Custard apple crop residues combustion: an overall study of their energy behaviour under different fertilisation conditions

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ABBREVIATIONS LIST

A: frequency factor.

DGT: derived thermogravimetric profiles.

$\mathrm{DTG}_{\mathrm{max}}$: maximum value reached of a DTG profile.

E_a: activation energy.

FWO: Ozawa-Flynn-Wall iso-conversional method.

HHV: high heating value.

KAS: Kissinger-Akahira-Sunose iso-conversional method.

M1: Casarabonela plot.

M2: Tolox plot.

R^2: correlation coefficients.

SC: seed sample under organic fertilizer.

SM: seed sample under mineral fertilizer.

TG: thermogravimetric profiles.

TGA: thermogravimetric analysis.

WC: pruning remain sample under organic fertilizer.

WM: pruning remain sample under mineral fertilizer.

α: conversion grade.

ABSTRACT

The current energy demand requires new energy sources. The use of biomass is an attractive option. In this work, the combustion thermal behaviour and kinetic of custard apple (*Annona cherimola*) crop remains derived from different plots fertilisation conditions (organic and inorganic) was studied. Thermogravimetry procedures were applied to seeds and wood under four heating rates (5, 10, 20 and 40ºC/min). Iso-conversional methods (Friedman, Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose) were used to determine the activation energy and the frequency factor. Fuel results showed a higher high heating value for seeds (~24.78MJ/mol) when compared with wood (~19.33MJ/mol). Thermogravimetric profiles denoted that, while seed samples were only affected by heating ramps, pruning remains were also influenced by the type of fertiliser. Organic fertiliser was responsible of higher maximum values on the second decomposition peak for wood samples, at 20 and 40ºC/min (56.78%/min and 23.03%/min). Kinetic indexes were also notably influenced by the fertiliser nature. Organic manure reduced the average activation energy results, being more perceptible in seeds (135.51kJ/mol –172.32kJ/mol) than wood (140.32kJ/mol – 144.43kJ/mol). Hence, it is proved that the type of fertilisation affects the thermal behaviour of custard apple residues.

Keywords: biomass, custard-apple, combustion, fertilisation, kinetic, thermogravimetry.

1. INTRODUCTION

Recently, and due to the rapid increase in the human population, the energy demand is raising drastically. Nevertheless, the amount of fossil fuels available in the world is depleting daily [1]. Therefore, the global energy structure needs a revolutionary transition from fossil fuels to renewable fuels based on green energy systems [2]. Within this transition, the scientific community agrees that biomass must play a key role. It has been the oldest humanity energy source and it is currently one of the alternatives with the greatest potential due to, among others, its availability, lower processing cost, high conversion and carbon-neutrality thorough its lifecycle [3]. Biomass is a group of organic materials which can be derived from wood industries (wood residues), animal farms, crops and agro-industries (agricultural residues) as well as from urban activities (municipal solid waste) [4]. Biomass combustion can be considered a process of energy transference in the form of heat and, in total, about 95–97% of the world's bioenergy is currently produced by direct combustion of biomass [5]. The thermal processing of the materials is related to the processes of depolymerization and destruction of their basic organic components: mainly lignin, cellulose, hemicellulose and pectins [6]. Hence, the biomass composition is a crucial parameter to be considered when studying the potential use as fuel of the different sources of biomass [7].

In this research work, the samples energy performance of custard apple crop residues (*Annona cherimola* Mill., 1978), also denominated cherimoya, were used as biomass source. This arboreal species is characterized by having a high water content, proteins, carbohydrates, vitamins and fibre, as well as a low percentage of fat and sterols [8]. Thus, due to its nutritional value and, furthermore, its pharmaceutical characteristics [9], commercial demand for this crop is increasing [10]. Spanish coastal areas, principally Granada, Málaga and Cádiz, **Fig. 1**, are one of the world´s largest production volumes of this fruit [11]. However, its use generates agricultural residues, mainly wood and seeds, that are considered useless waste products or by-products and they end up being burned directly on the crops or accumulated in landfills [12, 13]. Therefore, they must be managed correctly to avoid environment contamination [14]. Cherimoya yield crops depend on various environmental factors, highlighting the susceptibility to diseases [15], the availability of water or the type of fertilization applied [16]. Regarding this last aspect, traditionally, mineral fertiliser has been applied due to the higher yield obtained [17]. However, these synthetic fertilisers are associated to soil and water contamination, eutrophication and loss of biodiversity [18, 19]. Due to the existence of a current market in which organic products are more in demand, organic fertilisation appears as an effective alternative. The type of fertiliser can significantly affect the thermal properties of fuel samples as demonstrated by previous works of these authors for different biomass raw materials [20–23].

For studying the energy performance, thermogravimetric analysis (TGA) was used. Three different iso-conversional kinetic methods, Friedman, Kissinger-Akahira-Sunose (KAS) and Ozawa-Flynn-Wall (FWO) were adopted to determine the activation energy (E_a) and the pre-exponential value or frequency factor (A) under combustion reactions.

This way, the aim of this work was to study how the type of fertilisation applied in custard apple crops influenced the thermal behaviour of the generated residue (wood and seeds).

2- MATERIALS AND METHODS.

2.1 Raw material, plots and sampling.

Custard apple samples were taken from two different plots under different growing conditions. The first one (M1), located in Casarabonela (Málaga, Spain), had an organic production area of 0.25 ha and 20 trees of 19 years of age distributed in plantation frames of 8 x 8 meters. As fertilisation is concerned, it received an annual dose in December of 3 kg per tree and year of granulated phyto agricultural fertiliser 15+15+15 ($N+P_2O_5+K_2O$). The soil, mainly classified as a eutrophic vertisol [24], is characterized by low slopes (2-6%) allowing a useful depth of 87 cm, clayey texture, moderately stony (2-10%) and imperfectly well drained. It was mechanically cleared 3-4 times a year and the soil was tilled once every two years to prevent compaction. Irrigation rates varied according to annual rainfall. A 12,000 hl/ha was estimated. The second farm (M2), located in Tolox (Málaga, Spain), had an extension of 0.35 ha occupied by 45 trees of 21 years old distributed in plantation frames of 8 x10 meters. It was organically fertilised with an annual dose of 25 kg per tree and year. The fertiliser used was cow manure previously composted with the characteristics already published in [23]. The predominant soil was a eutrophic regosol [24], characterized also by low slopes (4-6%), which allowed a useful depth of 77 cm, sandy loam texture, moderately stony (2-10%) and well drained. It was cultivated using a conventional cultivation system characterized by 2-3 annual weeding operations of the ground vegetation cover with a mechanical weed cutter. As above, irrigation varied according to the annual rainfall, but was estimated at around 14,000 hl/ha. A more detailed description for the for both plots are shown in **Table 1**.

Annual pruning was carried out in spring and generated around 100-200 kg of wood per tree. Although the custard apple is mainly a table fruit, it is estimated that 10% of its production does not find an outlet on the market due to its low size or its lack of visual appeal, so this percentage would be used for its transformation through industrial processes for the production of juices, mousses, jams and pulps that, frozen and vacuum packed, are served to the market. Considering the high number of seeds inside the fruit, an average of 10-14 seeds per 100 g of pulp [25], it implies a high quantity of cherimoya seeds concentrated in the industrial transformation centres of this fruit, which, to date, is considered as a waste

In terms of production, it could be established average values of 250-350 kg of fruit per tree and year for the conventional system and 200-300 kg/tree·year for the organic system. Biomass sampling was carried out as described elsewhere [23] and following the guidelines by AENOR Standards [26]. 100 g of pruning remains and 100 g of seeds were collected from every plot which were properly managed and labelled, obtaining in this way the four samples of this work: SC (organic-seed), SM (mineral-seed), WC (organic-wood) and WM (mineral-wood). **Fig. 2** shows both the raw material as wells as an example of the *Annona cherimola* tree and fruit.

2.2 Thermo-chemical analysis.

To evaluate the fuel properties, thermo-chemical analysis was carried out from seeds and pruning remains. The analysed parameters, elemental and proximate analysis and calorific value, were estimated using 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) and carbon, hydrogen and nitrogen (UNE-EN ISO16948:2015).

2.3 Thermogravimetric analysis (TGA).

For thermogravimetric analysis, the samples were prepared ahead of time. To do this, firstly they were dried by air-drying for at least 72 hours. Then, they were milled on a Fritsch^{TM} mill Model P-19 to achieve a particle size of 1 mm. Finally, the samples underwent a second grinding process with a Retch^{TM} ball mill model MM200 to obtain particles size around lower than 0.2 mm. During thermogravimetric analysis, continuous measurement of sample weight as a function of time or temperature were obtained using a TA Instruments^{TM} TGA SDT2960 system. For the dynamic experiments, samples between 8-12 mg of milled samples (particle size less than 0.2 mm) were located on an Al_2O_3 crucible and heated from ambient temperature to 900ºC in ramps of 5ºC, 10ºC, 20ºC and 40ºC per minute, applying a flow of air of 100 ml·min^{-1} with a gauge pressure of 1 atm. These experimental conditions were maintained until the samples reached the common oxidative process of combustion. Mass-time and mass-temperature data obtained were treated by Universal Analysis 2000 TG software (TA Instruments, New Castl, EEUU). Thus, Thermogravimetric profiles of samples (TG) were obtained. To identify the different stages, it is advisable to derive these TG profiles (DTG profiles). With them, important parameters, as the temperature at which occur each stage as well as the mass loss, could be identified.

2.4 Kinetic parameters.

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

Generally, to determine the kinetics of reactions in solid-state is used the **Eq. (1)**:

$$\mathrm{d\alpha/dt = k(T)f(\alpha)} \tag{1}$$

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

For the custard apple samples analysed, the grade of conversion or volatile biomass fraction (α) was estimated applying the **Eq. (2)**:

$$\alpha(\mathrm{T}) = (\mathrm{m_0 - m_T})/(\mathrm{m_0 - m_F}) \tag{2}$$

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

Following the Arrhenius relationship, kinetic decomposition rate constant, **Eq. (3),** is a function of temperature $k(T)$:

$$\mathrm{k(T) = A\ e^{(-E/RT)}} \tag{3}$$

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

After combining **Eq. (1) and Eq. (3)**, the general expression of analytical methods to estimate kinetic parameters using TG results was obtained, **Eq. (4)**.

$$d\alpha/dt = A\, e^{(-E/RT)}\, f(\alpha) \tag{4}$$

This kinetic expression can be modified in non-isothermal TG experiments, due to the sample is heated at a constant rate or heating rate ($\beta = dT/dt$), causing **Eq. (5)**.

$$d\alpha/dT = 1/\beta\, (A\, e^{(-E/RT)})\, f(\alpha) \tag{5}$$

However, reaction function $f(\alpha)$ is usually unknown, so, if **Eq. (5)** is integrated up to conversion, **Eq. (6)** is attained:

$$\int_0^\alpha d\alpha/f(\alpha) \ = g(\alpha) = A/\beta \int_{T_0}^{T} e^{(-E/(RT))}\, dT \tag{6}$$

Finally, the chance of variable with the non-dimensional parameter $x = E/RT$ gives rise to **Eq. (7)**.

$$g(x) = (AE/\beta R) \int_0^\infty (e^{-x}/x^2\ dx) = AE/\beta R\, p(x) \tag{7}$$

Nevertheless, the integral of p(x) has no an analytical solution so it has to be approximated. In this way, diverse kinetic methods with different approximated formulas have been developed. In this work, Friedman, Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods were employed. All of them analysed the measurements for multiple conversion levels (0.1-0.9). The Friedman analyses is an isoconversional method whereas the Ozawa-Flynn-Wall (FWO) and Kissinger-Akahira-Sunose (KAS) analyses are integral isoconversional methods.

2.4.1 Friedman method.

This analysis is an isoconversional method [27]. Its approximated formula is based on **Eq. (5)**, performance the **Eq. (8)**.

$$\ln(\beta\, d\alpha/dT) = \ln[A_\alpha\, f(\alpha)] - E/RT \tag{8}$$

The activation energy uses the variation of conversion fraction regarding the temperature at a given heating rate and at a certain temperature. It requires at least two measurements.

2.4.2 Flynn-Wall-Ozawa (FWO) method.

Constitute an integral isoconversional method [28, 29] founded on Doyle's approximation [30], resulting in following **Eq. (9)**:

$$\ln(\beta) = \ln[AE/(Rg(\alpha))] - 5.331 - 1.052\,(E/RT) \qquad (9)$$

2.4.3 Kissinger-Akahira-Sunose (KAS) method.

Like the FWO method, it is an integral isoconversional anaylis. KAS is a differential method [31, 32] based on Coast-Redfern's approximation method [33]. The final expression is **Eq. (10)**.

$$\ln(\beta/T_\alpha{}^2) = \ln((A_\alpha R)/(E_\alpha g(\alpha))) - E/(RT_\alpha) \qquad (10)$$

Taking into account the previous equations, apparent activation energy was determined for α values between 0.1–0.9, with an estimated error sufficiently small.

2.4.4 Pre-exponential factor (A).

For the estimation of the pre-exponential factor, in terms of the activation energy, the Kissinger's equation, **Eq. (10)**, was applied, following literature recommendations [34, 35], and developing **Eq. (11)**.

$$A_\alpha(\beta) = \beta E/(RT^2{}_p)\,\exp(E/(RT_p)) \qquad (11)$$

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 result purposes, the average values of the results obtained for A in each heating rate for a same conversion level were estimated.

3. RESULTS AND DISCUSSION.

3.1 Fuel properties.

Results, **Table 2**, were very different according to the type of waste analysed. Focusing on custard apple seeds, they contained a very high quantity of carbon (~56%), a low percentage of hydrogen (~7%) and moderate amount of nitrogen (~2%). These values were in line with those obtained from other seeds, such us date seeds [36]. Studies have demonstrated that oil comprises a large part of the composition of this type of seeds [37], highlighting the long carbonated chains that form the palmitic, oleic and linoleic acids [38]. High carbon and nitrogen values revealed that custard apple seeds and pruning remains had properly fuel characteristics under combustion. The oxidation reactions of these elements were exothermic, releasing energy [39]. Although pruning samples mean values for the above mentioned parameters were lower when compared with seeds, all of them had slightly higher percentages than several common agricultural crops remains, olive, pear, vine, hazelnut and apple, that literature showed [40]. In respect of sulphur and chlorine content, low percentages were obtained. In the case of seeds, higher sulphur values stood out, while wood samples contained higher chlorine content. In both cases, the values were in line with other studies carried out with similar biomass sources [41, 42].

It was noticeable the difference in moisture content, registering dissimilar values between seed and wood samples (~1% vs ~8%). This resulted in significant differences in their calorific values (HHV). The higher the moisture, the less valid biomass is as a fuel because part of the heat generated in combustion is used to evaporate the water and not to produce energy, requiring burning of greater amounts of biomass to obtain the same value of energy [43]. Seed samples obtained best HHV values (~25MJ/kg) than wood pruning samples (~19MJ/kg). This HHV values achieved in seeds were remarkably high, closer to results of pelleted materials [44] rather than raw materials [45] or coal mixtures [46]. In the same way, seeds HHV results were greater than those of seeds from biomass sources already studied [47, 48]. However, custard apple seed HHV results were lower compared with seeds of other species included in the genre Annona (*Annona squamosa* L.) [49], mango [50], papaya or watermelon [51]. Likewise, similar findings of wood HHV results have been reported by other studies already published about biomass from diverse origins, such as olive tree [52], avocado [23] and vineyard [53] pruning remains.

Ashes, unburned solid waste, were undesirable when trying to energetically value a raw material. In fact, many of the equations used to calculate HHV recommend that the percentage of ash in the samples not exceed 11% [54]. The presence of compounds with a high content of chlorine and sulphur in ashes composition can result in acid gas emissions [55] and equipment corrosion due to slagging and fouling [56]. Far from having these critical values that cause these problems in combustion systems, custard apple residues values (~2%) were in line with results reached for similar biomass sources [57].

In this way, it was confirmed that *Annona cherimola* remains had good combustible properties, especially the seeds regardless of the type of fertiliser used.

3.2. TGA stages

TGA and DTG curves of custard apple biomass obtained under air atmospheric conditions at four heating rates (5, 10, 20 and 40°C/min) are shown in **Fig. 3 and 4**. The study was carried out from room temperature to up to 700°C. Within this range, various processes during the thermal decomposition of biomass took place. Three mass loss stages could be appreciated. Firstly, initial loss of biomass weight is attributed to the moisture evaporation and to very light volatile compounds release [58]. The presence of higher peaks in this first phase (ambient to 100ºC) was related to the content of the moisture samples.

The obtained profiles, TGA and DTG, were significantly different depending on the type of raw material studied: seed or wood. This is so because their chemical composition. Wood remains are composed mainly of cellulose, hemicellulose and lignin, whereas seeds contain a higher content of other components, such as oils and alcohols [59]. These differences were reflected with greater intensity on the second and third phases of mass loss of the TGA and DTG profiles.

The second phase is known as devolatilization and corresponds to the second DTG peak. This intense mass loss occurred between the temperatures of 250°C and 450°C, when easy-release components were emitted. In the case of the pruning remains, it was during this stage that the light volatile decomposition took place, releasing cellulose and hemicellulose components [60]. The third phase, fixed carbon combustion, occurred between 400 and 600°C, approximately. This last mass loss event encompassed the hard-to-decompose components. Thus, during this stage, lignin was released from pruning remains [61]. Thermal decomposition of both seed and wood samples ceased when temperature values above those mentioned previously were reached.

For seeds, the similar residues nature leaded to similar SC and SM profiles with close DTG_{max} values (**Table 3**). Under 40ºC/min heating rate, these values were higher (35.88 and 32.66%/min respectively). Heating rate influence was really evident for the second and third mass loss stages. As the heating rate increased, the maximum values of the peaks became larger and narrower, especially after 300ºC. Regardless of the heating rate, from 600ºC, the temperature at which the higher peaks in DTG profiles were managed for the second stage of combustion (230 – 340ºC), when TG profiles decreased significantly. Consequently, it can be stated that biomass from custard apple seeds had an upper percentage of easy-release components compared to the hard-decompose ones.

Concerning pruning remains, unlike of the behaviour experienced for the seeds, the different fertilisers applied caused differences in the profiles especially during high heating rates (20 and 40ºC/min). It would be appreciated how, for the DTG profiles (**Fig. 3**)**,** the maximum values of the second peak acquire higher figures, for these two ramps, when organic fertiliser was applied (56.78% min vs 54.97%/min and 23.03%/min vs 16.95%/min for 40 and 20ºC/min respectively).

The DTG profiles, **Fig. 3**, also showed how for all samples there was a gradual mass loss at the end of the process (components of difficult release). This can also be seen in the slopes plotted in TG profiles, **Fig. 4**. This behaviour was so similar with combustion profiles for raw materials with similar composition [62]. In this way, it can be stated that approximately between 450°C and 600°C, depending on the type of biomass and the heating rate, practically all of the mass had been released (**Table 3**), leaving a minimum amount of final residue (<4% weight). This means that all the biomass introduced into the boiler, except for a very small percentage, was used.

Thermal degradation results of custard apple samples were in line with the TGA profiles obtained in previous studies with similar biomass samples. In this way, it was found that willow and poplar wood reached close DTG_{max} values (~34% w/min) for the same temperature range (250-370°C) [63, 64]. However, if comparison with olive pruning remains is made [65], it was quickly verified that higher temperatures were demanded, requiring between 500°C and 670°C to achieve the decomposition of cellulose and hemicellulose, and more than 700°C for the release of lignin. The more temperature is required for the decomposition of the biomass components; the more energy the system needs to consume. This can be attributed to the fact that the efficiency of the heat transfer is lower when the heating rate is higher [61]. For this reason, and based on its good behaviour under slow ramps, it can be argued that custard apple pruning remains showed good thermal characteristics. On the other hand, the combustion results from seeds were really close to those obtained from peach seeds, with similar $\mathrm{DTG_{max}}$ value and temperature range, and also similar to those from its pyrolysis process [66]. A close trend was observed when a comparison with pyrolysis process is done. Custard apple seeds had similar DTG combustion profiles to *Mangifera indica* L. (mango), *Artocarpus heterofyllus* L. (jackfruit) and *Syzygium jambalonum* L. (java plum) seeds pyrolysis results [67], where the active pyrolysis zones were located below 500ºC and it was found that the best thermal behaviour were also related to the slower heating rates. Nevertheless, in this pyrolysis samples, together others [36], although $\mathrm{DTG_{mas}}$ values could be higher, final residues inside the burner were certainly bigger, varying between 17.76% and 21% of the sample weight and entailing that a large part of the biomass was not used.

Therefore, differences in thermal behaviour were observed according to the biomass used. While seed samples were only affected by heating ramps, pruning remains were also influenced by the type of fertiliser. For the release of seeds components, a slightly higher temperature range (550ºC – 600ºC) was needed when compared with wood (~500ºC). Thus, considering the highest $\mathrm{DTG_{max}}$ value, the fast compound release and the slow final residue, WC presented the best thermal profile. This result is crucial when using this type of waste in pilot plants or combustion boilers already implemented.

3.3. Kinetics.

Isoconversional methods were used to estimate the thermogravimetric analysis (TGA) and simultaneously obtain the effective activation energies for the custard apple samples. Hence, according to **Eq. (9) to (11)**, E_a was calculated plotting ln $(\beta\ d\alpha/dT)$, ln(β) and ln $(\beta/{T_\alpha}^2)$ vs 1/T for different conversion values (α = 0.1–0.9). The linear fitting equations following Friedman, FWO and KAS methods were thus achieved (**Fig. 5, 6 and 7**, respectively). The quality of the linear fit was also corroborated thorough the correlation coefficients (R^2) values between 0.958 and 0.999. For the given conversion values, the activation energies data were obtained by the linear slopes. **Table 4** shows the results.

Kinetic parameters and particularly activation energy provide indirectly the potential for the thermal conversion of biomass into fuel. In this work, slightly higher results of activation energy were achieved for the Friedman method. Although the Friedman differential isoconversional method is considered as one of the most suitable [68], all these methods are based on simplified approximations using different calculation techniques [69]. This way, all of them could have be faintly influenced by data noise [70, 71]. Thus, the small variances detected among the methods can be explained in this way.

Considerable differences were observed in the average E_a values between seeds (132.09kJ/mol - 175.30kJ/mol) and wood residues (137.66kJ/mol – 146.93kJ/mol). Organic manure decreased the average E_a values in all samples, greater extent in seeds than wood, highlighting this plunged in SC where a drop of 43.41 kJ/mol was registered. For seeds there was also a trend in which E_a raised for α interval from 0.1 to reaching the maximum values for 0.7 and then decreased for 0.8 and 0.9. Pruning remains showed a similar trend achieving the highest E_a for $\alpha = 0.6$. This fact has been found in another similar researches [72–74] and has been mainly ascribed to the development of endothermic reactions [75] related to hard-to-decompose components which slowed down the speed of the process. In contrast, for the highest conversion values, E_a decreased indicating the occurrence of exothermic reactions again [76]. In the present study, the values found for the activation energy were slightly different but lie in the range of previous results from literature for similar biomass. Thus, for instance, seed samples were in line with results achieved for oil palm kernels [77] and lower than for avocado stones [23], which also stand out for their high oil content. Pruning remains results were within the range of similar biomass such as the birch wood [78], the date palm pruning [79], and even the pine sawdust [80]. However, samples E_a average values were higher than data collected in literature for conventional fuels like coal (~100kJ/mol) [81] or crude oil (~45-95kJ/mol) [82].

If a comparison with other thermal processes is made, a remarkable contrast with the results obtained in this work can be appreciated. The atmosphere conditions clearly influenced the results. Literature E_a values for agricultural residues under pyrolysis thermal process were higher than the custard apples results here obtained. Namely straw mixture (~221.7kJ/mol) [83], pine pruning remains (~184.72kJ/mol) [84] grapes seeds or cherries stones (~186.6 and 272.2kJ/mol [85]. Similar values of E_a for custard apple were reached after the pyrolysis of poplar wood (134-142 kJ/mol) [86].

Regarding frequency factor (A), the values shown in the **Table 4** were the average result achieved in **Eq. (12)** for each heating rate and for a given conversion value. Hence, on average, higher A-results were obtained in seed samples ($3.66\text{x}10^{13} – 4.12\text{x}10^{18}$ 1/s) than in woods ($1.31\text{x}10^{14}$ – $2.52\text{x}10^{17}$ 1/s). As happened with E_a values, A results were also influenced by the type of fertilisation applied. Organic manure decreased the A-values in both seed and wood samples. Moreover, there was a trend in all cases in which a wide range variation among the different conversion values within each sample were registered. Maximum average A-results coincided with the highest E_a for $\alpha = 0.6$ and 0.7. These variations of frequency factor with conversion indicated that complex reactions occurred during decomposition processes [87]. The obtained A-values, between 10^9 and 10^{19} 1/s, were in line with values for sub-bituminous [88] and bituminous [89] coals.

Activation energy, E_a, values are closely related to the material performance in the combustion boilers [90]. A lower activation energy means that the combustion reaction starts more easily. Analysing **Table 3**, it can be seen how the temperatures at which the greatest energy release occurs practically do not vary depending on the type of fertilizer. The wood has lower final temperature values than the seeds. When considering the average values of E_a (**Table 4**), however, it can be seen how the seeds of the trees that have been subjected to organic treatment are, the ones that denote the lowest values (~135 kJ/mol) and, therefore, in the case of feeding a combustion boiler, those that require less energy expenditure to start said combustion reaction.

4. CONCLUSIONS.

This work encompassed thermogravimetric and kinetic analysis methods to investigate the thermochemical behaviour of custard apple crop residues. The results achieved showed better higher heating values for seed samples (~25MJ/kg) than woods (~19MJ/kg) independent of the fertiliser applied. TGA and DTG profiles obtained were notably different according to the chemical composition of the sample analysed. While seed samples were only affected by heating ramps, pruning remains were also influenced by the type of fertiliser. For the release of seeds components, a slightly higher temperature range (550ºC – 600ºC) was needed when compared with wood (~500ºC). All the samples had a final residue <4% weight. Regarding kinetic parameters, organic fertiliser reduced average E_a values in both seed (135.51kJ/mol – 172.32kJ/mol) and wood (140.32kJ/mol – 144.43kJ/mol) samples. This same trend was strongly detected in A-coefficient results where higher values than $>10^9$ 1/s in all samples corroborated that the thermal decomposition of this biomass was a complex process. Therefore, custard apple remains had properly fuel characteristics under combustion.

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CONTRIBUTIONS

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

COMPETING INTERESTS

The authors declare no competing interests.

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Highlights

- Custard apple remains had properly fuel characteristics under combustion.
- Seeds had higher HHV results (~25 vs ~19MJ/kg).
- In contrast to seeds, DTG wood profiles were influenced by the fertilizer used.
- Organic fertilizer reduced the activation energy in both seed and wood samples.
- Thermal decomposition of custard apple remains was a complex process.

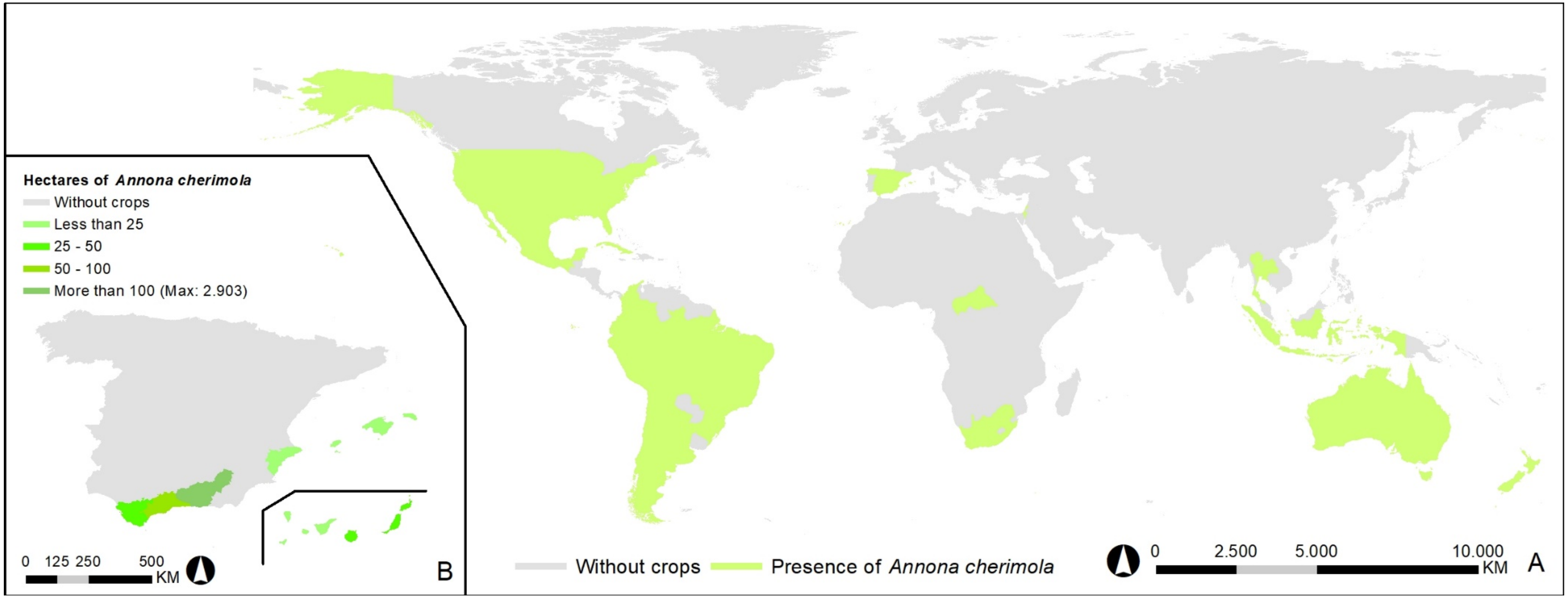


Fig. 1. – Custard apple world distribution and Spanish production volumes.

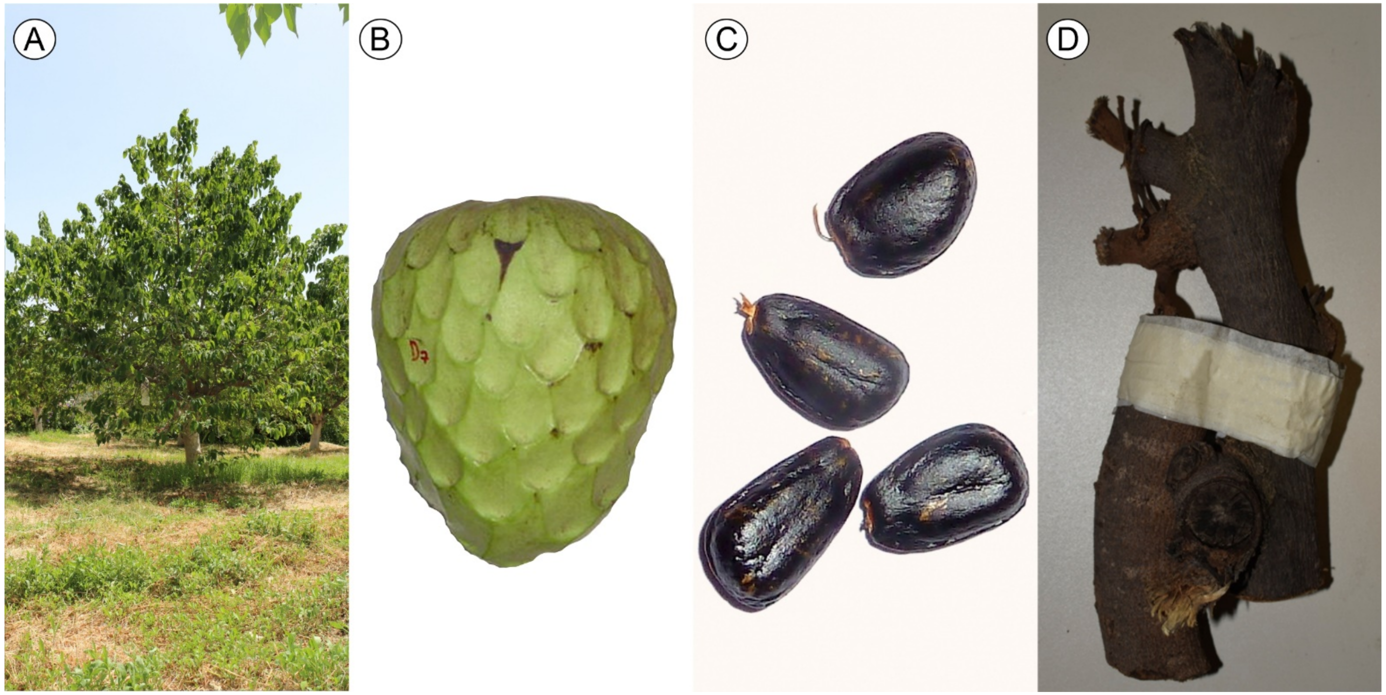


Fig. 2. – *Annona cherimola* tree (A), fruit (B), seeds (C) and pruning remains (D).

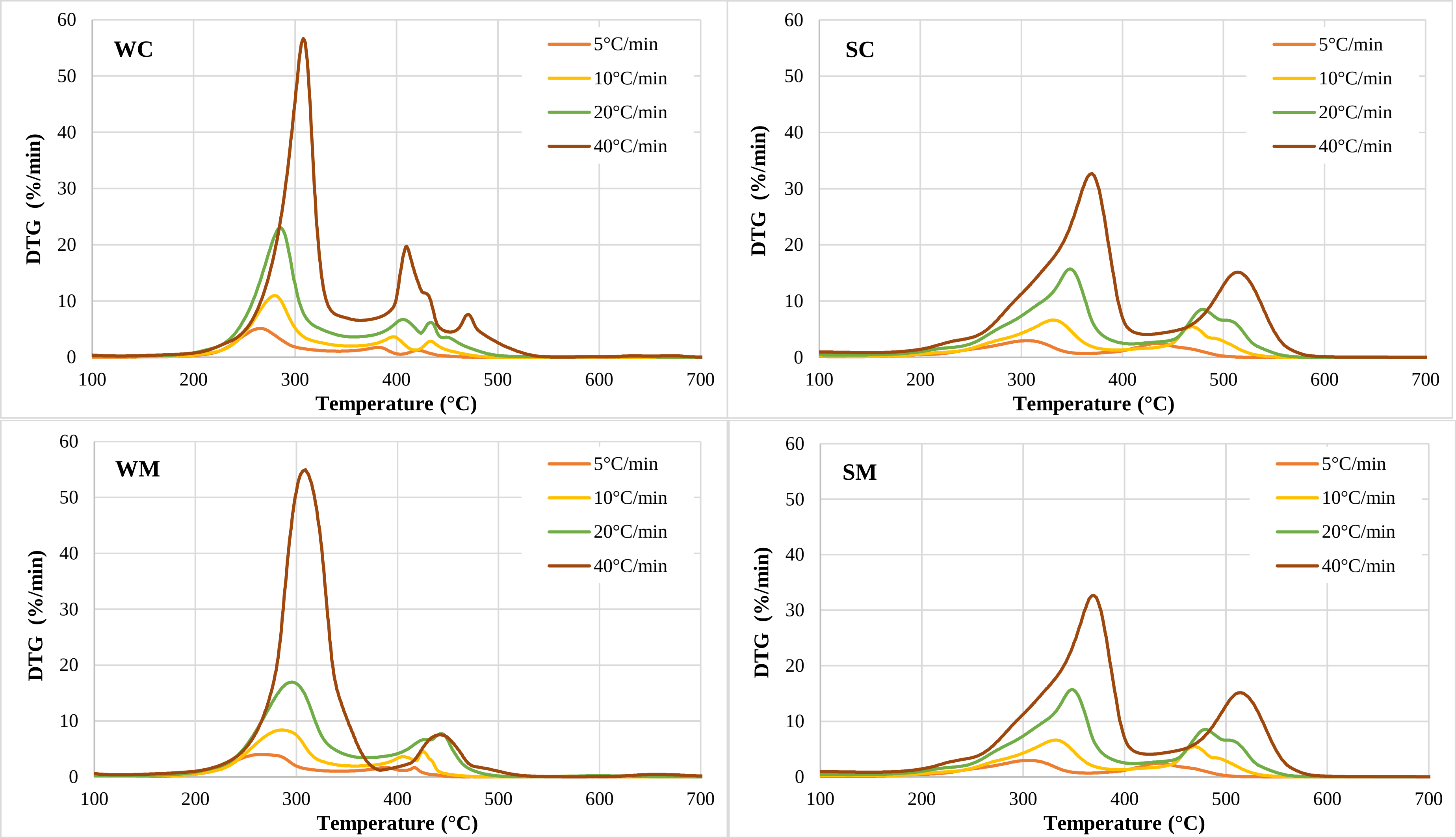


Fig. 3. – Custard apple residues DTG profiles for different heating rates.

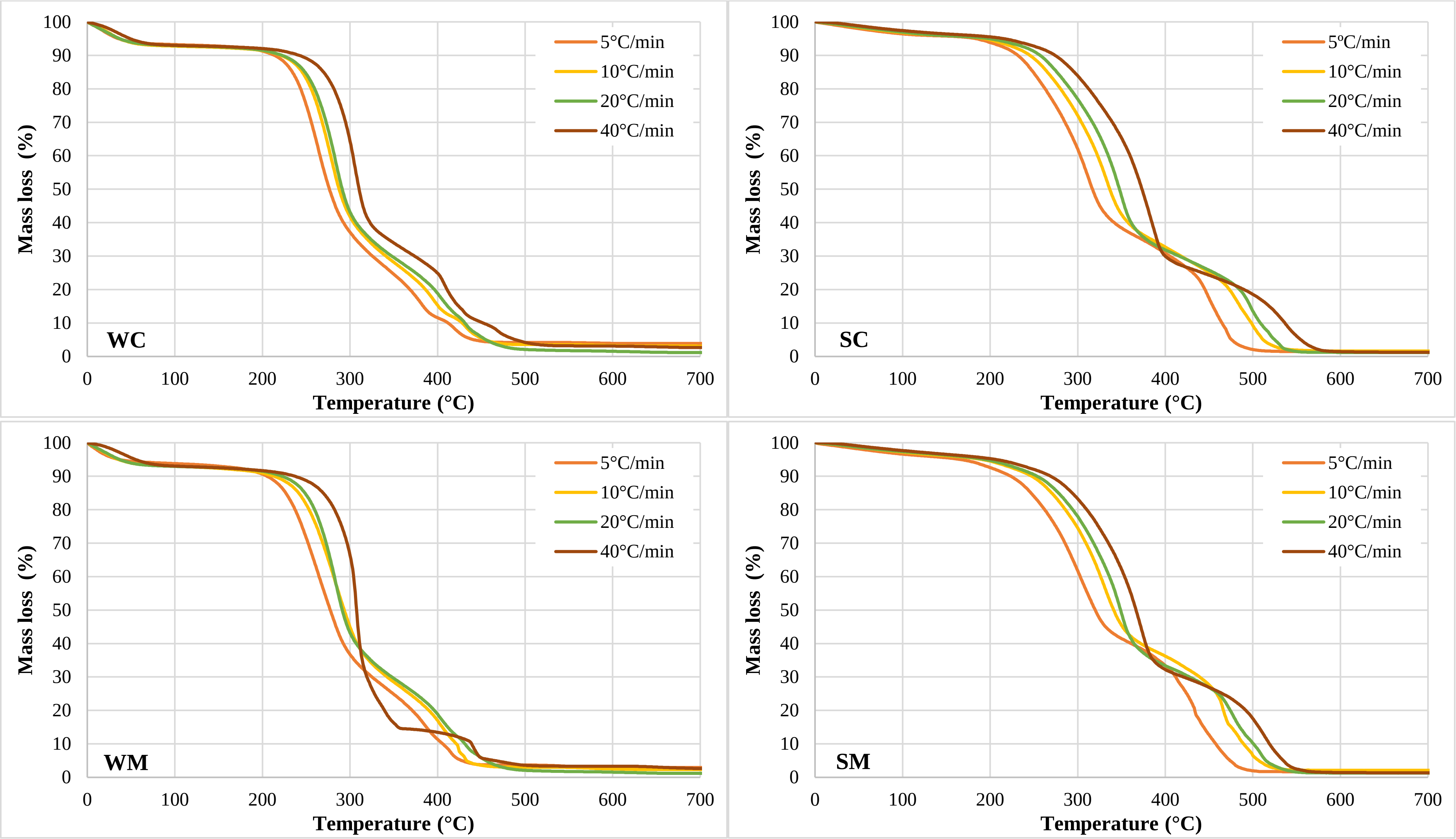


Fig. 4. – Custard apple residues TG profiles for different heating rates.

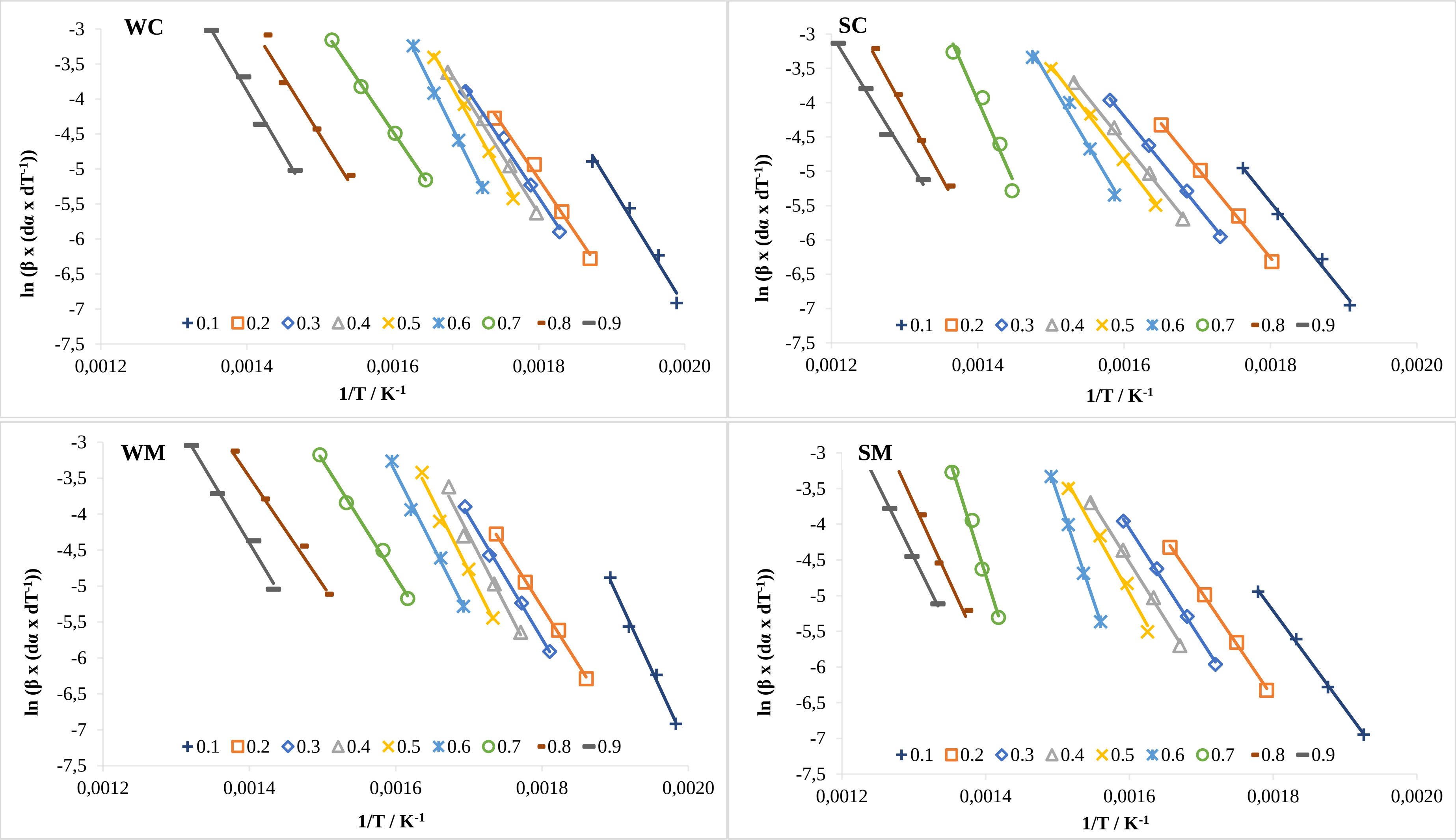


Fig. 5. – Custard apple linear regression results based on Friedman method.

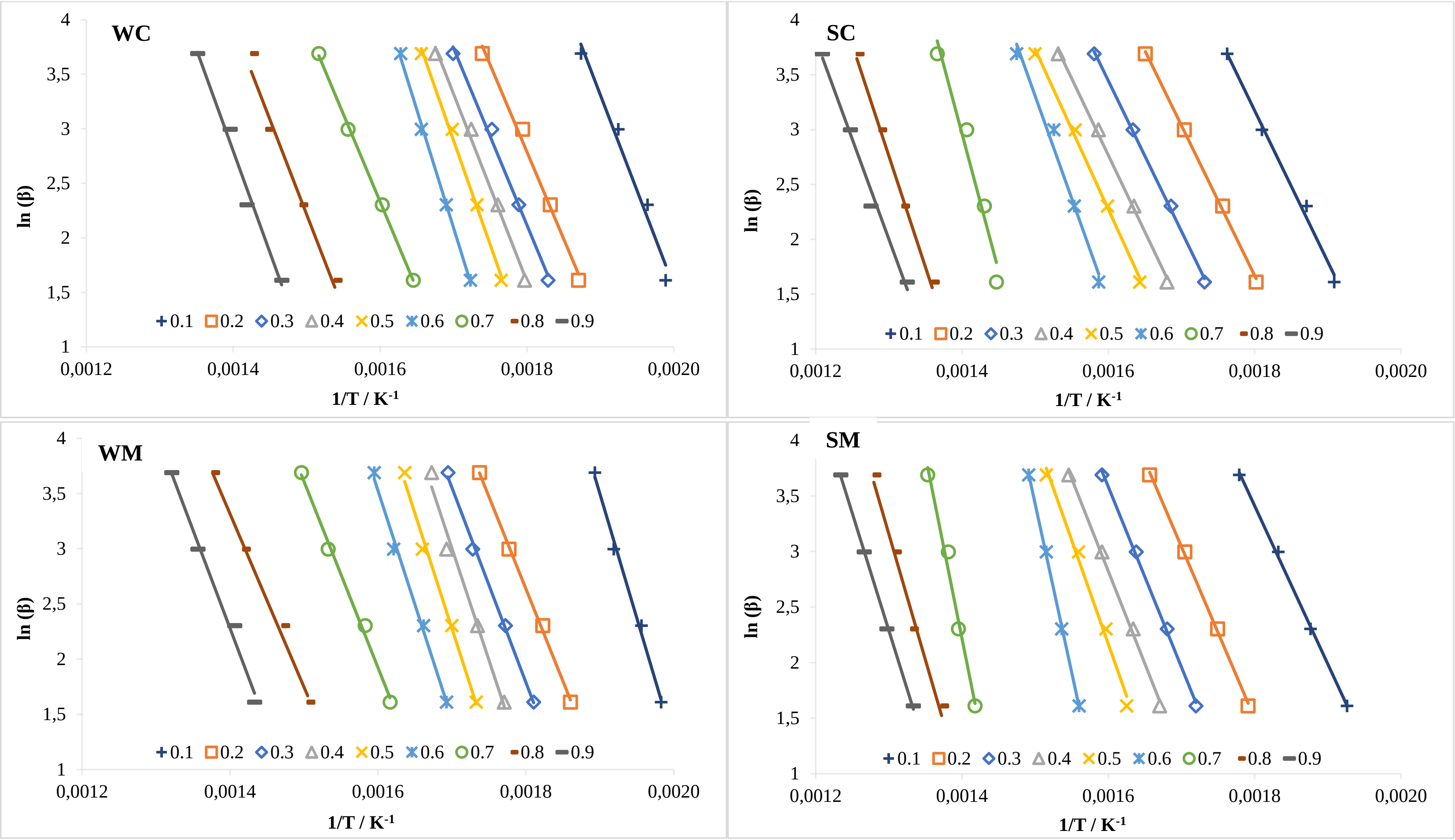


Fig. 6. – Custard apple linear regression results based on FWO method.

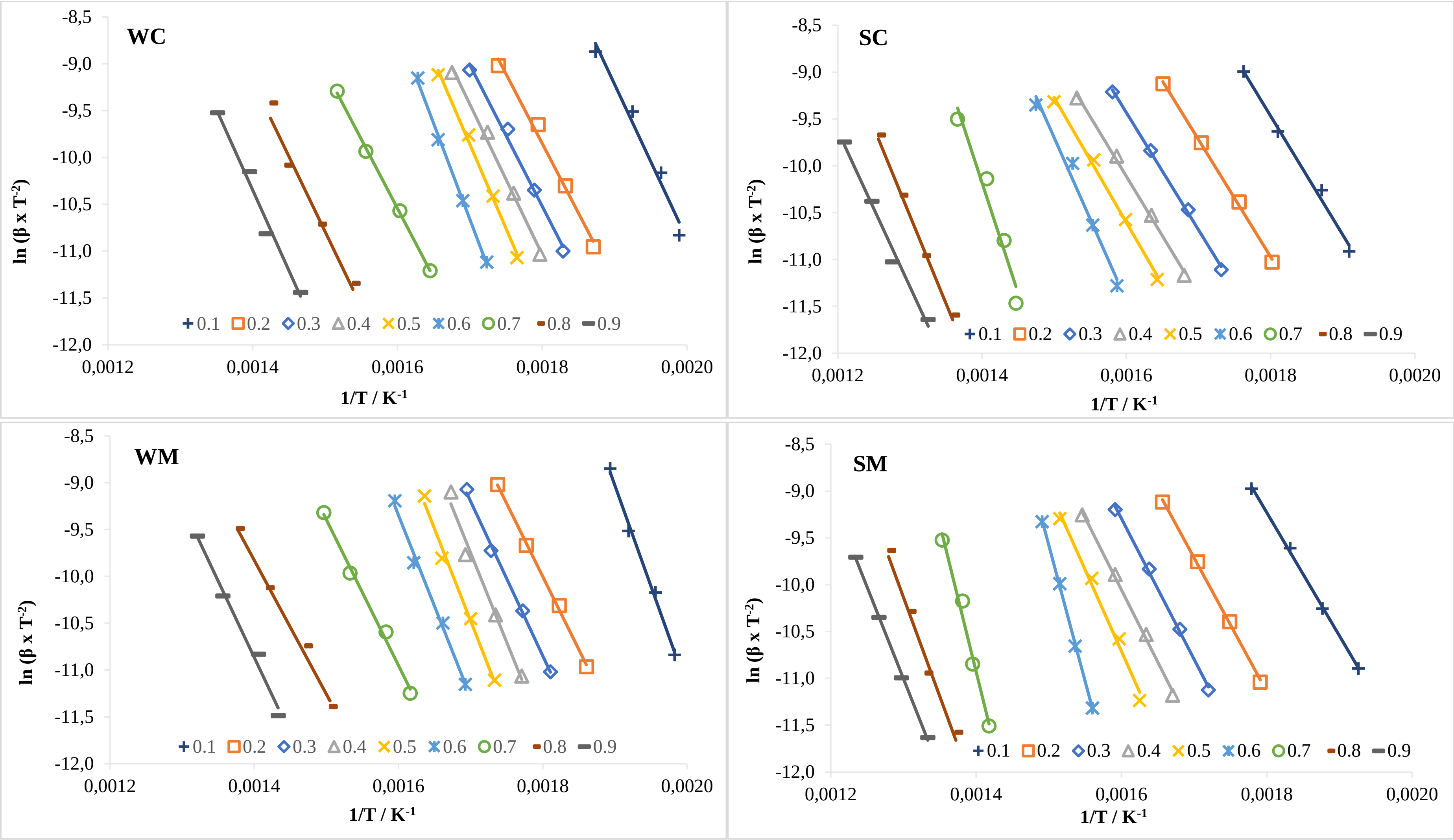


Fig. 7. – Custard apple linear regression results based on KAS method.

Table 1. Capacities and bases per horizon of the soil of the plots of Casarabonela (M1-mineral fertilizer) and Tolox (M2-organic fertilizer).

BASES											SOIL CAPACITY				
Crop	**Hor.**[a]	**Depth (cm)**	**pH**	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**K^{+}**	**C.E.C**[c]	**E.CD**	**Organic carbon (%)**	**N (%)**	**C/N**	**P_2O_5 (mg/100g)**	**K_2O (mg/100g)**	**$CaCO_3$ (%)**
M1	A_p	0-21	8.0	Sat[b]	5.54	0.30	0.53	29.57	0.46	0.57	0.089	6	13	27.9	16
	B_w	21-87	8.3	Sat	14.25	0.74	0.41	29.57	0.64	0.48	0.095	5	10	22.4	10
	C1	87-130	8.5	Sat	17.50	0.92	0.29	26.61	1.14	0.33	0.101	3	8	15.3	3
M2	A_p	0-18	7.4	Sat	1.54	0.14	0.15	13.15	0.81	0.95	0.065	15	13	3	1
	C	18-77	7.6	Sat	0.81	0.08	0.10	13.01	0.34	0.84	0.059	14	13	3	2

[a] Soil horizon. [b] Saturade. [c] Cation exchange capacity. [d] Soil electrical conductivity;

Table 2. Custard apple residues fuel properties.

	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[ab]	
SM	56.60 ± 0.36	7.49 ± 0.12	2.11 ± 0.11	0.13 ± 0.00	0.026 ± 0.005	33.64 ± 0.13	1.02 ± 0.08	1.44 ± 0.11	84.03 ± 1.71	14.53 ± 0.32	24.81 ± 0.37
SC	56.60 ± 0.44	7.56 ± 0.15	2.07 ± 0.09	0.12 ± 0.00	0.022 ± 0.003	33.63 ± 0.19	1.08 ± 0.03	1.38 ± 0.11	83.10 ± 1.56	15.52 ± 0.40	24.75 ± 0.36
WM	49.00 ± 0.57	5.83 ± 0.08	0.80 ± 0.04	0.03 ± 0.00	0.110 ± 0.001	44.23 ± 0.17	7.66 ± 0.14	1.81 ± 0.12	77.62 ± 1.33	20.57 ± 0.40	19.38 ± 0.39
WC	48.90 ± 0.29	5.80 ± 0.04	0.62 ± 0.03	0.04 ± 0.00	0.180 ± 0.002	44.46 ± 0.26	8.55 ± 0.19	2.15 ± 0.16	78.51 ± 1.48	19.34 ± 0.39	19.29 ± 0.39

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

Table 3. Characteristic parameters obtained from TGA and DTG combustion profiles of custard apple samples under different heating rates.

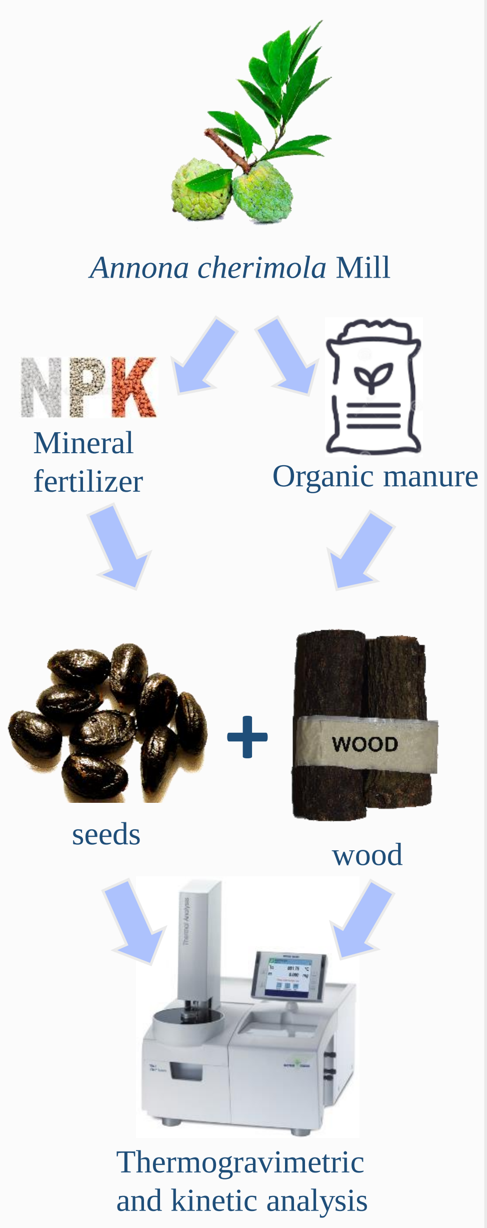
Sample	**β (ºC·min^{-1})**	**DTGmax (%·min^{-1})**	**T$_{DTGmax}$ (ºC)**	**Main region (ºC)**	**Final solid residue (%)**	**Mass loss (%)**
SC	5	3.827	331	231-504	1.767	89.45%
	10	7.573	350	239-545	1.970	90.22%
	20	17.430	372	252-566	1.304	92.13%
	40	35.880	407	237-598	1.343	93.05%
SM	5	2.962	328	217-523	1.908	91.22%
	10	6.630	344	218-543	2.426	91.61%
	20	15.710	366	208-564	1.429	93.43%
	40	32.660	389	225-581	1.423	93.12%
WC	5	5.122	283	200-461	3.503	87.22%
	10	10.940	296	196-487	2.564	88.00%
	20	23.030	309	210-515	0.912	89.69%
	40	56.670	327	200-530	2.019	88.59%
WM	5	4.011	291	200-469	2.431	88.41%
	10	8.382	306	205-470	2.007	87.93%
	20	16.950	320	180-500	2.271	88.89%
	40	54.970	328	180-525	2.166	88.88%

Table 4. Kinetic parameters for the different residues derived from the custard apple crop residues.

		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)**
SC	0.1	110.03	0.9924	2.32E+10	108.90	0.9932	1.79E+10	105.50	0.9917	8.16E+09
	0.2	108.89	0.9986	3.74E+09	108.09	0.9987	3.14E+09	104.07	0.9984	1.31E+09
	0.3	109.10	0.9986	1.43E+09	108.48	0.9987	1.26E+09	104.07	0.9984	5.01E+08
	0.4	110.94	0.9977	1.02E+09	110.38	0.9979	9.11E+08	105.75	0.9974	3.56E+08
	0.5	116.02	0.9964	1.70E+09	115.32	0.9967	1.48E+09	110.73	0.9959	5.94E+08
	0.6	149.92	0.9818	6.34E+11	147.68	0.9831	4.13E+11	144.48	0.9803	2.24E+11
	0.7	201.84	0.9582	5.41E+14	197.49	0.9605	2.53E+14	195.92	0.9556	1.92E+14
	0.8	162.21	0.9954	5.42E+10	160.23	0.9957	3.93E+10	155.85	0.9950	1.92E+10
	0.9	144.89	0.9876	1.47E+09	143.96	0.9885	1.27E+09	135.83	0.9865	3.47E+08
	*****	**137.97**		**6.02E+13**	**136.45**		**2.81E+13**	**132.09**		**2.14E+13**
SM	0.1	113.90	0.9988	7.09E+10	112.54	0.9989	5.17E+10	109.41	0.9987	2.50E+10
	0.2	123.58	0.9989	8.59E+10	122.05	0.9990	6.18E+10	118.75	0.9988	3.03E+10
	0.3	129.92	0.9983	1.08E+11	128.28	0.9984	7.66E+10	124.90	0.9981	3.80E+10
	0.4	133.27	0.9974	9.55E+10	131.61	0.9977	6.83E+10	128.10	0.9972	3.37E+10
	0.5	149.95	0.9900	1.35E+12	147.57	0.9907	8.49E+11	144.66	0.9892	4.79E+11
	0.6	247.03	0.9930	4.75E+19	240.01	0.9993	1.27E+19	241.58	0.9992	1.71E+19
	0.7	267.39	0.9840	2.06E+19	259.88	0.9847	5.73E+18	261.39	0.9833	7.41E+18
	0.8	182.18	0.9834	2.09E+12	179.14	0.9844	1.27E+12	175.92	0.9824	7.45E+11
	0.9	169.06	0.9986	1.01E+11	166.86	0.9987	7.10E+10	162.58	0.9985	3.58E+10
	*****	**175.30**		**7.57E+18**	**171.93**		**2.05E+18**	**169.73**		**2.72E+18**
WC	0.1	141.61	0.9763	1.96E+14	138.71	0.9778	9.76E+13	137.31	0.9748	6.97E+13
	0.2	128.01	0.9905	7.80E+11	126.06	0.9912	5.72E+11	123.40	0.9897	3.13E+11
	0.3	130.25	0.9924	7.32E+11	128.29	0.9930	4.76E+11	125.52	0.9918	2.58E+11
	0.4	138.35	0.9937	2.64E+12	136.07	0.9942	1.61E+12	133.56	0.9932	9.35E+11
	0.5	154.47	0.9961	5.11E+13	151.46	0.9963	2.69E+13	149.61	0.9958	1.82E+13
	0.6	175.07	0.9985	1.71E+15	171.13	0.9986	7.57E+14	170.10	0.9984	6.12E+14
	0.7	128.10	0.9991	2.04E+10	126.77	0.9991	1.57E+10	122.84	0.9990	7.20E+09
	0.8	139.04	0.9718	2.68E+10	137.51	0.9738	2.02E+10	133.43	0.9696	9.49E+09
	0.9	148.73	0.9830	4.37E+10	146.99	0.9842	3.21E+10	142.83	0.9816	1.54E+10
	*****	**142.75**		**2.18E+14**	**140.54**		**9.82E+13**	**137.66**		**7.79E+13**
WM	0.1	183.19	0.9941	4.08E+18	178.21	0.9944	1.25E+18	178.90	0.9938	1.47E+18
	0.2	134.21	0.9987	3.04E+12	131.97	0.9988	1.84E+12	129.59	0.9986	1.08E+12
	0.3	141.87	0.9974	7.04E+12	139.37	0.9975	4.08E+12	137.13	0.9972	2.51E+12
	0.4	163.46	0.9810	3.82E+14	159.97	0.9820	1.82E+14	158.63	0.9799	1.36E+14
	0.5	168.14	0.9912	4.83E+14	164.52	0.9916	2.27E+14	163.20	0.9907	1.73E+14
	0.6	166.67	0.9934	1.53E+14	163.25	0.9938	7.60E+13	161.62	0.9930	5.45E+13
	0.7	134.82	0.9941	5.13E+10	133.24	0.9945	3.77E+10	129.47	0.9936	1.81E+10
	0.8	124.64	0.9932	1.09E+09	123.99	0.9938	9.66E+08	118.87	0.9925	3.81E+08
	0.9	141.62	0.9876	7.32E+09	140.37	0.9886	5.89E+09	135.58	0.9865	2.57E+09
	*****	**146.93**		**4.54E+17**	**144.58**		**1.38E+17**	**141.76**		**1.63E+17**

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

Custard apple crop residues combustion: an overall study of their energy behaviour under different fertilisation conditions.



Annona cherimola Mill

Mineral fertilizer

Organic manure

seeds

+

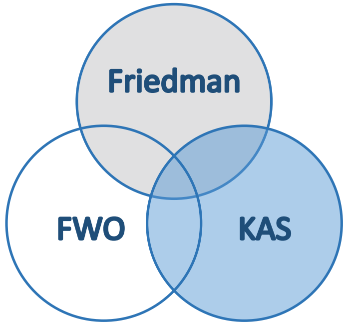
wood

Thermogravimetric and kinetic analysis

A. Fuel Properties:

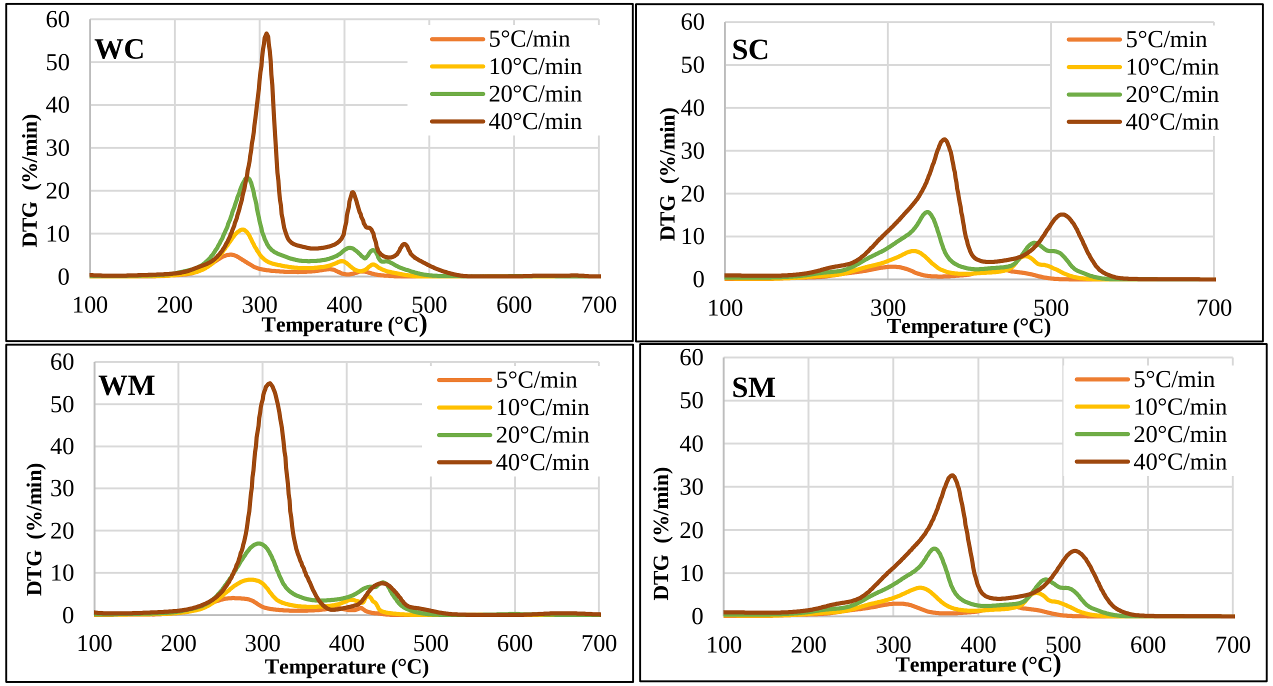
Seeds HHV results were higher than the wood one regardless of the fertilizer employed.

C. Kinetic analysis:



Organic manure decreased the activation energy in all cases, highlighting the seed samples.

B. Thermogravimetric analysis: TG and DTG profiles



CONCLUSION:
Custard apple remains had properly fuel characteristics under combustion. Organic manure decreased the average activation energy in all samples.