Combustion of avocado crop residues: varieties and nature of nutrients influence

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ABSTRACT.

The thermal behaviour of avocado crop residues was studied. The seeds and the pruning remains from Hass and Bacon varieties were analysed to know their fuel properties. The influence of the fertiliser nature was also studied thorough the application of cow manure and inorganic products. Thermogravimetric analysis (TGA) was carried out under 10, 20 and 40 ºC/min heating rates. Kinetics was also estimated according to the Friedman, Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods. Results indicated the good fuel performance of the samples. Higher heating values (HHV) were higher for pruning remains (19.43 MJ/kg) when compared to seeds (18.74 MJ/kg). Cow manure improved the behaviour of all avocado samples regardless of the varieties. Average action energy was lower for wood (143.89 – 211.04 kJ/mol) than seeds (174.05 - 279.99 kJ/mol). Regarding TGA, this analysis showed three different mass loss associated to hemicellulose, cellulose and lignin release. TGA profiles were so different for the different biomass sources according to the fertiliser employed. Hence, the heating rate influenced the thermal behaviour of the samples, highlighting the fast release of the SBC and WHM for the 10 and 20ºC/min ramps respectively.

Keywords: Avocado crop residues; Bacon; combustion; fertiliser influence; Hass; kinetics.

1. INTRODUCTION.

Energy issues play an increasingly important role in contemporary developed and developing societies [1]. In a world with increasing pollution and the depletion of fossil fuels, countries across the globe have arrived at a consensus to replace fossil fuels with renewable resources [2–4]. Among them, biomass has been widely recognized due to its huge, cheap and readily availability [5,6] as well as its consolidated technology for bioenergy use, especially when talking about the thermo-chemical processes applied to lignocellulosic biomass [7]. Moreover, they possess the advantage of being ‘carbon-neutral’ and biodegradable and of reducing greenhouse gas (GHG) emission [8].

Biomass has different components such as cellulose, hemicellulose, lignin etc.; and therefore, it is important to know its thermal decomposition behaviour during combustion [9]. Hence, sufficient knowledge of the thermal decomposition kinetics of biomass provides essential information to evaluate the energy potential of feedstocks [10]. For this reason, a complete understanding of combustion behaviour of a biomass and the process conditions are necessary prior to utilization of a particular biomass for energy purpose [11,12].

In this work, samples energy performance was carried out by thermogravimetric analysis (TGA). It is used in the real-time monitoring of the relationship between feedstock physicochemical properties and temperature for different thermal processes [13]. Generally, the TGA data is plotted with y-variables of mass change rates and x-variables of temperatures. Thus, these curves are used to determine the apparent mass loss of sample with increasing temperature [14]. Furthermore, thermoanalytical techniques are well adapted to describe the thermal decomposition and to extract kinetic parameters of a particular fuel [15]. This way, three different iso-conversional kinetic methods such as Friedman, Kissinger-Akahira-Sunose (KAS) and Ozawa-Flynn-Wall (OFW) were adopted to determine the activation energy (E_a) and the pre-exponential value or frequency factor (A) of the combustion reaction [16–19]. The advantage of determining the kinetic parameters such as the above mentioned from TG-DTG is that only fewer data are required for calculating the kinetics over specific temperature range [20].

Avocado (*Persea americana* Mill., 1768) crop residues have been used as biomass source. With a great increase in its commercialization due, in part, to its nutritional value [21], Spain is, within the European continent, the country with the most hectares dedicated to its cultivation [22,23], **Supp.1.** The avocado crop generates a large amount of waste [24]. While seeds represent about 13–17 % of the fresh fruit [25], the pruning of the trees generates large quantities of wood that, if not valued, could involve a problem for the environment [26]. Hass and Bacon avocado varieties are two of the most consumed based on their nourishing properties and adaptation to different conditions and environments [27–30]. On the other hand, the type of fertiliser was another parameter considered. Inorganic fertilisers (also called mineral) have been applied for a long time due to, among others, the demonstrated increase in yield associated with them [31]. However, current customers are demanding more organic products. This fact is causing a grow in the number of farmers who select this type of culture [32]. Besides, despite environmental benefits [33], previous research studies carried out affirmed the existence of a relation between several biomass sources and the type of fertiliser employed [34–37].

The purpose of the present work is to investigate the thermal behaviour and kinetic analysis of Hass and Bacon avocado varieties under different types of fertilizer via thermogravimetry together with the application of different kinetic and heating rates.

2. MATERIAL AND METHODS.

2.1 Raw material, plots and sampling.

The samples of the Hass and Bacon avocado varieties were taken from two different plots first planted in 2001. One of them (1.66 ha) was fertilized exclusively with inorganic fertiliser and the second one (2.68 ha) with cow manure. All of them were adjacent to each other in the municipality of Alozaina (Málaga, Spain). The planting arrangement was 156 trees/ha (8 x 8 m). The crops were handled by mechanical weeding from January to June. The predominant soils were Calcic Cambisols and Calcaric Regosols [38], with an average depth of 66.4 ± 30.9 cm and an average organic carbon content of 20.3 ± 13.5 g/kg. The climate is temperate Mediterranean, with an average annual temperature of 18.4° C and mean annual precipitation of 636 mm with a prolonged water deficit, from April to September. The biomass samples, **Supp. 2**, were taken in 2020.

Thus, while the inorganic crop was irrigated annually with 15000 hl/ha, the organic crop received 10000 hl/ha. Following the recommendation of Trehan [39], for mineral fertiliser conditions, each tree received 6 kg 17-17-17 (N-P_2-O_5 - K_2-O) in two applications, one in June and other in October. Related to organic plots, the farmers applied a dose of 25 kg/(tree·year) of cow fertiliser which characteristics are specified in **Table 1.** The following standard methods were used for the determination of the different parameters: moisture (UNE-EN 13040:2008), organic matter (UNE-EN 13039:2012), total nitrogen (UNE-EN 13654-1: 2002), N-NH_4^+ (UNE-EN 15475:2009), phosphorus (UNE-EN 15958:2012), potassium (UNE-EN 15477:2009), organic carbon (UNE 77321:2003) and pH (UNE-EN 13037:2012).

In the same way, the orchard received all standard grower management practices including the pruning. This pruning was yearly carried out in spring generating between 50 - 75 kg wood/adult tree for the two varieties for both types of fertiliser. Considering the production, the Bacon variety had a higher yield than the Hass variety. The highest values were reached for the inorganic cultivation of Bacon variety (between 200 and 300 kg/(tree·year). The rest of varieties - fertiliser combinations provided average productivity values of 150-180 kg/(tree·year).

Both seeds (S) and pruning wood remains (W) were sampled ensuring that two consecutive trees were never selected and following the standard UNE-EN ISO 18135:2018. 100 g of pruning wood were taken for each variety, Hass (H) or (Bacon), and fertilizer type, mineral (M) or cow manure (C). In addition, one mature avocado fruit was collected per each tree previously selected sampling unit. Then, samples of the same variety and fertilizer type were mixed, dried by air-drying for a minimum of 72 hours and milled on a Fritsch™ mill Model P-19 to a 1 mm particle size. Later, using a Retch™ ball mill model MM200, particle sizes lower than 0.2 mm were obtained. Thus, the eight samples employed in this word have the following name: SBM, SBC, SHM, SHC, WBM, WBC, WHM, WHC.

2.2 Hemicellulose, cellulose, lignin and extractives content.

Additionally, samples composition in terms of hemicellulose, cellulose, was also estimated by atomic balance of the components elemental formula following the method of Ranzi et al. [40]. 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) [41]. 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. The relative amount of each of these monomeric lignin precursors and the total lignin content mostly depend on wood species. Lignins from softwood consist mainly of G structures whereas hardwood consists of various amounts of G and S units [42]. Water and ethanol extractive contents were determined, in triplicates, according to the procedure described for lignocellulosic biomass by Hann and Rowell [43] following Eq. (1):

$$\text{Extractives (\%)} = 100 - (\text{Weight}_{\text{sample after extraction}} / \text{Weight}_{\text{initial sample}}) * 100 \tag{1}$$

2.3 Thermo-chemical analysis.

Both the seeds and the avocado pruning remains of the different plantations were analysed to know their fuel properties (**Table 2**). The elemental and proximate analysis together with the calorific value were estimated following a series of standard methods. 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).

2.4 Thermogravimetric analysis (TGA).

Before this analysis, samples were prepared. They were dried by air-drying for a minimum of 72 hours and milled on a Fritsch™ mill Model P-19 to a 1 mm particle size. Later, using a Retch™ ball mill model MM200, particle sizes around lower than 0.2 mm were obtained.

Thermogravimetric analysis was carried employing a TA Instruments™ TGA SDT2960 system, which was able to supply a continuous measurement of sample weight as a function of time or temperature. The dynamic experiments were performed with approximately 8 mg of milled samples placed in an Al_2O_3 crucible and heated from ambient to 700 ºC at 10, 20 and 40 ºC/min. This heating was carried out under a flow of 100 mL min^{-1} of air (at a gauge pressure of 1 atm) to achieve the oxidative process that takes place at combustion. Mass and time/temperature data were recorded using Universal Analysis 2000 TG software (TA Instruments, New Castl, EEUU) to yield the mass loss (TG) and differential mass loss (DTG) curves.

2.5 Kinetic parameters.

The isoconversional methods Fiedman, FWO and KAS were compared to determined different kinetic parameters that occurring throughout the combustion process of the different avocado residues.

As a general rule, the kinetics of reactions in solid-state can be described by Eq. 2:

$$\mathrm{d\alpha/dt = k(T)f(\alpha)} \qquad (2)$$

where α is the grade of conversion, t is the time, $\mathrm{f(\alpha)}$ is the reaction function and $\mathrm{k(T)}$ is the decomposition rate constant.

For this study, the above grade of conversion or volatile biomass fraction (α) is estimated with Eq. 3:

$$\mathrm{\alpha(T) = (m_0 - m_T)/(m_0 - m_F)} \qquad (3)$$

where $\mathrm{m_T}$ is the biomass mass at the working temperature during TGA test, $\mathrm{m_0}$ and $\mathrm{m_F}$ represent the initial and final solid-sample mass through combustion process, respectively.

The kinetic decomposition rate constant is a function of temperature $k(T)$ according to the Arrhenius relationship:

$$\mathrm{k(T) = A\ e^{(\ -E/RT)}} \qquad (4)$$

Being T the absolute temperature (K), A is the pre-exponential factor (s^{-1}), R is the ideal gas constant (8.31446 J/(mol·K)) and E is the activation energy (J/mol).

The combination of Eqs. (2) and (4) provides the general expression (5) of analytical methods to calculate kinetic parameters employing TG results:

$$\mathrm{d}\alpha/\mathrm{dt} = \mathrm{A}\,\mathrm{e}^{(-\mathrm{E}/\mathrm{RT})}\,\mathrm{f}(\alpha) \tag{5}$$

For non-isothermal TG experiments, in which a sample is heated at a constant rate or heating rate ($\beta = \mathrm{dT}/\mathrm{dt}$), the kinetic expression can be written as follows:

$$\mathrm{d}\alpha/\mathrm{dT} = 1/\beta\,(\mathrm{A}\,\mathrm{e}^{(-\mathrm{E}/\mathrm{RT})})\,\mathrm{f}(\alpha) \tag{6}$$

Commonly, the reaction function $f(\alpha)$ is unknown. Hence, if Eq. (6) is integrated up to conversion, α, Eq. (7) is obtained:

$$\int_0^{\alpha} d\alpha/f(\alpha) = g(\alpha) = A/\beta \int_{T_0}^{T} e^{(-E/(RT))}\,dT \tag{7}$$

Performing a change of variable with the following non-dimensional parameter $x = E/RT$;

$$\mathrm{g(x)} = (\mathrm{AE}/\beta\mathrm{R}) \int_0^{\infty} (\mathrm{e}^{-\mathrm{x}}/\mathrm{x}^2\ \mathrm{dx}) = \mathrm{AE}/\beta\mathrm{R}\,\mathrm{p(x)} \tag{8}$$

Integral of $p(x)$ must be approximated due to it has no analytical solution. Thus, there are different methods with their approximation formulas. For this work, Friedman, Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods were employed. The Friedman analysis is an isoconversional method whereas the Ozawa-Flynn-Wall (OFW) and Kissinger-Akahira-Sunose (KAS) analyses are integral isoconversional methods. In all methods, the measurements are analyzed for multiple conversion levels. Friedman requires at least two measurements.

2.5.1 Friedman method.

This is one of the earliest isoconversional methods [44]. The activation energy uses the variation of conversion fraction regarding the temperature at a given heating rate and at a certain temperature. It is founded on the following Eq. (6) it is obtained the following result:

$$\ln(\beta\, d\alpha/dT) = \ln[A_\alpha\, f(\alpha)] - E/RT \qquad (9)$$

2.5.2 Flynn-Wall-Ozawa (FWO) method.

This method [45,46] is based on the Doyle's approximation [47] and results in the following Eq. (10):

$$\ln(\beta) = \ln[AE/(Rg(\alpha))] - 5.331 - 1.052\,(E/RT) \qquad (10)$$

2.5.3 Kissinger-Akahira-Sunose (KAS) method.

The KAS is a differential method [48,49] based on the approximation of Coats-Redfern method [50] which final expression is the Eq. (11):

$$\ln(\beta/T_\alpha{}^2) = \ln((A_\alpha R)/(E_\alpha g(\alpha)) - E/(RT_\alpha) \qquad (11)$$

Knowing the previous equations, apparent activation energy was determined for α values between 0.2–0.7, where each isoconversional methods were in agreement and the estimated error was sufficiently small, by plotting $\ln(\beta\, d\alpha/dT)$, $\ln(\beta)$ and $\ln(\beta/T_\alpha{}^2)$ vs 1/T for the Friedman, FWO and KAS methods respectively.

2.5.4 Pre-exponential factor (A).

The pre-exponential factor (in terms of the value of the activation energy), was estimated by the Kissinger's equation Eq. (11) following literature recommendation [51,52]:

$$A_\alpha(\beta) = \beta E/(RT^2{}_p)\, \exp(E/(RT_p)) \qquad (12)$$

where T_p is the peak temperature which is placed at the highest point in the $d\alpha/dT$ vs T curve at a specific heating rate. For comparison purposes, the middle heating rate (β=20°C min^{-1}) has been selected for this work.

3. RESULTS AND DISCUSSION.

3.1 Fuel properties.

Results were shown in **Tables 2 and 3**. The different nature of the biomass samples analysed had influence over the values here obtained. Related to the avocado seeds, they had a high quantity of carbon (≈ 47%) and low percentages of hydrogen (≈ 6.2 %) and nitrogen (≈ 0.5 %). These values were in line with Domínguez et al. [53] and influenced by the high starch concentration in the seeds of this species [54]. Although results were so similar according to the fertilized employed, Nitrogen, however, is showing effect of fertilizer manure used. Specifically, when compared WHM and WHC. As the sulphur and chlorine was concerned, low values for both elements are desirable because during combustions process they are generally transformed into sulphur dioxides and chlorides. These elements as well as their reaction products may be related to heating equipment corrosion and damaging emissions in SO_x form. Based on their average sulphur (0.03%) and chlorine (0.012%) values, lower than several straws and trees [55,56], it can be stated that both seeds and tree pruning remains can be a suitable option for their use as fuels [57–59].

The differentiation between seeds and wood was maintained considering their calorific power values. Seed HHV results (≈ 19 MJ/kg) were according to the same species already published values [60] and so similar to mango [61], apricot or cherry stones [62]. However, avocado seeds HHV results were lower compared with olive or peach stones [62,63]. Pruning values here calculated were also in line with commonly energy crops standards. For instance, wood derived from the genres *Paulownia*, *Populus*, *Eucalyptus* or *Pinus* [64] had similar HHV values to avocado. Moreover, these pruning residues had relatively higher mean calorific values (19.43 MJ/kg) than seeds (18.74 MJ/kg).

Likewise, cow manure application improved slightly HHV for both seeds and pruning. This increase was especially noticeable for SHC (19.25 MJ/kg), practically 0.5 MJ/kg more than SHM. This organic nature fertilizer increased the volatile matter content, especially for wood (approx. 3% higher) and reduced ashes of all samples when compared to mineral fertilizer. Moisture content was very similar for all cases (the seeds had lower values than the wood).

In addition to being able to interpret the chemical composition of the samples based on an elemental and immediate analysis, it is also interesting to know their composition of holocellulose (hemicellulose and cellulose), lignin and extractive compounds (in water and ethanol), **Table 3**. Results linked to these analyses clearly evidenced the difference between avocado wood and seeds. Both biomass sources showed results in line literature for samples with similar nature [58,65,66]. Despite the fact that extractive compounds represent a low percentage in biomass materials such as straw or wood, in materials such as avocado pit they take on a much greater importance [67]. Likewise, and as expected, the holocellulose and lignin content was higher for the woods due to the lower proportion of extractive elements. This last fact can be related to the presence of more uniform peaks in the DTG profiles, **Fig. 2**. On the other hand, the DTG of the seeds showed greater fluctuation in their emission peaks due to the high content of extractives (always greater than 30%).

Thus, it can be stated than Hass and Bacon had good fuel properties as well as so similar between them. As well as having a higher HHV and volatiles percentage, it is also desirable (among others) a high C content together with a low moisture and ash values. Hence, SHC was, by far, the sample with better results for the seeds (probably due to its higher C content, 48.22 %) whereas WBC and WHC were the ones with better fuel properties for the pruning woods.

3.2 TGA stages.

TG and DTG curves in air under three heating rates (10, 20 and 40 ºC min^{-1}) were illustrated up to 700 ºC, **Figs. 1 and 2**. Thermal decomposition behaviours may be explained by the individual components of both wood and seeds, where cellulose, hemicellulose and lignin are the main components [68,69]. Thus, different TG and DTG profiles were observed for wood and seeds based on the different nature of raw materials.

Within the thermal profiles, three different mass loss stages can be identified [70]. The first one is linked to the loss of moisture and very light volatile compounds. Low moisture contents are desirable for combustion. For this reason, the drying of avocado residues is crucial, not only to eliminate microorganisms but also to achieve a greater energy use [71]. The temperature range of the first stage was from ambient temperature to about 100 °C. According to the second peak, more intense mass loss occurred between the temperatures of 150 and 450 °C. The mass loss during this stage is due to the decomposition of hemicellulose and cellulose, which are generally the components lost in this temperature range and are commonly grouped as volatile matter [72]. The third and last mass loss event is known as fixed carbon combustion. It took place from 400 to 600 °C and was related to the decomposition of lignin. Once the temperature was higher than this value, mass loss was brought to an end by thermal decomposition. Readers should consider that biomass mass lost is not an isolated process. Due to the different decomposition temperature intervals for hemicellulose (190 – 320 °C), cellulose (280 – 400 °C) and lignin (320 – 450 °C) [73], each particular stage can be the result of the decomposition of both elements simultaneously.

For the seeds, cow manure application reduced the main region temperature interval for both varieties. Bacon seeds had higher DTG_{max} (maximum value achieved for DTG profiles) values compared to Hass. Organic fertiliser also increased these values being SBC the sample associated with the maximum for all samples studied in this work (1.904 %/°C). Heating rate influence was clearly more evident for Bacon seeds profiles. Whereas different heating rate plotted lines were so similar for Hass (only 20 °C/min was different), working with Bacon samples the same did not happened. Overall, the best behaviour for this biomass was achieved under a slow heating rate (10 °C/min) for SBC sample. It also had a very low final residue (0.238%). Chemical properties influence thermal profiles. Consequently, the Bacon variety, which hocellulose (hemicellulose + cellulose) content was higher than that of the Hass variety, presented higher peaks (higher DTG_{max} values) for the interval associated with the release of these compounds (190 - 400°C). However, this same Bacon variety, having a lower lignin content, had an emission value for the stage from 400ºC lower than that of Hass.

Regarding wood, the above trend was maintained. Here, both the heating ramp and the type of fertilizer played an important role, being the cow manure and the 10ºC/min heating rate the ones associated with the best thermal behaviour. Once this organic fertiliser was used, it was so remarkable that a 96 % of the initial WBC sample mass was released at 326 °C. This performance was not achieved for any other wood sample. However, when Hass variety was analysed, and similar to this variety seeds activity, cow manure it did not have as much influence as for the Bacon variety. It was the combination WHM and 20 °C/min the one with the higher DTG_{max} for all wood samples (1.581 °C/min). Hass variety presented a higher holocellulose content. Likewise, for the different varieties, mineral fertilization was related to a higher content of this component, which is observed with a higher value of the area under the peak of the samples.

DTG samples profiles, **Fig. 2**, showed a very steep slope in the final mass loss. The hearing rate influenced this fact. Readers can realize the effect of 10ºC/min heating rate for SBC and WBC and 20ºC/min for WBM, WHM and WHC in **Fig.1**. This contrasted with the progressive mass loss experienced in conventional profiles [74]. As consequence, it can be stated that practically all of the biomass was released at temperatures below 450ºC. This has the associated advantage that almost all of the material introduced into the burner is used.

On balance, the heating rate and fertiliser type influenced differently the thermal behaviour of the different varieties of avocado crop residues. That way, in addition to the largest sample mass release possible, higher DTG_{max} values together with a fast hemicellulose, cellulose and lignin liberation was desirable. SBC at 10ºC/min and WHM Hass at 20 °C/min were the samples that fitted best with this pattern.

Avocado wood TGA profiles were in line with the characteristic profiles for wood under these same working conditions [75]. If a comparison with wood furniture waste is made, it was shown that the slowest heating rate was related with the higher DTG_{max} values along with a faster compounds release [76].

If a comparison with pyrolysis is made, while wood pyrolysis processes showed less differentiable release peaks with a higher final residue [77], avocado seeds had similar DTG combustion profiles than almond shells and olive stones pyrolysis results [78] as well as similar DTG_{max} values than cherry seeds [79]. Besides, for combustion process, the decomposition process above

400 ºC could be faster than that observed under nitrogen atmosphere because of the oxidation of the residual material [80]. If a is analysis with gasification thermal process is done, values here obtained were quite different from the biomass typical ones under this semi-inert thermal process. Thereby, compared with sugarcane bagasse [81], DTG_{max} results were higher for this above raw material in the same way that temperature linked with these maximum values were, by miles, higher than the achieved for avocado residues.

3.3 Kinetics.

Apparent activation energy was estimated plotting ln $(\beta \, d\alpha/dT)$, ln(β) and ln $(\beta/{T_\alpha}^2)$ vs 1/T for different conversion values (α = 0.2–0.7). Linear regression results are shown in **Figs. 3-5**. Thus, once the slope was known, numerical data can be obtained for the Friedman, FWO and KAS methods respectively (**Table 4**). The straight lines were observed at each conversion level assumed with correlation coefficients (R^2) in the range of 0.9116–0.9999.

Starink [82] affirmed that KAS and FWO were more accurate than Friedman model. For this work, although results obtained for Friedman method were slightly higher than the achieved for the rest, we found similar trends for the activation energy issued from all the methods applied. The small differences observed can be explained based on the calculations techniques and principles of the three methods applied [83]. For seeds there was also a trend in which E_a increased for the α interval between 0.2 - 0.5 to finally decrease with the 0.6 and 0.7 conversion degrees.

Average E_a values were lower for pruning wood (143.89 – 211.04 kJ/mol) when compared with seeds (174.05 - 279.99 kJ/mol). Cow manure decreased the average E_a values for all avocado samples. The case of its application to Bacon variety pruning wood was especially remarkable. An average drop of 60 kJ mol^{-1} was shown considering WBM and WBC samples. It was just this variety (Bacon) the one related with the lowest E_a values. Avocado pruning results were in line with the reflected by literature for wood feedstock [73,84–86]. Wood biochar had [87], however, higher values than the obtained for this work. As for seeds, olive stones had similar E_a combustion values [88]. The overall E_a results were higher than the typical ones for fossil fuels such as lignite [89] or bituminous coals [90].

Kinetics values here obtained were so different when a comparison with other thermal processes is done. Thus, literature associated with pyrolysis indicated that, for instance, olive stones [91], horse chestnuts seeds [92], sugarcane bagasse [93] or waste wood [94] had lower E_a values than the obtained in this work.

As the frequency factor values are concerned, wood samples ($8.7 \times 10^{17} – 3.8 \times 10^{29}$ 1/s) had lower values than seeds ($6.1 \times 10^{13} – 2.8 \times 10^{22}$ 1/s). Once again, cow manure application modified these results. For this A parameter, organic fertiliser decreased, regardless of the variety and biomass raw material, all the samples outcomes. This parameter is clearly influenced by the formula used for its estimation Eq. (12) which consider the employment of one certain heating rate (20ºC/min for this work).

4. CONCLUSIONS.

This work investigated the thermochemical behaviour under combustion for avocado wood and seeds via thermogravimetric analysis. Hass and Bacon varieties were studied together with different fertilizer types (mineral and cow manure). Obtained results denoted that pruning wood had relatively higher mean calorific values (19.43 MJ/kg) than seeds (18.74 MJ/kg). Cow manure improved the behaviour of all avocado samples regardless of the varieties. The above trend was also maintained for E_a. Hence, average E_a values were lower for pruning wood (143.89 – 211.04 kJ/mol) when compared with seeds (174.05 - 279.99 kJ/mol). In the same sense, considering this kinetic parameter values, Bacon variety had also the lowest results. Regarding DTG profiles, they were different because of the different hollocellulose, lignin and extractive contents clearly influenced by the different varieties and types of fertilizer. The lower amount of extractive elements in wood led to more uniform release stages in contrast with seeds. Heating rate also had an effect on samples thermal performance. This way, results achieved advised the use of Bacon seeds employing cow manure and a 10 °C/min ramp as well as Hass wood under mineral fertilisation at 20 °C/min.

ACKNOWLEDGMENTS.

F. Lima investigation was conducted within the framework of a predoctoral contract (A.2) under the I Research and Transfer Plan of the University of Málaga

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Sergio Paniagua: Conceptualization, Investigation, Methodology, Writing - review & editing, **Sergio Reyes**: Resources, Investigation, Visualization. **Francisco Lima**: Resources, Investigation, Methodology. **Luis F. Calvo**: Conceptualization, Supervision, Review & editing, Project administration,

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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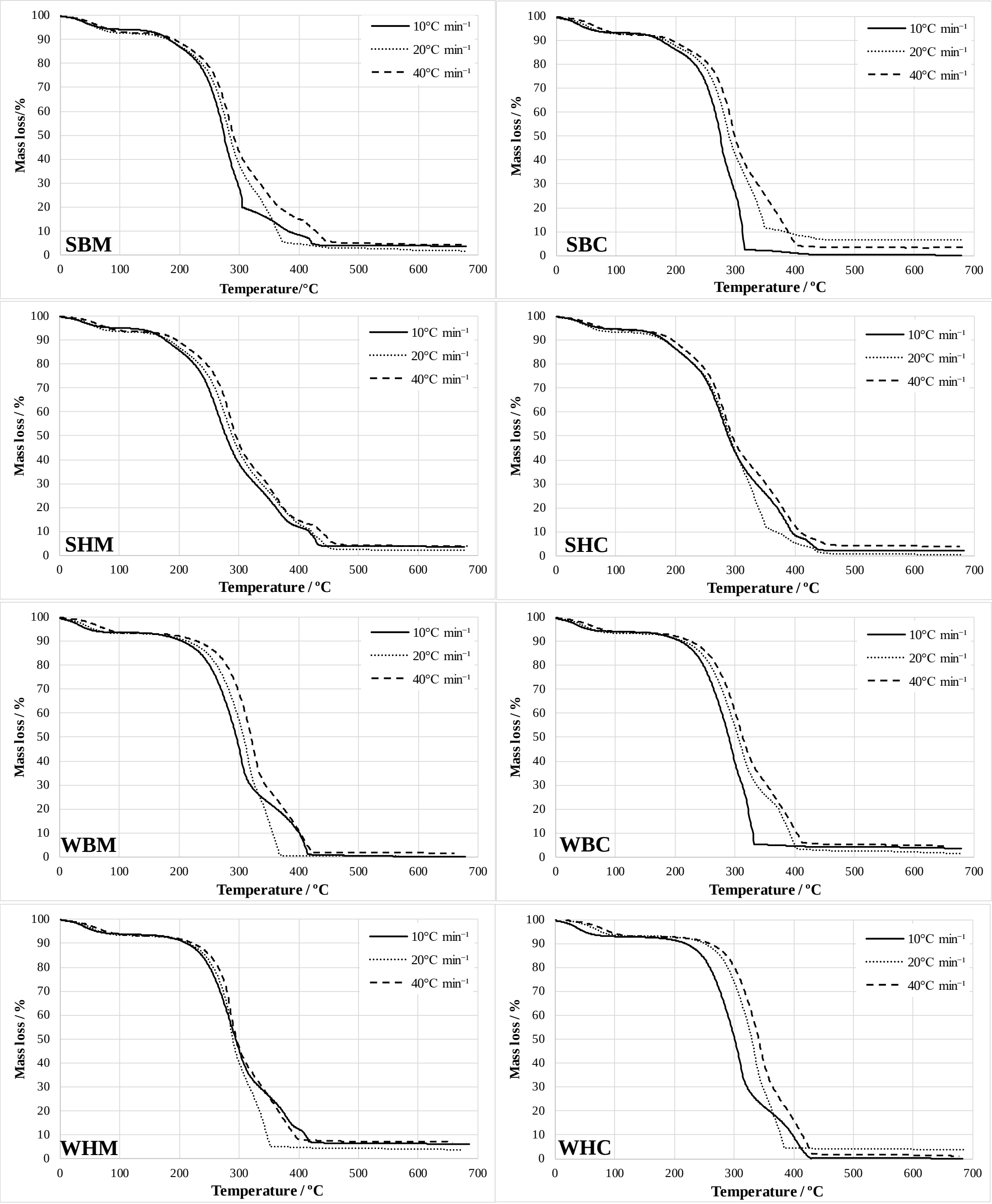


Fig. 1 - TG profiles under three different heating rates from the avocado crop residue samples.

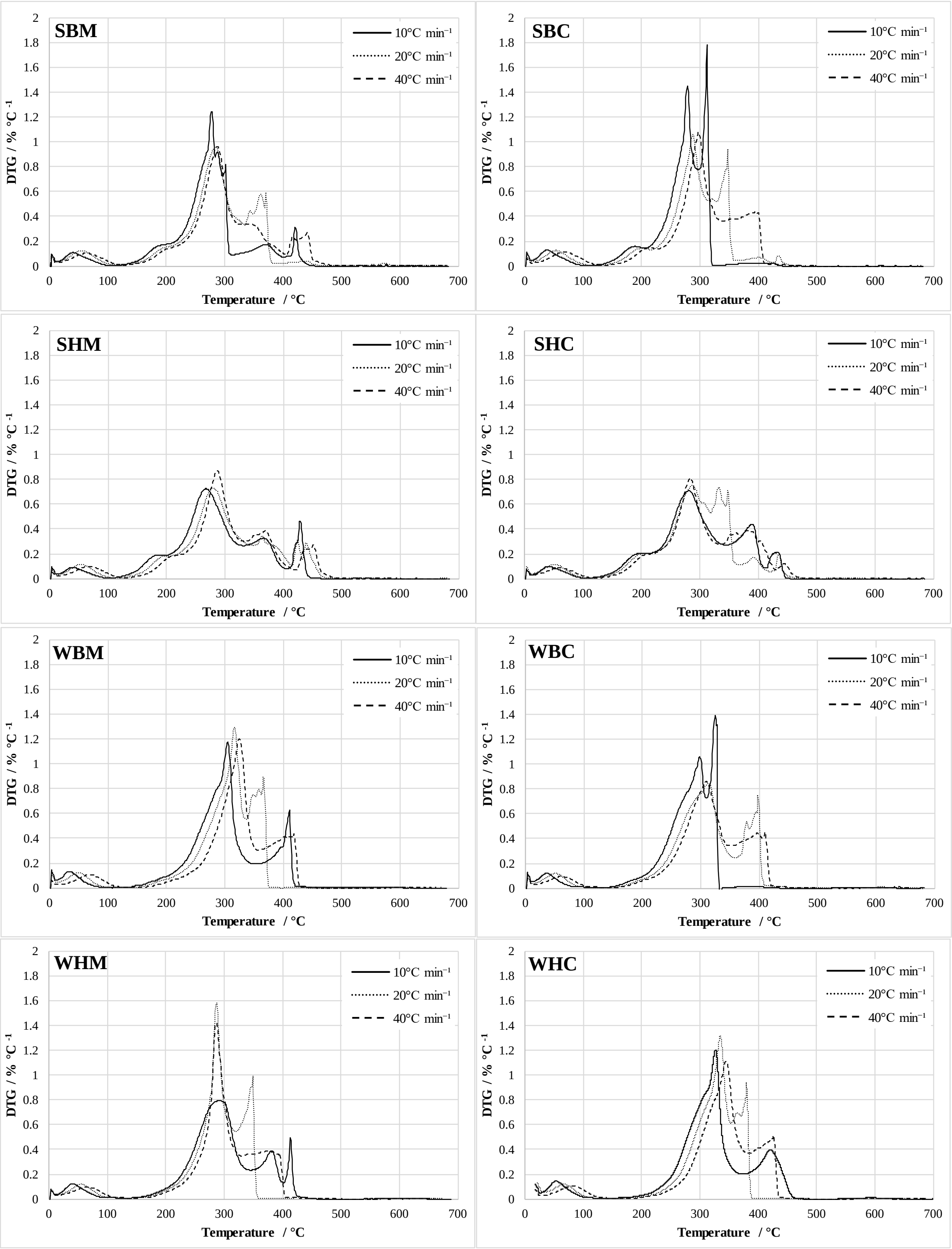


Fig. 2 - DTG profiles under three different heating rates from the avocado crop residue samples.

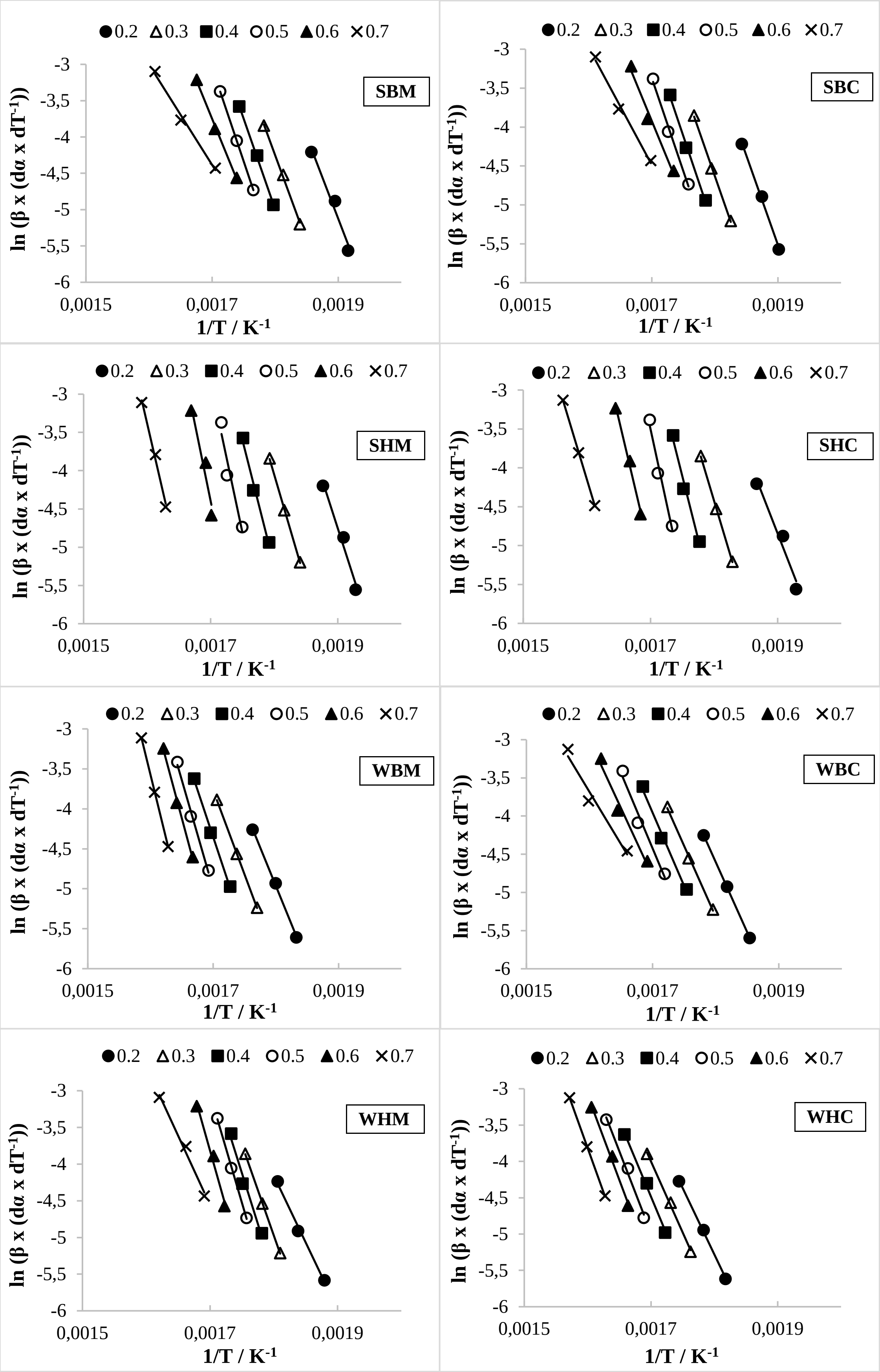


Fig. 3 - Avocado residues linear regression results based on Friedman method.

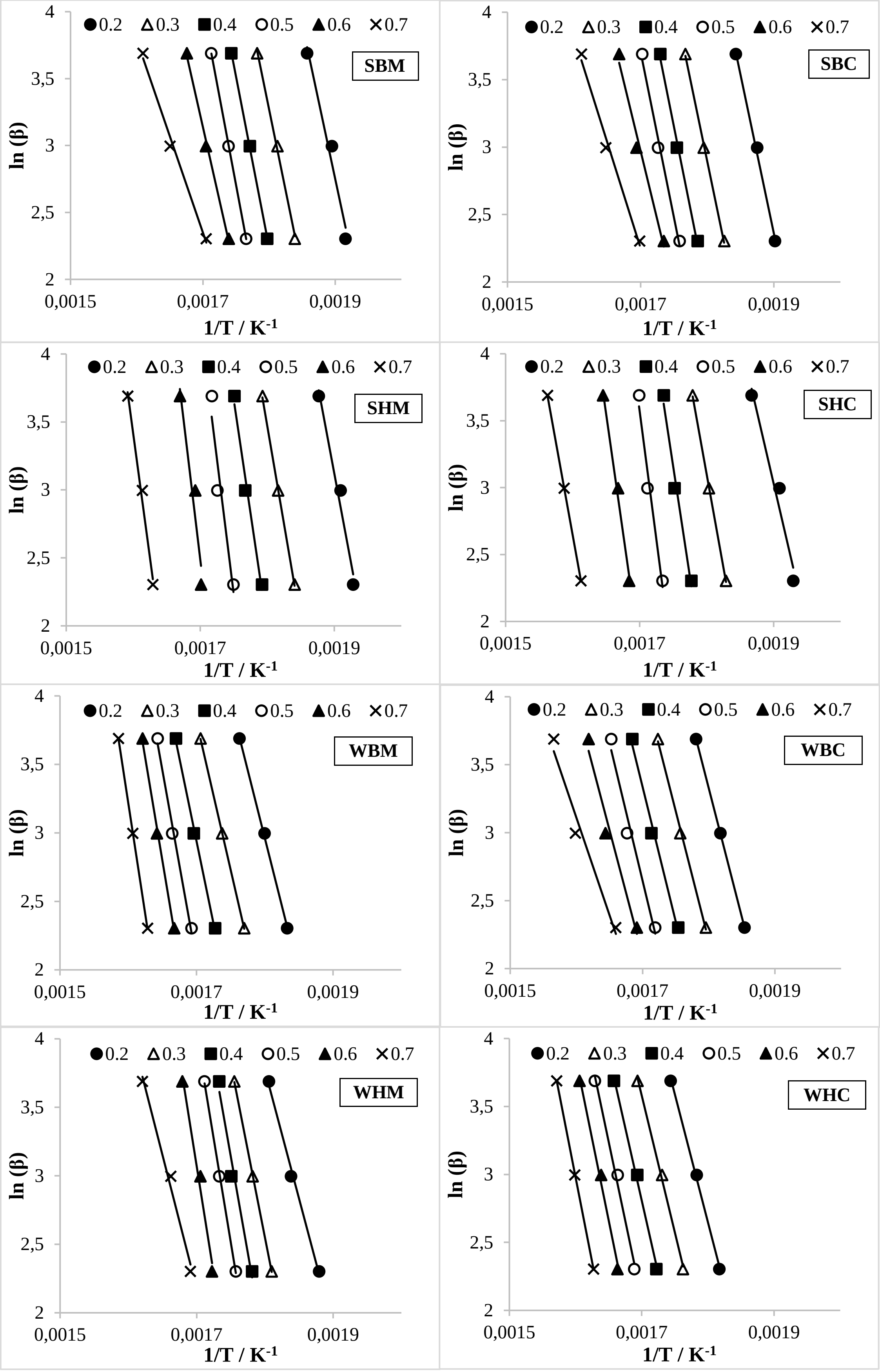


Fig. 4 - Avocado residues linear regression results based on FWO method.

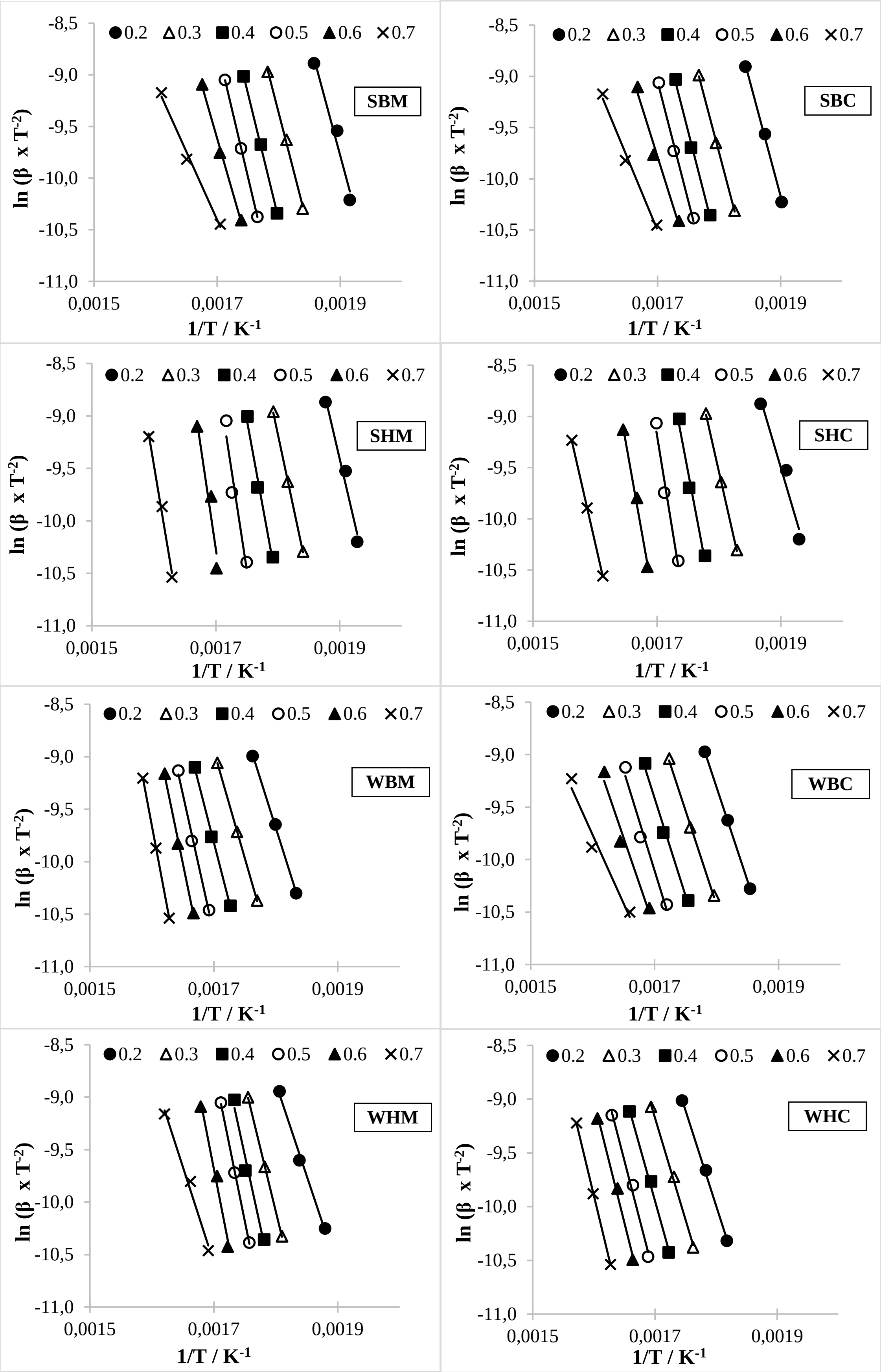


Fig. 5 - Avocado residues linear regression results based on KAS method.

Table 1. Properties of the cow manure employed as organic fertilizer.

	Moisture (%)	**OM (%)**	**Total N (%)**	**N-NH_4^+ (%)**	**P_2O_5 (%)**	**K_2O (%)**	**C/N**	**pH**
Cow manure	60.8 ± 4.3	35.2 ± 2.1	1.03 ± 0.11	0.78 ± 0.08	0.36 ± 0.02	1.37 ± 0.18	19.9 ± 2.3	7.6 ± 0.7

All data appear in dry basis, except moisture, with their standard deviation.

Table 2. Avocado residues properties.

Code	**Proximate analysis (%)**						**Ultimate analysis (%)**				**HHV[c] (MJ/kg)**
	C[a]	H[a]	N[a]	S[a]	Cl[a]	O[b]	Moisture[a]	Ash[a]	Volatiles[a]	FC[b]	
SBM	46.59 ± 0.34	6.23 ± 0.11	0.55 ± 0.02	0.03 ± 0.00	0.014 ± 0.001	46.59 ± 0.18	3.78 ± 0.16	2.30 ± 0.14	77.6 ± 1.62	16.32 ± 0.36	18.43 ± 0.37
SBC	46.71 ± 0.43	6.25 ± 0.13	0.49 ± 0.01	0.03 ± 0.00	0.012 ± 0.001	46.51 ± 0.25	4.31 ± 0.15	1.66 ± 0.11	77.9 ± 1.42	16.13 ± 0.40	18.50 ± 0.36
SHM	47.00 ± 0.53	6.20 ± 0.10	0.56 ± 0.02	0.04 ± 0.00	0.011 ± 0.001	46.19 ± 0.13	3.54 ± 0.10	2.43 ± 0.15	76.4 ± 1.30	17.63 ± 0.37	18.77 ± 0.38
SHC	48.22 ± 0.29	6.26 ± 0.09	0.51 ± 0.03	0.04 ± 0.00	0.011 ± 0.002	44.96 ± 0.26	3.58 ± 0.13	1.99 ± 0.16	77.0 ± 1.41	17.43 ± 0.37	19.25 ± 0.39
WBM	49.16 ± 0.47	5.92 ± 0.14	0.28 ± 0.01	0.03 ± 0.00	0.013 ± 0.002	44.60 ± 0.33	5.02 ± 0.11	1.61 ± 0.13	79.5 ± 1.71	13.87 ± 0.26	19.35 ± 0.39
WBC	49.29 ± 0.62	6.03 ± 0.14	0.29 ± 0.02	0.02 ± 0.00	0.014 ± 0.002	44.36 ± 0.46	4.99 ± 0.12	0.88 ± 0.09	82.4 ± 2.03	11.73 ± 0.19	19.57 ± 0.42
WHM	48.82 ± 0.45	5.91 ± 0.13	0.56 ± 0.04	0.02 ± 0.00	0.011 ± 0.001	44.68 ± 0.32	5.15 ± 0.18	2.35 ± 0.11	79.4 ± 1.96	13.10 ± 0.30	19.26 ± 0.30
WHC	49.40 ± 0.60	6.00 ± 0.10	0.44 ± 0.02	0.03 ± 0.00	0.010 ± 0.001	44.12 ± 0.40	5.06 ± 0.16	1.22 ± 0.09	82.8 ± 2.03	10.92 ± 0.21	19.54 ± 0.39

[a] In percentage. All values are in dry basis except moisture. [b] Estimated by difference. [c] HHV: high heating value.

Table 3. Avocado residues hemicellulose, cellulose, lignin and extractives content.

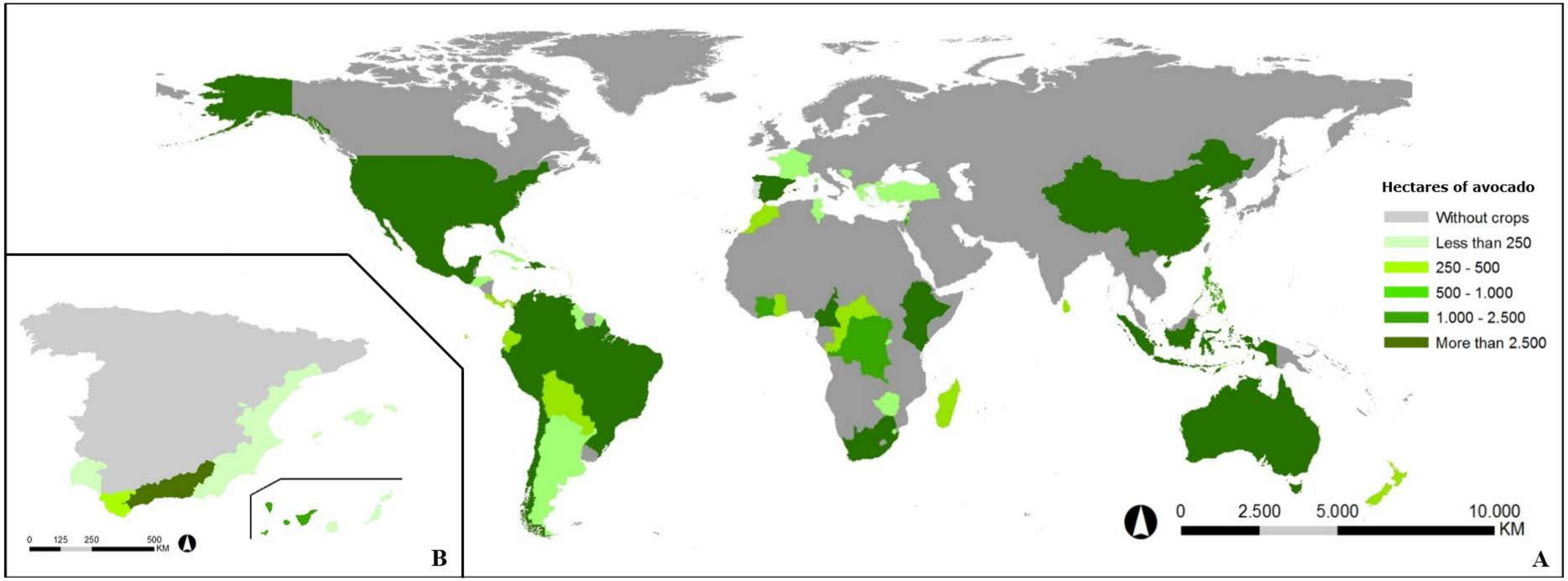
Code	**Hemicellulose (%)**[a]	**Cellulose (%)**[a]	**Lignin (%)**[a]	**Extractives (%)**[a]
SBM	40.21 ± 1.28	16.90 ± 0.23	7.47 ± 0.10	35.42 ± 1.03
SBC	48.11 ± 1.23	11.86 ± 0.12	6.40 ± 0.16	33.63 ± 0.82
SHM	43.06 ± 1.19	11.11 ± 0.10	13.97 ± 0.23	31.86 ± 0.79
SHC	44.57 ± 1.31	11.76 ± 0.09	11.26 ± 0.13	32.41 ± 0.97
WBM	30.14 ± 1.16	39.41 ± 0.42	27.01 ± 0.42	3.44 ± 0.12
WBC	28.07 ± 1.14	38.16 ± 0.33	23.87 ± 0.50	9.9 ± 0.14
WHM	37.02 ± 1.34	45.20 ± 0.63	15.41 ± 0.12	2.37 ± 0.10
WHC	30.82 ± 1.23	42.51 ± 0.54	23.41 ± 0.63	3.26 ± 0.13

[a] Daf (dry ash free).

Table 4. Kinetic parameters for the different avocado samples.

		Friedman			FWO			KAS		
Sample	**α**	**E$_a$ (kJ/mol)**	**R^2**	**A(1/s)**	**E$_a$ (kJ/mol)**	**R^2**	**A(1/s)**	**E$_a$ (kJ/mol)**	**R^2**	**A(1/s)**
SBM	0.2	188.30	0.9720	7.1 x 10^{18}	183.19	0.9733	2.2 x 10^{18}	183.90	0.9706	2.5 x 10^{18}
	0.3	196.92	0.9976	6.9 x 10^{18}	191.55	0.9977	2.1 x 10^{18}	191.58	0.9975	2.1 x 10^{18}
	0.4	207.58	0.9994	2.5 x 10^{19}	201.79	0.9994	7.1 x 10^{18}	202.89	0.9993	9.0 x 10^{18}
	0.5	214.32	0.9999	4.6 x 10^{19}	208.27	0.9999	1.3 x 10^{19}	209.54	0.9999	1.6 x 10^{19}
	0.6	177.05	0.9971	7.2 x 10^{15}	172.93	0.9972	3.0 x 10^{15}	172.18	0.9969	2.6 x 10^{15}
	0.7	114.74	0.9928	5.9 x 10^{09}	113.84	0.9934	4.9 x 10^{09}	109.73	0.9922	2.1 x 10^{09}
	*	**183.15**		**1.4 x 10^{19}**	**178.59**		**4.0 x 10^{18}**	**178.30**		**5.0 x 10^{18}**
SBC	0.2	190.87	0.9969	8.0 x 10^{18}	185.66	0.9746	2.4 x 10^{18}	186.43	0.9722	2.9 x 10^{18}
	0.3	193.61	0.9991	2.1 x 10^{18}	188.44	0.9991	6.8 x 10^{17}	188.98	0.9990	7.6 x 10^{17}
	0.4	200.01	0.9960	3.2 x 10^{18}	194.62	0.9962	9.8 x 10^{17}	195.28	0.9958	1.1 x 10^{18}
	0.5	199.06	0.9920	1.3 x 10^{18}	193.79	0.9923	4.1 x 10^{17}	194.26	0.9916	4.5 x 10^{17}
	0.6	164.03	0.9820	3.7 x 10^{14}	160.57	0.9830	1.8 x 10^{14}	159.15	0.9810	1.3 x 10^{14}
	0.7	125.23	0.9901	4.9 x 10^{10}	123.81	0.9908	3.7 x 10^{10}	120.20	0.9893	1.7 x 10^{10}
	*	**178.80**		**2.4 x 10^{18}**	**174.48**		**7.4 x 10^{17}**	**174.05**		**8.7 x 10^{17}**
SHM	0.2	210.19	0.9760	1.7 x 10^{21}	208.21	0.9770	1.1 x 10^{21}	210.30	0.9750	1.7 x 10^{21}
	0.3	235.39	0.9996	4.0 x 10^{22}	228.11	0.9960	7.8 x 10^{21}	230.81	0.9996	1.4 x 10^{22}
	0.4	272.47	0.9847	2.9 x 10^{25}	263.46	0.9852	4.1 x 10^{24}	267.77	0.9842	1.0 x 10^{25}
	0.5	325.09	0.9288	4.7 x 10^{29}	313.58	0.9307	4.1 x 10^{28}	320.30	0.9269	1.7 x 10^{29}
	0.6	338.19	0.9368	1.8 x 10^{30}	326.16	0.9385	1.5 x 10^{29}	333.25	0.9350	6.6 x 10^{29}
	0.7	298.58	0.9919	2.7 x 10^{25}	288.73	0.9922	3.9 x 10^{24}	293.42	0.9116	9.8 x 10^{24}
	*	**279.99**		**3.8 x 10^{29}**	**271.37**		**3.2 x 10^{28}**	**275.97**		**1.4 x 10^{29}**
SHC	0.2	174.66	0.9624	4.0 x 10^{17}	170.19	0.9642	1.4 x 10^{17}	170.28	0.9605	1.4 x 10^{17}
	0.3	227.07	0.9996	4.3 x 10^{21}	220.23	0.9996	9.5 x 10^{20}	222.47	0.9996	1.6 x 10^{21}
	0.4	269.58	0.9833	9.3 x 10^{24}	260.75	0.9839	1.4 x 10^{24}	264.85	0.9827	3.4 x 10^{24}
	0.5	314.46	0.9733	2.9 x 10^{28}	303.52	0.9741	2.9 x 10^{27}	309.61	0.9725	1.1 x 10^{28}
	0.6	287.66	0.9909	2.2 x 10^{25}	278.19	0.9912	3.2 x 10^{24}	282.67	0.9906	8.0 x 10^{24}
	0.7	225.11	0.9999	6.3 x 10^{18}	218.96	0.9999	1.9 x 10^{18}	219.87	0.9999	2.3 x 10^{18}
	*	**249.76**		**4.8 x 10^{27}**	**241.97**		**4.9 x 10^{26}**	**244.96**		**1.8 x 10^{27}**
WBM	0.2	159.98	0.9991	1.4 x 10^{15}	156.47	0.9992	6.2 x 10^{14}	155.36	0.9990	4.9 x 10^{14}
	0.3	175.13	0.9999	1.0 x 10^{16}	171.02	0.9999	4.1 x 10^{15}	170.35	0.9999	3.6 x 10^{15}
	0.4	195.95	0.9975	3.1 x 10^{17}	190.92	0.9976	1.1 x 10^{17}	191.06	0.9973	1.1 x 10^{17}
	0.5	226.02	0.9936	6.7 x 10^{19}	219.58	0.9938	1.8 x10^{19}	221.03	0.9933	2.4 x 10^{19}
	0.6	243.00	0.9968	1.1 x 10^{21}	235.80	0.9938	2.6 x 10^{20}	237.94	0.9967	3.9 x 10^{20}
	0.7	266.13	0.9487	3.6 x 10^{22}	257.90	0.9999	7.1 x 10^{21}	260.96	0.9999	1.3 x 10^{22}
	*	**211.04**		**6.2 x 10^{21}**	**205.28**		**1.2 x 10^{21}**	**206.11**		**2.2 x 10^{21}**
WBC	0.2	152.96	0.9999	4.1 x 10^{14}	149.75	0.9999	2.0 x 10^{14}	148.38	0.9999	1.4 x 10^{14}
	0.3	154.12	0.9983	1.6 x 10^{14}	151.00	0.9984	8.1 x 10^{13}	149.39	0.9982	5.7 x 10^{13}
	0.4	159.54	0.9909	2.1 x 10^{14}	156.24	0.9914	1.1 x 10^{14}	154.71	0.9903	7.7 x 10^{13}
	0.5	163.73	0.9725	2.4 x 10^{14}	160.31	0.9740	1.2 x 10^{14}	158.80	0.9709	8.7 x 10^{13}
	0.6	148.36	0.9694	5.3 x 10^{12}	145.80	0.9713	3.1 x 10^{12}	143.33	0.9674	1.9 x 10^{12}
	0.7	113.90	0.9673	2.3 x 10^{09}	113.17	0.9698	2.0 x 10^{09}	108.76	0.9643	8.1 x 10^{08}
	*	**148.77**		**1.7 x 10^{14}**	**146.04**		**8.4 x 10^{13}**	**143.89**		**6.1 x 10^{13}**
WHM	0.2	151.48	0.9945	4.3 x 10^{14}	148.28	0.9947	2.1 x 10^{14}	146.97	0.9941	1.6 x 10^{14}
	0.3	205.97	0.9999	2.3 x 10^{19}	200.22	0.9999	6.7 x 10^{18}	202.13	0.9999	1.0 x 10^{19}
	0.4	230.12	0.9758	1.9 x 10^{21}	223.25	0.9767	4.3 x 10^{20}	225.39	0.9748	6.9 x 10^{20}
	0.5	246.63	0.9988	3.8 x 10^{22}	238.99	0.9989	7.5 x 10^{21}	241.83	0.9988	1.4 x 10^{22}
	0.6	256.42	0.9842	1.3 x 10^{23}	248.25	0.9848	2.3 x 10^{22}	251.37	0.9836	4.4 x 10^{22}
	0.7	156.93	0.9883	4.4 x 10^{13}	153.95	0.9890	2.4 x 10^{13}	151.91	0.9874	1.6 x 10^{13}
	*	**207.92**		**2.8 x 10^{22}**	**202.16**		**5.1 x 10^{21}**	**203.27**		**9.7 x 10^{21}**
WHC	0.2	151.89	0.9984	1.6 x 10^{14}	144.87	0.9985	3.5 x 10^{13}	147.22	0.9983	5.8 x 10^{13}
	0.3	162.43	0.9976	5.7 x 10^{14}	158.98	0.9977	2.7 x 10^{14}	157.62	0.9974	2.0 x 10^{14}
	0.4	173.79	0.9964	2.8 x 10^{15}	169.88	0.9966	1.2 x 10^{15}	168.87	0.9962	1.0 x 10^{15}
	0.5	187.47	0.9914	2.4 x 10^{16}	182.97	0.9918	9.7 x 10^{15}	182.46	0.9908	8.7 x 10^{15}
	0.6	194.01	0.9930	5.1 x 10^{16}	189.25	0.9934	1.9 x 10^{16}	188.92	0.9926	1.8 x 10^{16}
	0.7	201.84	0.9999	9.0 x 10^{16}	196.80	0.9999	3.3 x 10^{16}	196.64	0.9999	3.2 x 10^{16}
	*	**178.57**		**2.8 x 10^{16}**	**173.79**		**1.1 x 10^{16}**	**173.62**		**1.0 x 10^{16}**

(*) Average E$_a$ and A values for each case.



Supp. 1 - Global avocado crops (A). Particular situation in Spain (B) – Data obtained from [22]

Supp. 2 - Avocado residues analysed. The first capital letter is linked to the biomass source (seeds, S, or pruning wood, W), the second one refers to the variety (Bacon, B or Hass, H) and finally, the last initial informs the reader about the type of fertilizer (mineral, M or cow manure, C).