Fuel 291 (2021) 119660

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Combustion of avocado crop residues: Effect of crop variety and nature of nutrients

Sergio Paniagua [a], Sergio Reyes [b], Francisco Lima [b], Nadezhda Pilipenko [c], Luis F. Calvo [a,*]

[a] University of León, Department of Chemistry and Applied Physics, Chemical Engineering Area, IMARENABIO, Avda. Portugal 41 (24071), León, Spain
[b] University of Málaga, Department of Geography, Geographic Analysis Research Group, Faculty of Philosophy and Letters, Campus of Teatinos, s/n. (29071), Málaga, Spain
[c] Kuban State Agrarian University, Department of Agronomy and Ecology, Kalinina Str.,13, (350044), Krasnodar, Russia

ARTICLE INFO

Keywords:
Avocado crop residues
Bacon
Combustion
Fertiliser influence
Hass
Kinetics

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 °C/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 analysed 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 20 °C/min ramps respectively.

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 thermochemical 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

* Corresponding author. Tel.: +34 987291844.
E-mail address: lfcalp@unileon.es (L.F. Calvo).

https://doi.org/10.1016/j.fuel.2020.119660
Received 13 July 2020; Received in revised form 15 September 2020; Accepted 1 November 2020
Available online 6 February 2021

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 × 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 15,000 hl/ha, the organic crop received 10,000 hl/ha. Following the recommendation of Trehan [39], for mineral fertiliser conditions, each tree received 6 kg 17-17-17 (N-P_2O_5 - K_2O) 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 and 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 as sampling unit. Then, samples of the same variety and fertilizer type were mixed, dried by air-drying for a minimum of 72 h 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):

$$Extractives\ (\%) = 100 - \left(Weight_{sample\ after\ extraction} / Weight_{initial\ sample}\right) * 100 \quad (1)$$

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 h 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 °C at 10, 20 and 40 °C/min. This heating was carried out under a flow of 100 mL

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 deviations.

Table 2
Avocado residues properties.

Code	Proximate analysis (%)						Ultimate analysis (%)				HHVc (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.

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):

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

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

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

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

where $m_T$is the biomass mass at the working temperature during TGA test, m_0 and 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:

$$k(T) = Ae^{(-E/RT)} \tag{4}$$

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:

$$d\alpha/dt = Ae^{(-E/RT)}f(\alpha) \tag{5}$$

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

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

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 $x = E/RT$;

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

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:

$$\ln(\beta d\alpha/dT) = \ln[A_\alpha f(\alpha)] - E/RT \tag{9}$$

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):

$$\ln(\beta) = \ln[AE/(Rg(\alpha))] - 5.331 - 1.052(E/RT) \tag{10}$$

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):

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

Knowing the previous equations, apparent activation energy was determined for α values between 0.2 and 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]:

$$A_{\alpha}(\beta) = \beta E/(RT^{2}_{p})\exp(E/(RT_{p})) \quad (12)$$

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 ($\beta = 20\ ^{\circ}C\ min^{-1}$) 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 (≈ 19MJ/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 °C min^{-1}) were illustrated up to 700 °C, 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 loss 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 the samples studied in this work

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	9.90 ± 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).

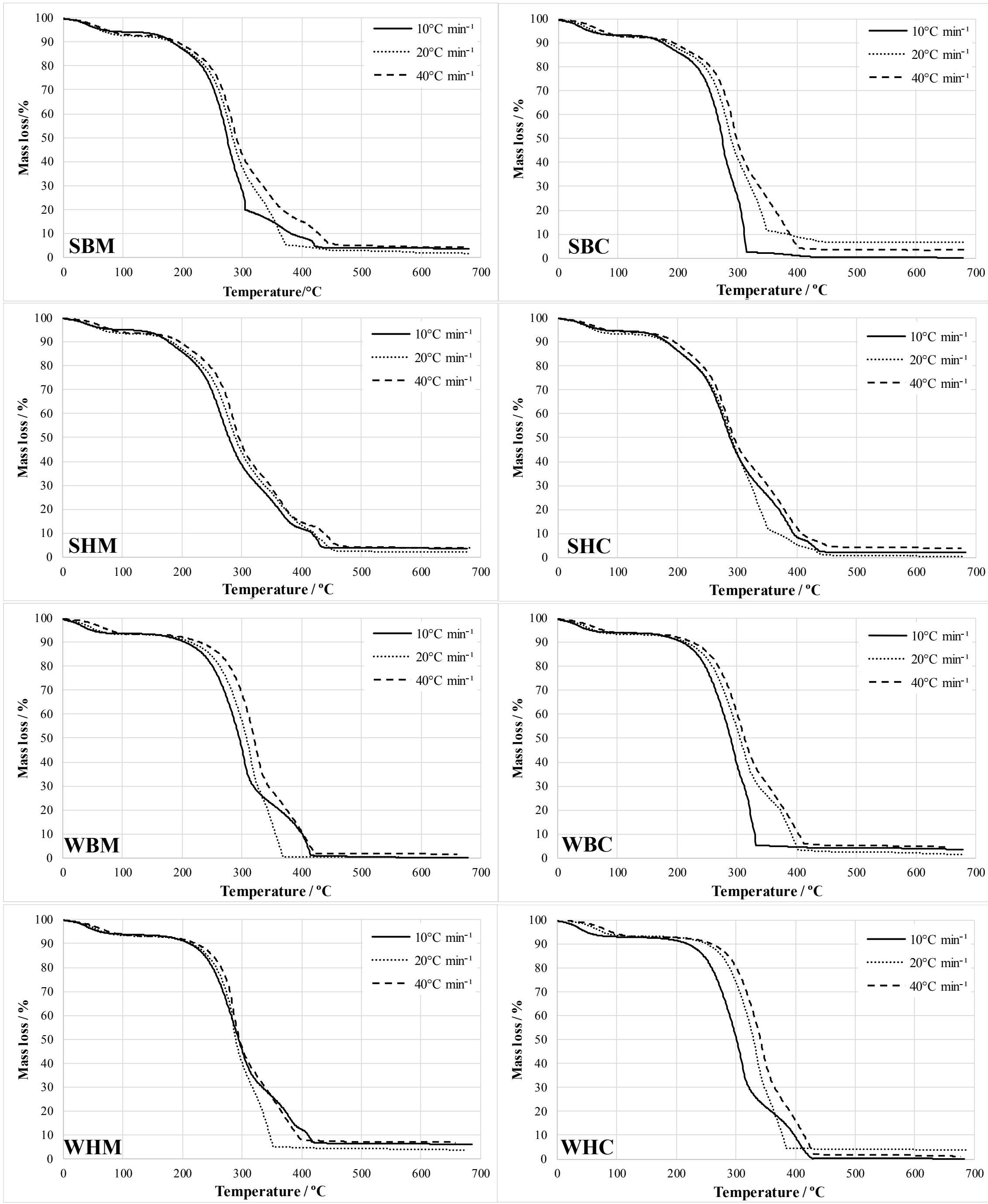

Fig. 1. TG profiles under three different heating rates from the avocado crop residue samples.

(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 400 °C 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 10 °C/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

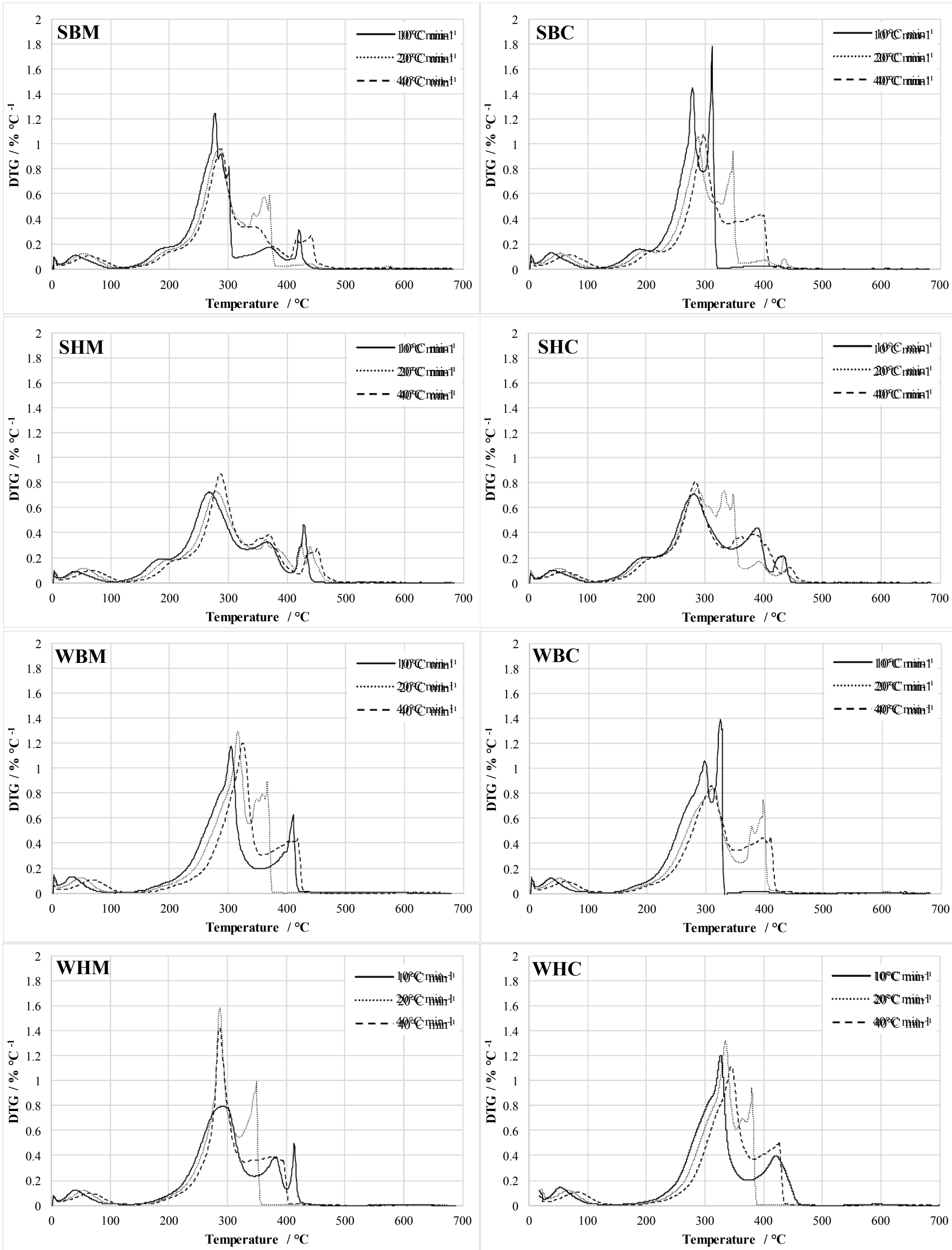

Fig. 2. DTG profiles under three different heating rates from the avocado crop residue samples.

peak of the samples.

DTG samples profiles, Fig. 2, showed a very steep slope in the final mass loss. The heating rate influenced this fact. Readers can realize the effect of 10 °C/min heating rate for SBC and WBC and 20 °C/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 450 °C. 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 10 °C/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 °C could be faster than that observed under nitrogen atmosphere because of the oxidation of the residual material [80]. If a comparison 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.

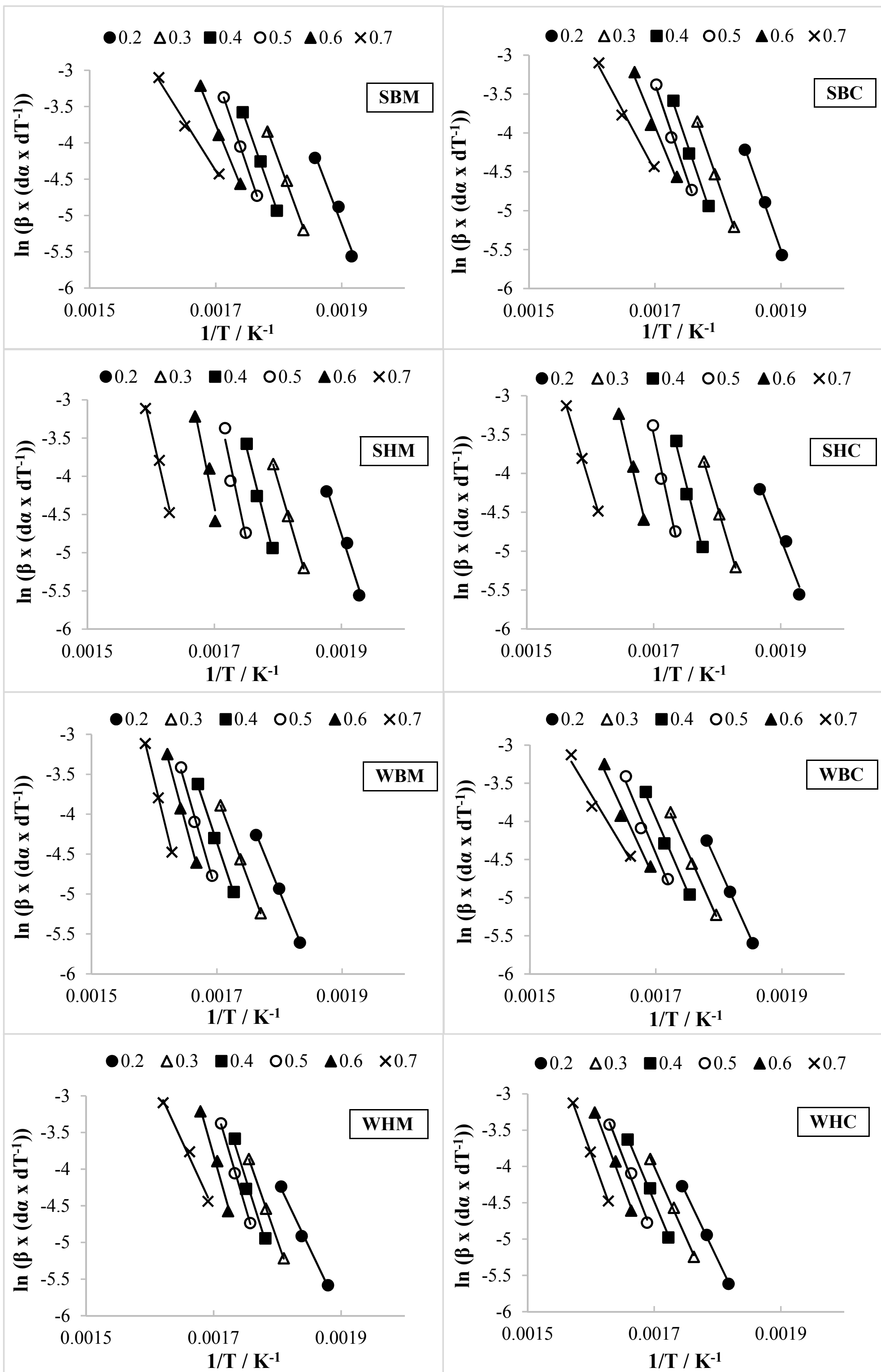

Fig. 3. Avocado residues linear regression results based on Friedman method.

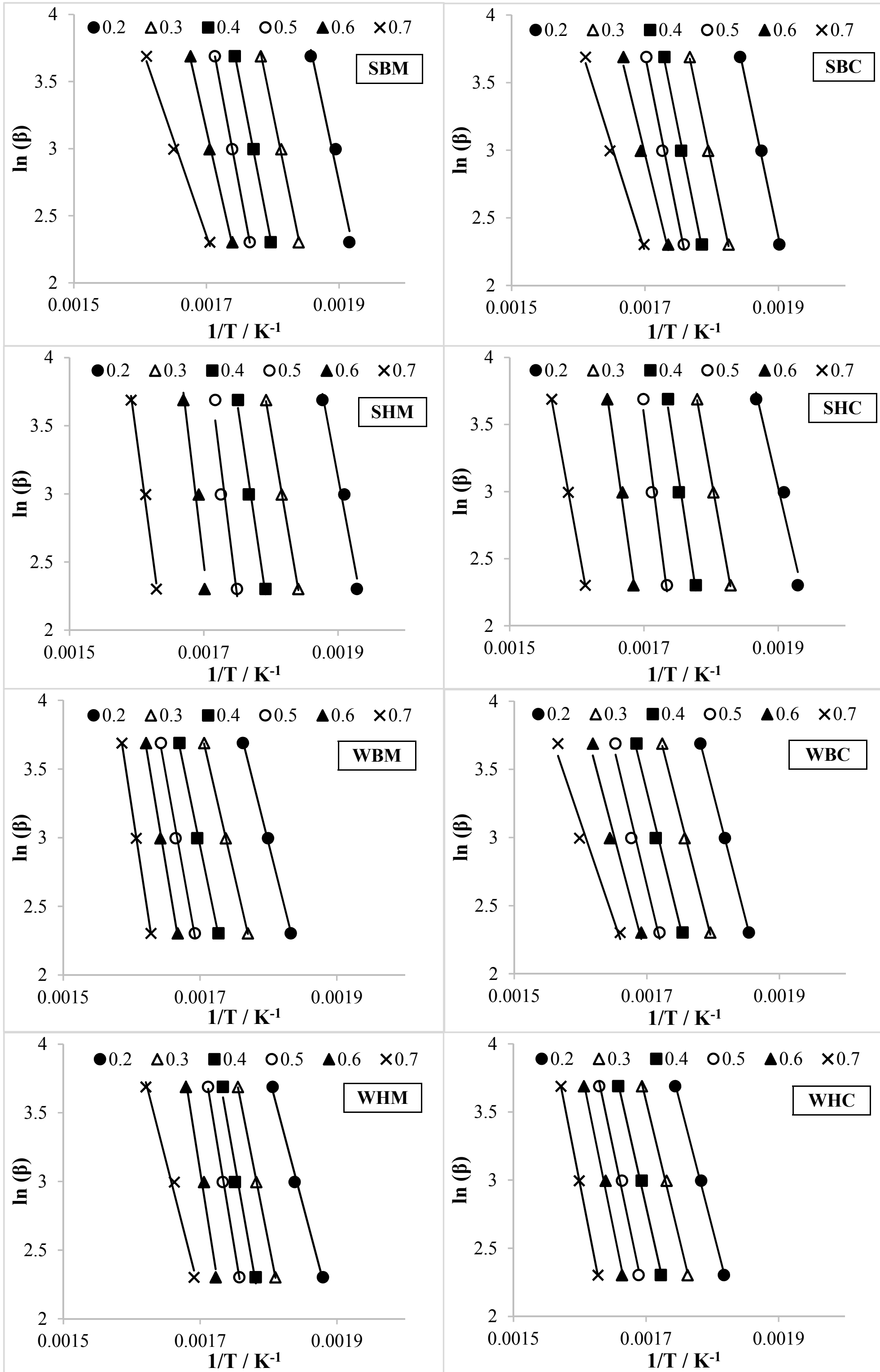

Fig. 4. Avocado residues linear regression results based on FWO method.

3.3. Kinetics.

Apparent activation energy was estimated plotting $\ln(\beta d\alpha/dT)$, $\ln(\beta)$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

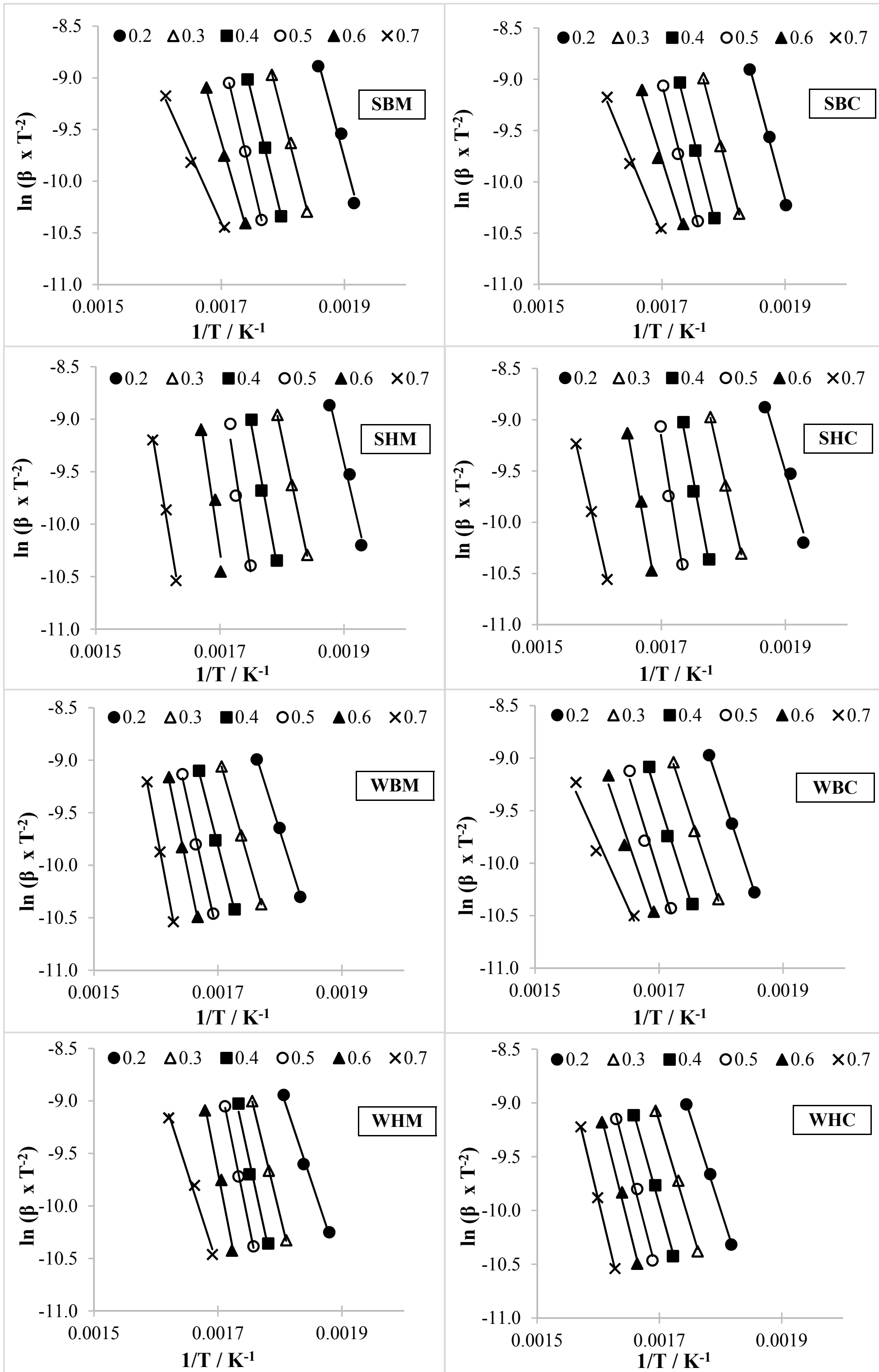

Fig. 5. Avocado residues linear regression results based on KAS method.

interval between 0.2 and 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

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

(*) Average E_a and A values for each case.

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 (8.7×10^{17}–3.8×10^{29} 1/s) had lower values than seeds (6.1×10^{13}–2.8×10^{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 (20 °C/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.

CRediT authorship contribution statement

Sergio Paniagua: Conceptualization, Investigation, Methodology, Writing - review & editing. **Sergio Reyes:** Resources, Investigation, Visualization. **Francisco Lima:** Resources, Investigation, Methodology. **Nadezhda Pilipenko:** Formal analysis, Writing - review & editing. **Luis F. Calvo:** Conceptualization, Supervision, 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.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2020.119660.

References

[1] Gago A, Labandeira X, López-Otero X. A panorama on energy taxes and green tax reforms. Hacienda Pública Española 2014;208:145–90.
[2] Bilandzija N, Voca N, Jelcic B, Jurisic V, Matin A, Grubor M, Kricka T. Evaluation of Croatian agricultural solid biomass energy potential. Renew Sustain Energy Rev 2018;93:225–30. https://doi.org/10.1016/j.rser.2018.05.040.
[3] Xiao R, Yang W. Kinetics characteristics of straw semi-char gasification with carbon dioxide. Bioresour Technol 2016;207:180–7. https://doi.org/10.1016/j.biortech.2016.02.010.
[4] Sobek S, Werle S. Solar pyrolysis of waste biomass: Part 1 reactor design. Renewable Energy 2019;143:1939–48. https://doi.org/10.1016/j.renene.2019.06.011.
[5] Setter C, Borges FA, Cardoso CR, Mendes RF, Oliveira TJP. Energy quality of pellets produced from coffee residue: Characterization of the products obtained via slow pyrolysis. Ind Crops Prod 2020;154:112731. https://doi.org/10.1016/j.indcrop.2020.112731.
[6] Loy ACM, Gan DKW, Yusup S, Chin BLF, Lam MK, Shahbaz M, Unrean P, Acda MN, Rianawati E. Thermogravimetric kinetic modelling of in-situ catalytic pyrolytic conversion of rice husk to bioenergy using rice hull ash catalyst. Bioresour Technol 2018;261:213–22. https://doi.org/10.1016/j.biortech.2018.04.020.
[7] Anca-Couce A, Tsekos C, Retschitzegger S, Zimbardi F, Funke A, Banks S, Kraia T, Marques P, Scharler R, de Jong W, Kienzl N. Biomass pyrolysis TGA assessment with an international round robin. Fuel 2020;276:118002. https://doi.org/10.1016/j.fuel.2020.118002.
[8] Yuan R, Yu S, Shen Y. Pyrolysis and combustion kinetics of lignocellulosic biomass pellets with calcium-rich wastes from agro-forestry residues. Waste Manage 2019;87:86–96. https://doi.org/10.1016/j.wasman.2019.02.009.
[9] Boubacar Laougé Z, Merdun H. Pyrolysis and combustion kinetics of Sida cordifolia L. using thermogravimetric analysis. Bioresour Technol 2020;299:122602. https://doi.org/10.1016/j.biortech.2019.122602.
[10] Islam MA, Auta M, Kabir G, Hameed BH. A thermogravimetric analysis of the combustion kinetics of karanja (Pongamia pinnata) fruit hulls char. Bioresour Technol 2016;200:335–41. https://doi.org/10.1016/j.biortech.2015.09.057.
[11] Maia AAD, de Morais LC. Kinetic parameters of red pepper waste as biomass to solid biofuel. Bioresour Technol 2016;204:157–63. https://doi.org/10.1016/j.biortech.2015.12.055.
[12] Brown RC. Thermochemical processing of biomass: conversion into fuels, chemicals and power. Wiley; 2019.
[13] Song Y, Liu J, Evrendilek F, Kuo J, Buyukada M. Combustion behaviors of Pteris vittata using thermogravimetric, kinetic, emission and optimization analyses. J Cleaner Prod 2019;237:117772. https://doi.org/10.1016/j.jclepro.2019.117772.
[14] Balasundram V, Ibrahim N, Kasmani RM, Hamid MKA, Isha R, Hasbullah H, Ali RR. Thermogravimetric catalytic pyrolysis and kinetic studies of coconut copra and rice husk for possible maximum production of pyrolysis oil. J Cleaner Prod 2017;167:218–28. https://doi.org/10.1016/j.jclepro.2017.08.173.
[15] Boumanchar I, Chhiti Y, M'hamdi Alaoui FE, Elkhouakhi M, Sahibed-dine A, Bentiss F, Jama C, Bensitel M. Investigation of (co)-combustion kinetics of biomass, coal and municipal solid wastes. Waste Manage 2019;97:10–8. https://doi.org/10.1016/j.wasman.2019.07.033.
[16] He Q, Ding Lu, Gong Y, Li W, Wei J, Yu G. Effect of torrefaction on pinewood pyrolysis kinetics and thermal behavior using thermogravimetric analysis. Bioresour Technol 2019;280:104–11. https://doi.org/10.1016/j.biortech.2019.01.138.
[17] Kaur R, Gera P, Jha MK, Bhaskar T. Pyrolysis kinetics and thermodynamic parameters of castor (Ricinus communis) residue using thermogravimetric analysis. Bioresour Technol 2018;250:422–8. https://doi.org/10.1016/j.biortech.2017.11.077.
[18] Ma J, Meng X, Guo X, Lan Y, Zhang S. Thermal analysis during partial carbonizing process of rhubarb, moutan and burnet. PLoS One 2017; 12: e0173946.
[19] Zou H, Zhang J, Liu J, Buyukada M, Evrendilek F, Liang G. Pyrolytic behaviors, kinetics, decomposition mechanisms, product distributions and joint optimization of Lentinus edodes stipe. Energy Convers Manage 2020;213:112858. https://doi.org/10.1016/j.enconman.2020.112858.
[20] El-Sayed SA, Mostafa ME. Kinetic Parameters Determination of Biomass Pyrolysis Fuels Using TGA and DTA Techniques. Waste Biomass Valor 2015;6(3):401–15. https://doi.org/10.1007/s12649-015-9354-7.
[21] Hurtado-Fernández E, Fernández-Gutiérrez A, Carrasco-Pancorbo A. Avocado fruit—Persea americana. Exot. Fruits, Elsevier; 2018, p. 37–48.
[22] Altés GV. Proyecto del sistema de riego de un cultivo de aguacate en la partida de l'Arap en el TM de Quartell de les Valls (Valencia). Universidad Politécnica de Valencia 2018.
[23] Serra Bonvehi J, Ventura Coll F, Orantes Bermejo JF. Characterization of avocado honey (Persea americana Mill.) produced in Southern Spain. Food Chem 2019;287:214–21. https://doi.org/10.1016/j.foodchem.2019.02.068.
[24] Wang W, Bostic TR, Gu L. Antioxidant capacities, procyanidins and pigments in avocados of different strains and cultivars. Food Chem 2010;122(4):1193–8. https://doi.org/10.1016/j.foodchem.2010.03.114.
[25] Abubakar ANF, Achmadi SS, Suparto IH. Triterpenoid of avocado (Persea americana) seed and its cytotoxic activity toward breast MCF-7 and liver HepG2 cancer cells. Asian Pacific J Trop Biomed 2017;7(5):397–400. https://doi.org/10.1016/j.apjtb.2017.01.010.
[26] Chel-Guerrero L, Barbosa-Martín E, Martínez-Antonio A, González-Mondragón E, Betancur-Ancona D. Some physicochemical and rheological properties of starch isolated from avocado seeds. Int J Biol Macromol 2016;86:302–8. https://doi.org/10.1016/j.ijbiomac.2016.01.052.
[27] Litz RE. Avocado. Compend Transgenic Crop Plants 2009:175–84.
[28] Rodríguez-Carpena J-G, Morcuende D, Andrade M-J, Kylli P, Estévez M. Avocado (Persea americana Mill.) Phenolics, In Vitro Antioxidant and Antimicrobial Activities, and Inhibition of Lipid and Protein Oxidation in Porcine Patties. J Agric Food Chem 2011;59(10):5625–35. https://doi.org/10.1021/jf1048832.
[29] Kondo T, Honsho C. Effect of shading on low-temperature damage in 'Bacon' avocado (Persea americana). Trop Agric Dev 2018;62:132–5.
[30] Acosta-Rangel AM, Li R, Celis N, Suarez DL, Santiago LS, Arpaia ML, Mauk PA. The physiological response of 'Hass' avocado to salinity as influenced by rootstock. Sci Hortic 2019;256:108629. https://doi.org/10.1016/j.scienta.2019.108629.
[31] Gellings C. Efficient use and conservation of energy - volume II. Eolss Publishers 2009.
[32] Willer H, Lernoud J, Kemper L. The world of organic agriculture 2018: Summary. World Org. Agric. Stat. Emerg. Trends 2018, Research Institute of Organic Agriculture FiBL and IFOAM-Organics International; 2018, p. 22–31.
[33] Meng F, Qiao Y, Wu W, Smith P, Scott S. Environmental impacts and production performances of organic agriculture in China: A monetary valuation. J Environ Manage 2017;188:49–57. https://doi.org/10.1016/j.jenvman.2016.11.080.
[34] Zhang Y, Li C, Wang Y, Hu Y, Christie P, Zhang J, et al. Maize yield and soil fertility with combined use of compost and inorganic fertilizers on a calcareous soil on the North China Plain. Soil Tillage Res 2016;155:85–94. https://doi.org/10.1016/j.still.2015.08.006.
[35] Cavaleri MA, Gilmore DW, Mozaffari M, Rosen CJ, Halbach TR. Hybrid poplar and forest soil response to municipal and industrial by products: A greenhouse study. J Environ Qual 2004;33:1055–61. https://doi.org/10.2134/jeq2004.1055.
[36] Paniagua S, Zanfaño L, Calvo LF. Influence of the fertilizer type in the agronomic and energetic behaviour of the residues coming from oleander, cypress and quinoa. Fuel 2020;272:117711. https://doi.org/10.1016/j.fuel.2020.117711.
[37] Paniagua S, Escudero L, Escapa C, Coimbra RN, Otero M, Calvo LF. Effect of waste organic amendments on Populus sp biomass production and thermal characteristics. Renew Energy 2016;94:166–74. https://doi.org/10.1016/j.renene.2016.03.019.
[38] FAO. World Reference Base for Soil Resources 2014. Uptade 2015. 3th editio. Rome; 2015.
[39] Trehan SP, Roy SK, Sharma RC. Potato variety differences in nutrient deficiency symptoms and responses to NPK. Better Crop Int 2001;15:18.
[40] Ranzi E, Cuoci A, Faravelli T, Frassoldati A, Migliavacca G, Pierucci S, et al. Chemical kinetics of biomass pyrolysis. Energy Fuels 2008;22:4292–300. https://doi.org/10.1021/ef800551t.

[41] Boerjan W, Ralph J, Baucher M. Lignin Biosynthesis. Annu Rev Plant Biol 2003;54: 519–46. https://doi.org/10.1146/annurev.arplant.54.031902.134938.
[42] Ralph J, Lundquist K, Brunow G, Lu F, Kim H, Schatz PF, et al. Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenyl-propanoids. vol. 3; 2004.
[43] Han JS, Rowell JS. Chemical composition of fibers. Pap Compos from Agro-Based Resour 1997:83–134.
[44] Friedman HL. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. J Polym Sci Polym Symp vol. 6, Wiley Online Library; 1964, p. 183–95.
[45] Flynn JH, Wall LA. A quick, direct method for the determination of activation energy from thermogravimetric data. J Polym Sci Part C Polym Lett 1966;4:323–8.
[46] Ozawa T. A new method of analyzing thermogravimetric data. Bull Chem Soc Jpn 1965;38:1881–6.
[47] Doyle CD. Series approximations to the equation of thermogravimetric data. Nature 1965;207:290–1.
[48] Kissinger HE. Variation of Pedk Temperature With Hedting Rote in Differentidl Thermal Andlysis. J Res Natl Bur Stand 1934;1956(57):217.
[49] Kissinger HE. Reaction kinetics in differential thermal analysis. Anal Chem 1957; 29:1702–6.
[50] Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. Nature 1964;201:68–9.
[51] Yuan X, He T, Cao H, Yuan Q. Cattle manure pyrolysis process: Kinetic and thermodynamic analysis with isoconversional methods. Renew Energy 2017;107: 489–96. https://doi.org/10.1016/j.renene.2017.02.026.
[52] Mishra RK, Mohanty K, Wang X. Pyrolysis kinetic behavior and Py-GC–MS analysis of waste dahlia flowers into renewable fuel and value-added chemicals. Fuel 2020; 260:116338. https://doi.org/10.1016/j.fuel.2019.116338.
[53] Domínguez MP, Araus K, Bonert P, Sánchez F, San Miguel G, Toledo M. The avocado and its waste: an approach of fuel potential/application. In: Lefebvre G, Jiménez J, Cabañas B, editors. Environ. Energy Clim. Chang. II, Switzerland: Springer, Cham; 2014, p. 199–223. Doi: 10.1007/698_2014_291.
[54] Lacerda LG, Colman TAD, Bauab T, Da Silva Carvalho Filho MA, Demiate IM, De Vasconcelos EC, et al. Thermal, structural and rheological properties of starch from avocado seeds (Persea americana, Miller) modified with standard sodium hypochlorite solutions. J Therm Anal Calorim 2014; 115: 1893–9. Doi: 10.1007/s10973-013-3349-z.
[55] Cuiping L, Chuangzhi W, Yanyongjie Haitao H. Chemical elemental characteristics of biomass fuels in China. Biomass Bioenergy 2004;27:119–30. https://doi.org/10.1016/j.biombioe.2004.01.002.
[56] Paniagua S, Otero M, Coimbra RNR, Escapa C, García AAI, Calvo LFL. Simultaneous thermogravimetric and mass spectrometric monitoring of the pyrolysis, gasification and combustion of rice straw. J Therm Anal Calorim 2015; 121:603–11. https://doi.org/10.1007/s10973-015-4632-y.
[57] El-Sayed SA, Mostafa ME. Pyrolysis characteristics and kinetic parameters determination of biomass fuel powders by differential thermal gravimetric analysis (TGA/DTG). Energy Convers Manag 2014;85:165–72. https://doi.org/10.1016/J.ENCONMAN.2014.05.068.
[58] Demirbas A. Combustion characteristics of different biomass fuels. Prog Energy Combust Sci 2004;30:219–30. https://doi.org/10.1016/J.PECS.2003.10.004.
[59] Saleh SB, Flensborg JP, Shoulaifar TK, Sárossy Z, Hansen BB, Egsgaard H, et al. Release of chlorine and sulfur during biomass torrefaction and pyrolysis. Energy Fuels 2014;28:3738–46. https://doi.org/10.1021/ef4021262.
[60] Perea-Moreno A-J, Aguilera-Ureña M-J, Manzano-Agugliaro F. Fuel properties of avocado stone. Fuel 2016;186:358–64. https://doi.org/10.1016/J.FUEL.2016.08.101.
[61] Perea-Moreno A-J, Perea-Moreno M-Á, Dorado MP, Manzano-Agugliaro F. Mango stone properties as biofuel and its potential for reducing CO2 emissions. J Clean Prod 2018;190:53–62. https://doi.org/10.1016/J.JCLEPRO.2018.04.147.
[62] Küçükbayrak S, Dürüs B, Meríçboyu AE, Kadioglu E. Estimation of calorific values of Turkish lignites. Fuel 1991;70:979–81. Doi: 10.1016/0016-2361(91)90054-E.
[63] Yin C-Y. Prediction of higher heating values of biomass from proximate and ultimate analyses. Fuel 2011;90:1128–32. Doi: 10.1016/j.fuel.2010.11.031.
[64] Villanueva M, Proupín J, Rodríguez-Añón JA, Fraga-Grueiro L, Salgado J, Barros N. Energetic characterization of forest biomass by calorimetry and thermal analysis. J. Therm. Anal. Calorim 2011;104:61–7. https://doi.org/10.1007/s10973-010-1177-y.
[65] Poletto M, Zattera AJ, Santana RMC. Thermal decomposition of wood: kinetics and degradation mechanisms. Bioresour Technol vol. 126, Elsevier Ltd; 2012, p. 7–12. Doi: 10.1016/j.biortech.2012.08.133.
[66] Elizalde-González MP, Hernández-Montoya V. Characterization of mango pit as raw material in the preparation of activated carbon for wastewater treatment. Biochem Eng J 2007;36:230–8. https://doi.org/10.1016/j.bej.2007.02.025.
[67] Arukwe U, Amadi BA, Duru MKC, Agomuo EN, Adindu EA, Odika PC, et al. Chemical composition of Persea americana leaf, fruit and seed. Ijrras 2012;11: 346–9.
[68] Chen WH, Kuo PC. A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry. Energy 2010; 35:2580–6. https://doi.org/10.1016/j.energy.2010.02.054.
[69] González JF, Encinar JM, Canito JL, Sabio E, Chacón M. Pyrolysis of cherry stones: Energy uses of the different fractions and kinetic study. J Anal Appl Pyrolysis 2003; 67:165–90. https://doi.org/10.1016/S0165-2370(02)00060-8.
[70] Magdziarz A, Wilk M. Thermal characteristics of the combustion process of biomass and sewage sludge. J Therm Anal Calorim 2013;114:519–29. https://doi.org/10.1007/s10973-012-2933-y.
[71] Avhad MR, Marchetti JM. Mathematical modelling of the drying kinetics of Hass avocado seeds. Ind Crops Prod 2016;91:76–87. https://doi.org/10.1016/j.indcrop.2016.06.035.
[72] Reis JS, Araujo RO, Lima VMR, Queiroz LS, da Costa CEF, Pardauil JJR, et al. Combustion properties of potential Amazon biomass waste for use as fuel. J Therm Anal Calorim 2019;138:3535–9. https://doi.org/10.1007/s10973-019-08457-5.
[73] Magdziarz A, Wilk M, Straka R. Combustion process of torrefied wood biomass: A kinetic study. J Therm Anal Calorim 2017;127:1339–49. https://doi.org/10.1007/s10973-016-5731-0.
[74] Paniagua S, Prado-Guerra A, García AI, Calvo LF. Bioenergy derived from an organically fertilized poplar plot: overall TGA and index estimation study for combustion, gasification, and pyrolysis processes. Biomass Convers Biorefinery 2019:1–12. https://doi.org/10.1007/s13399-019-00392-7.
[75] Boukaous N, Abdelouahed L, Chikhi M, Meniai A-H, Mohabeer C, Bechara T. Combustion of flax shives, beech wood, pure woody pseudo-components and their chars: a thermal and kinetic study. Energies 2018;11:2146. https://doi.org/10.3390/en11082146.
[76] Haobin P, Li Y, Li Y, Yuan F, Chen G. Experimental investigation of combustion kinetics of wood powder and pellet. J Combust 2018;2018:5981598. https://doi.org/10.1155/2018/5981598.
[77] Trinh T, Jensen P, Risbjerg H, Dam-Johansen K, Hvilsted S. Flash pyrolysis properties of algae and lignin residue. 20th Eur Biomass Conf Exhib 2012.
[78] Caballero JA, Conesa JA, Font R, Marcilla A. Pyrolysis kinetics of almond shells and olive stones considering their organic fractions. J Anal Appl Pyrolysis 1997;42: 159–75.
[79] Duman G, Okutucu C, Ucar S, Stahl R, Yanik J. The slow and fast pyrolysis of cherry seed. Bioresour Technol 2011;102:1869–78. https://doi.org/10.1016/j.biortech.2010.07.051.
[80] Al-Badri HT, Lafta SJ, Barbooti MM, Al-Sammerrai DA. The thermogravimetry and pyrolysis of date stones. Thermochim Acta 1989;147:283–9. https://doi.org/10.1016/0040-6031(89)85183-4.
[81] Edreis EMA, Yao H. Kinetic thermal behaviour and evaluation of physical structure of sugar cane bagasse char during non-isothermal steam gasification. J Mater Res Technol 2016;5:317–26. Doi; 10.1016/j.jmrt.2016.03.006.
[82] Starink MJ. The determination of activation energy from linear heating rate experiments: A comparison of the accuracy of isoconversion methods. Thermochim Acta 2003;404:163–76. https://doi.org/10.1016/S0040-6031(03)00144-8.
[83] Fernandez A, Ortiz LR, Asensio D, Rodriguez R, Mazza G. Kinetic analysis and thermodynamics properties of air/steam gasification of agricultural waste. J Environ Chem Eng 2020;8:103829. https://doi.org/10.1016/j.jece.2020.103829.
[84] Popova E, Chernov A, Maryandyshev P, Brillard A, Kehrli D, Trouvé G, et al. Thermal degradations of wood biofuels, coals and hydrolysis lignin from the Russian Federation: Experiments and modeling. Bioresour Technol 2016;218: 1046–54. https://doi.org/10.1016/j.biortech.2016.07.033.
[85] Mureddu M, Dessì F, Orsini A, Ferrara F, Pettinau A. Air- and oxygen-blown characterization of coal and biomass by thermogravimetric analysis. Fuel 2018; 212:626–37. https://doi.org/10.1016/j.fuel.2017.10.005.
[86] Pereira S, Costa M. Short rotation coppice for bioenergy: From biomass characterization to establishment – A review. Renew Sustain Energy Rev 2017;74: 1170–80. https://doi.org/10.1016/j.rser.2017.03.006.
[87] Yu Y, Fu • Xiaoxu, Yu L, Liu R, Cai J. Combustion kinetics of pine sawdust biochar Data smoothing and isoconversional kinetic analysis n.d. Doi: 10.1007/s10973-016-5296-y.
[88] Costa FF, Wang G, Costa M. Combustion kinetics and particle fragmentation of raw and torrified pine shells and olive stones in a drop tube furnace. Proc Combust Inst 2015;35:3591–9. https://doi.org/10.1016/j.proci.2014.06.024.
[89] Magalhães D, Kazanç F, Riaza J, Erensoy S, Kabaklı Ö, Chalmers H. Combustion of Turkish lignites and olive residue: Experiments and kinetic modelling. Fuel 2017; 203:868–76. https://doi.org/10.1016/j.fuel.2017.05.050.
[90] Gil M V, Casal D, Pevida C, Pis JJ, Rubiera F. Thermal behaviour and kinetics of coal/biomass blends during co-combustion. Bioresour Technol 2010;101:5601–8 Doi: 10.1016/j.biortech.2010.02.008.
[91] Martín-Lara MA, Ronda A, Blázquez G, Pérez A, Calero M. Pyrolysis kinetics of the lead-impregnated olive stone by non-isothermal thermogravimetry. Process Saf Environ Prot 2018;113:448–58. https://doi.org/10.1016/j.psep.2017.11.015.
[92] Zaman F, Akhtar N, Guan Y, Huang Y. Thermal degradation kinetic analysis and conversion of Aesculus indica to porous carbon. Ind Crops Prod 2020;153:112555. https://doi.org/10.1016/j.indcrop.2020.112555.
[93] Zanatta ER, Reinehr TO, Awadallak JA, Kleinübing SJ, dos Santos JBO, Bariccatti RA, et al. Kinetic studies of thermal decomposition of sugarcane bagasse and cassava bagasse. J Therm Anal Calorim 2016;125:437–45. https://doi.org/10.1007/s10973-016-5378-x.
[94] da Silva JCG, Alves JLF, Galdino WV de A, Andersen SLF, de Sena RF. Pyrolysis kinetic evaluation by single-step for waste wood from reforestation. Waste Manag 2018;72:265–73. https://doi.org/10.1016/j.wasman.2017.11.034.