, *R^2:* adjusted R-squared

Table 6. Combustion characteristic parameters.

PLANT	PART	FERTILIZER	T_i	Tb	DTG_{max}	$S \cdot 10^{-7}$	$R_w \cdot 10^3$	H_f
Cypress	*Biomass*	Control	536.37	762.72	5.052	2.06	4.94	0.98
		Manure	517.12	764.87	4.399	2.03	4.61	1.11
		Mineral	523.16	758.80	4.783	2.18	5.00	1.03
Oleander	*Leaves*	Control	512.18	727.95	4.677	2.89	5.57	0.95
		Manure	507.90	721.76	4.575	3.04	5.44	1.08
		Mineral	504.19	723.31	4.671	2.52	5.39	0.95
	Stems	Control	524.82	759.26	5.782	3.06	5.98	0.92
		Manure	517.84	767.12	5.412	3.23	5.57	0.99
		Mineral	522.42	766.24	5.519	2.91	5.72	0.95
Quinoa	*Husk*	Control	503.91	707.65	4.958	3.25	6.47	0.81
		Manure	502.04	711.32	4.577	3.52	5.72	0.95
		Mineral	497.08	720.05	4.272	2.65	5.27	0.97
	Stems	Control	527.55	710.23	7.436	4.59	8.14	0.62
		Manure	534.13	703.95	7.753	5.04	8.05	0.68
		Mineral	532.23	706.98	7.698	4.81	8.21	0.63

T_i: ignition temperature (℃), T_b: burnout temperature (℃), DTG_{max}: maximum value of DTG (%/min), S: combustion characteristic factor (%^{2}/(min·℃^{3})), R_w: combustion stability index (%/(min·℃^{2})), H_f: ignition combustion parameter.

HIGHLIGHTS

1.- Oleander, quinoa and cypress biomass residues were analysed.

2.- NPK and cow manure were the fertilizers employed for comparison purposes.

3.- Agronomic and thermal behaviour was improved after fertilizer application.

4.- TGA and kinetics revealed that all new crops had acceptable fuel properties.

5.- Fertilizer application decreased E_a values for almost all cases.

CRediT author statement

Sergio Paniagua: Conceptualization, Methodology, Trial experiment, Data analysis, Writing- Reviewing and Editing. **Laura Zanfaño:** Trial experiment, statistical analysis**. Luis F. Calvo:** Supervision, Methodology, Study design, Funder.