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Thermochemical decomposition of coffee ground residues by TG-MS: a kinetic study

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Abstract

Dynamic pyrolysis tests of coffee grounds residues (CGR) at heating rates in the range from 5 – 100 °C/min and at maximum temperature of 500 °C were carried out using a thermogravimetric analyser coupled to a mass spectrometer (TG-MS), for online evolved gas analysis, to determine kinetic parameters of thermochemical decomposition of CGR and its biopolymer constituents. During the pyrolysis, the maximum decomposition rate of each biomass component increased linearly with the heating rate. The slope increased with the biopolymer reactivity in the following sequence: hemicellulose > cellulose > lignin. Main gases produced during the pyrolysis of CGR were oxygen containing species derived from parent biopolymers and primary and secondary vapours (250 – 425 °C), with H₂O being the most important, followed by CO and CO₂. The use of the Beta zeolite had only negligible effect on deoxygenation reactions, however it significantly promoted cracking reactions of pyrolysis vapours increasing the light hydrocarbons (C₁-C₂) formation with the subsequent improvement in the heating value of the pyrolysis gas. Kinetic parameters for any of the individual biopolymers in CGR were estimated using the model-free isoconversional dynamic methods: Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO) models. The average value for the apparent activation energy of the individual biopolymers (hemicellulose, cellulose and lignin) in CGR calculated by KAS and FWO methods: were estimated as 214, 241 and 266 kJ/mol, respectively; whilst for the CGR as a whole it was 242 kJ/mol. The two model-free isoconversional dynamic methods have been shown to be useful tools for assessment of biomass pyrolysis kinetic parameters, as they can provide E_a values for use in reactor design models.

Keywords	coffee ground residues; TG-MS; catalytic pyrolysis; cracking; kinetics; isoconversional methods.
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Suggested reviewers	D Beneroso, Beatriz Fidalgo, Aimaro Sanna

Submission Files Included in this PDF

File Name [File Type]

Cover Letter - revised - 111217.docx [Cover Letter]

Respos to REVIEWERS - 111217.docx [Response to Reviewers]

Manuscript - revised - 111217.docx [Revised Manuscript with Changes Marked]

Highlights_revised - 111217.docx [Highlights]

Pyrolysis kinetics of coffee ground residues - final.docx [Manuscript File]

Figures - revised - 111217.docx [Figure]

Supporting information - 111217.docx [Figure]

Table 1.docx [Table]

Table 2.docx [Table]

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December 11th, 2017

Dear Dr. Dufour

Enclosed you can find the electronic files of the revised version of our manuscript entitled “Thermochemical decomposition of coffee ground residues by TG-MS: a kinetic study”, resubmitted to be considered for publication in *Journal of Analytical and Applied Pyrolysis*, which has been agreed by all authors.

As you may note we have carefully taken into account all the reviewer’s comments making necessary changes where possible or providing suitable rebuttals where relevant.

Moreover, according to your recommendations, we have included more experimental results on MS analysis of the gaseous products (new Figs. 4 and 5) with the subsequent further improved discussion on the volatiles formation, thermally and catalytically. On the other hand, we have also moved some thermal modelling results to the new Supporting Information file (former Fig. 4 appears now as Fig. S1, and Table 3 appears now as Table S1).

Therefore, as you may note in the revised version of our manuscript it is devoted to study the thermochemical coffee ground residues decomposition by TG-MS. Main evolved gases online analysed by MS were oxygenates (H₂O, CO and CO₂), which overlapped with main CGR degradation regime (250 – 425 °C). Catalytic pyrolysis improved deoxygenation only negligibly but importantly enhanced vapours cracking increasing the light hydrocarbons (C₁-C₂) formation with the subsequent improvement in the heating value of the pyrolysis gas.

Kinetic parameters of the thermochemical decomposition of coffee ground residues (CGR) and those corresponding to the biopolymers comprising them were estimated by two model-free isoconversional dynamic methods: Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) models. These, were satisfactorily employed resulting average apparent activation energy (E_a) values of 242 kJ/mol (for the entire CGR), and 214, 241 and 266 kJ/mol for its hemicellulose, cellulose and lignin components, respectively.

The use of model-free isoconversional dynamic methods proved to be valuable to assess the kinetic parameters of CGR as it is for other biomasses whatever their structural complexity. The E_a values for pyrolysis of CGR are important input parameters for modelling and design of reactors and their optimisation for production of biochar, fuels or high added-value chemicals.

Keywords: coffee ground residues; TG-MS; catalytic pyrolysis; cracking; kinetics; isoconversional methods.

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Looking forward to hearing from you,

Yours sincerely,

Dr. Javier Feroso

Dear Dr Anthony Dufour,

We thank you and the reviewers for your helpful comments on our manuscript. We have carefully taken into account all of them making necessary changes where possible or providing suitable rebuttals where relevant. Below you can find our point-to-point response to the comments.

I hope that the revised manuscript can be accepted for publication.

Yours sincerely,

Dr. Javier Feroso

Comments from the editors and reviewers:

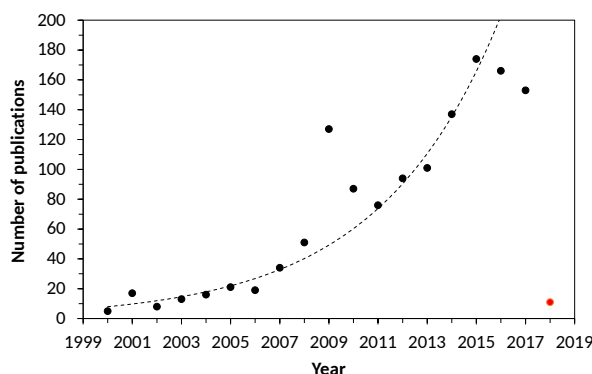
* Reviewer 1

This manuscript deals with thermogravimetric analysis of coffee ground residues. The evolved gases were analysed by using mass spectrometry. The manuscript is well prepared, and the discussion and presentations are clear. However, this work lacks novelty or even interesting findings. Several similar articles can be found elsewhere. Therefore, the manuscript is not recommended to be published in the Journal of Analytical and Applied Pyrolysis.

Answer:

We thank Reviewer 1 for the time dedicated to reviewing our manuscript. However, we do not fully agree with the statement of lack of novelty or interesting findings. To start with, coffee is the second most traded commodity in the world after oil, and one of the most widely consumed beverages [1]; and therefore, we believe that the potential utilization of the generated residues for fuels or high value-added chemicals production by means of its pyrolysis can be an attractive solution for this residue, whose worldwide production is still increasing. Therefore, the first, but not last step for its utilization on the pyrolysis process would be its kinetics study to understand the complex reaction mechanism of its different biopolymers decomposition to help on the design of an adequate reactor.

Although this kind of kinetics study is not new, it does not mean that it is no longer necessary and interesting for the research community, which helps to understand the pyrolysis process itself, whose complex reaction mechanism is still under debate and remains unknown. The importance of such kinetic studies can be evidenced in the available literature, where the number of published studies on pyrolysis showed exponential growth in the past 15 years as shown in the following figure (number of publications from 2000 to present based on search results from SCOPUS on: "thermogravimetric analysis", "biomass pyrolysis" and "kinetics").



Number of annual publications from 2000 to present on: "thermogravimetric analysis", "biomass pyrolysis" and "kinetics" (based on search results from SCOPUS).

*** Reviewer 2**

This paper investigated the kinetic of coffee ground residues pyrolysis. But there are no any meanings about the 1-3 highlights, and distributed activation energy model (DAEM) is more suitable than Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) models for coffee ground residues pyrolysis. The review could not identify the challenges of the present topic and position of this study. What's more, the review could not see sufficient discussions and useful conclusion.

Answer:

We thank Reviewer 2 for reviewing our manuscript.

Firstly, we consider the statement: "the distributed activation energy model (DAEM) is more suitable than those employed in our work, Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) models" as a personal assessment from the reviewer. We believe that there are still a lot of controversy and contradictory information in the literature regarding which models fit better the pyrolysis kinetics of lignocellulosic biomass. There are several review works published during the last 5-6 years in which those methods and some others are described and compared without any resolute statement selecting one over the others [2-4]. As we have already discussed answering to the Reviewer 1, we think that the focus covered in this work is actually of great interest within the research community as demonstrate the previous figure that shows the annual number of publications on this topic.

On the other hand, more MS results and further discussion about the evolved gaseous species during the non-catalytic and catalytic pyrolysis of CGR have been included in the revised manuscript.

*** Reviewer 3**

A solid work on fundamental investigations concerning an interesting topic, the potential utilization of coffee ground residues for pyrolytic processes. I have only three points, which the authors should consider:

1) Figure 1B: The authors claim that there are "clearly three conversion peaks" in the DTG curve visible. However, the second and third "peak" are hardly visible as shoulders on the first larger peak. I also wonder why with lower heating rates the distinction between the

peaks is not getting better, i.e. at 5K/min it is even less pronounced than at 25 and 50 K/min, respectively.

Answer:

In accordance with the reviewer's statement, we have modified our claims in the revised version of the manuscript. So, where it said: "...clearly showing three conversion peaks corresponding to the well-established order of biopolymers decomposition: hemicellulose, cellulose and lignin [28–30]. As the figure shows, the three peaks can be clearly distinguished for all the heating rates, with the exception of 100 °C/min"; now it reads: "...showing a first large peak with two remarkable shoulders corresponding to the well-established order of biopolymers decomposition: hemicellulose, cellulose and lignin [28–30]. As the figure shows, the peak with the subsequent shoulders can be clearly distinguished for all the heating rates, with the exception of 100 °C/min."

Regarding the second question, it is well documented that it is not always the case that the lower the heating rate the better the separation of biomass decomposition peaks. It depends on the biomass source and other experimental conditions, etc. This has been demonstrated in the literature, where different types of biomass were thermally decomposed at different heating rates [5–8]. In these papers it can be also observed that the best distinction of the decomposition peaks does not correspond to the lowest heating rate.

2) Figure 3: The temperature axis seems to be misplaced in this diagram, it should be on the x-axis parallel to the time axis, not to the MS-signal.

Answer:

We agree with this reviewer that the suggested way could also be used, however we believe that the way we used is advantageous as in this figure we want to show how the TGA (conversion and DTG curves) and MS (different gaseous evolved from the CGR decomposition results), but also the sample temperature progress with reaction time. As can be seen in that figure there is a non-isothermal step (during the heating up of the sample) but also a 30 min isothermal step which could not be properly plotted if temperature were on the X-axis parallel to the time axis.

3) It should be mentioned what type of ionization and mass analyser have been used for the MS analysis (I guess electron ionization and quadrupole). In this regard, have the authors considered to look deeper into the organic composition of the evolved gases by doing pyrolysis GC-MS for instance (or, if they have the opportunity, by coupling soft ionization MS or GC to the thermobalance)?

Answer:

In accordance with the reviewer's suggestion, we have included in the revised version of the manuscript the type of ionization source and mass analyzer that was used for the MS analysis. We thank the reviewer for the suggestions regarding further in-depth study of the pyrolysis gas and vapors and we will take these into consideration in future works focused on the bio-oil production from coffee ground residues.

*** Reviewer 4**

1. The apparent activation energy for the whole process was estimated as 244 and 241 kJ/mol for KAS and FWO methods, respectively. How this value was calculated from the activation energies of three components?

Answer:

These values of the apparent activation energy for the whole pyrolysis process for KAS and FWO methods were calculated as the average value of the activation energies obtained at conversion levels from 5 to 90 % as summarizes Table 3, in a similar way to other works found in the literature [9,10].

2. In "2.2. Analytical techniques," "asses" → "assess"

Answer:

We have replaced "asses" by "assess" in the 2.2 Analytical techniques section according to the Reviewer comment.

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Title page

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Thermochemical decomposition of coffee ground residues by TG-MS: a kinetic study

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Thermochemical decomposition of coffee ground residues by TG-MS: a kinetic study

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Abstract

Dynamic pyrolysis tests of coffee grounds residues (CGR) at heating rates in the range from 5 – 100 °C/min and at maximum temperature of 500 °C were carried out using a thermogravimetric analyser coupled to a mass spectrometer (TG-MS), for online evolved gas analysis, to determine kinetic parameters of thermochemical decomposition of CGR and its biopolymer constituents. During the pyrolysis, the maximum decomposition rate of each biomass component increased linearly with the heating rate. The slope increased with the biopolymer reactivity in the following sequence: hemicellulose > cellulose > lignin.

Main gases produced during the pyrolysis of CGR were oxygen containing species derived from parent biopolymers and primary and secondary vapours (250 – 425 °C), primarily H₂O, followed by CO and CO₂. The use of the Beta zeolite had only negligible effect on deoxygenation reactions, however it significantly promoted cracking reactions of pyrolysis vapours increasing the light hydrocarbons (C₁-C₂) formation with the subsequent improvement in the heating value of the pyrolysis gas.

Kinetic parameters for any of the individual biopolymers in CGR were estimated using the model-free isoconversional dynamic methods: Kissinger–Akahira–Sunose (KAS) and

Flynn–Wall–Ozawa (FWO) models. The average value for the apparent activation energy of the individual biopolymers (hemicellulose, cellulose and lignin) in CGR calculated by KAS and FWO methods: were estimated as 214, 241 and 266 kJ/mol, respectively; whilst for the CGR as a whole it was 242 kJ/mol. The two model-free isoconversional dynamic methods have been shown to be useful tools for assessment of biomass pyrolysis kinetic parameters, as they can provide E_a values for use in reactor design models.

Keywords: coffee ground residues; TG-MS; catalytic pyrolysis; cracking; kinetics; isoconversional methods.

1. Introduction

The depletion of fossil fuel reserves and the environmental problems derived from their utilization have made necessary the use of alternative fuels. Biomass is a clean and renewable energy source leading to environmental, technical and economic benefits. Residues from agricultural production and processing industries are readily available in large quantities. Coffee is the second most traded commodity in the world after oil, and one of the most widely consumed beverages in the world [1]. Moreover, the residues derived from its production are steadily increasing in proportion to the coffee consumption growth [1–3]. Coffee silverskin and spent coffee grounds are the main coffee industry residues [4]. The latter is a residue with fine particle size, high humidity (≈ 80 wt%), organic load and acidity, obtained during the treatment of raw coffee powder with hot water or steam for the instant coffee preparation. Therefore, this residue is generated in large amounts, with a worldwide annual generation of 8 million tons [3]. On an average one ton of green coffee generates about 650 kg of spent coffee ground and about 2 kg of wet spent coffee ground are generated per kg of soluble coffee produced [5]. Coffee grounds are disposed as household waste that may be incinerated and/or

moved to landfill [4]. Some alternative applications for coffee ground residues are their utilisation to produce compost [6], deodorizer or adsorbents [7,8], as well as source of renewable energy or for the synthesis of high value-added chemicals [9,10]. In this latter regard, the pyrolysis is a thermochemical conversion process that, depending on the reaction conditions, can be used to transform biomass directly into solid, gaseous or liquid biofuels, being the latter also a promising feedstock for chemicals synthesis [11]. In this respect, a systematic understanding of pyrolysis kinetics is a key factor for the assessment of feasibility, design, and scale-up of such biomass conversion processes for energy applications [12]. Therefore, we believe that the potential utilization of the generated residues for fuels or high value-added chemicals production by means of its pyrolysis results at least an attractive and challenging solution for this residue, whose worldwide production is still increasing. Therefore, the first, but not last step for its utilization on the pyrolysis process would be its kinetics study to understand the complex reaction mechanism of its different biopolymers decomposition to help on the design of an adequate reactor. Therefore, thermogravimetric analysis (TGA) is the most commonly used technique to study the solid-phase thermal decomposition reactions [13]. Although it typically operates in a different form in comparison to a real reactor (pyrolyzer, gasifier or combustor), it provides an understanding of thermal degradation processes occurring during the fuel conversion. In addition, as this study is focused on slow pyrolysis conversion of coffee grounds to solid and gaseous products, the conditions in the TGA represented real reactor conditions much more realistically that would be the case for processes deploying high heating rates, such as fast pyrolysis and gasification.

The thermal decomposition of biomass proceeds via a very complex set of competitive and concurrent reactions and thus, the exact mechanism for biomass pyrolysis remains unknown. Each step likely has its own single apparent activation energy, and thus the use

of an average, global apparent activation energy to define the kinetics of such processes could be interpreted as an inadequate simplification at best [14]. Furthermore, the DTG curves from these models may hide the true multi-stage character of pyrolytic reactions under a single peak [15].

During the second half of the 20th century several novel methods for determining Arrhenius parameters based on a single parameter emerged. These so-called “model-free” methods are founded on an isoconversional basis, wherein the degree of conversion, X , for a reaction was assumed to be constant and therefore the reaction rate, k , depended exclusively on the reaction temperature, T . By allowing apparent activation energy (E_a) to be calculated a priori, these approaches eliminate the need to initially hypothesize a form and rate order for the kinetic equation. Hence, isoconversional methods do not require previous knowledge of the reaction mechanism for biomass thermal degradation. Another advantage of such approaches is that the systematic error resulting from the kinetic analysis during the estimation of the Arrhenius parameters is eliminated [16]. Isoconversional models can follow either a differential or an integral approach to the treatment of TGA data. So, they are considered as a helpful solution for truly determining apparent activation energy [13].

During pyrolysis, due to the poor thermal conductivity of biomass, a temperature gradient is normally developed through the biomass sample between the external surface and the internal part. This gradient may be assumed to be proportional to the particle size, and decreases with reducing heating rate to the point that both, the external surface and the internal part of the biomass particles attains same temperature at a certain reaction time when appropriate time is given for heating [17]. Therefore, a defined particle size range was selected in this study to avoid the effect of the particle size on the determination of kinetic parameters under dynamic conditions of different heating rates.

Therefore, the main objectives of this study were, on the one hand to determine the kinetic parameters for the slow pyrolysis of such promising lignocellulosic residue, coffee ground residues, and its individual biopolymer components (cellulose, hemicellulose and lignin) employing isoconversional model-free dynamic methods: Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO), due to the advantages they offer in determining Arrhenius equation parameters without the need to make choices regarding kinetic models to be used [18]. The peak decomposition rates of biopolymers constituting the CGR and associated temperatures during pyrolysis process were evaluated. On the other hand, the non-condensable gases generated during the non-catalytic and catalytic tests were also monitored with reaction time and temperature by MS.

The obtained data and models provide important basis for design and operation of slow pyrolysis or staged pyrolysis systems using coffee ground residues for production of biochar and biofuels or high value-added chemicals.

2. Materials and methods

2.1. Materials

The biomass employed in this study was coffee ground residue (CGR), collected from local canteen at the University, ensuring that one type of beans was used. As the pre-dried CGR still contained ≈ 15 wt% of moisture, the material was air dried for 24 hours at 105 °C in a laboratory oven before further use. To avoid the effect of the particle size on the kinetic parameters determination, the CGR was crushed and sieved to collect particles in the range of 250 – 500 μm .

For the catalytic pyrolysis test, a Beta zeolite (Si/Al =150) in pellet form supplied by CLARIANT was employed. Prior to the catalytic pyrolysis test, the zeolite was crushed and sieved at same particle size as CGR sample.

2.2. Analytical techniques

The proximate analysis was determined according to European standards: moisture content (UNE-EN 14774-1:2010), ash content (UNE-EN 14775:2010), volatile matter (UNE-EN 15148:2010) and fixed carbon (determined by difference). A thermogravimetric analyzer, TGA (Mettler-Toledo TGA/DSC1) equipped with automatic sample handling was employed to assess the volatile matter and the ash contents of the coffee ground residue. This is a well established thermoanalytical technique for thermal degradation studies of solid materials, such as biomass pyrolysis [13].

A quadrupole mass spectrometer, MS (HIDEN Analytical HPR-20) with an electron ionisation source (70 eV) coupled to the TGA was employed for evolved gas analysis during the pyrolysis experiments. The ultimate analysis of feedstock and was carried out in a micro-elemental analyzer (Thermo Scientific) in order to determine content of C, H, N, S and O (by difference). The higher heating value (HHV) of CGR was calculated using the formula developed by Channiwala and Parikh [19]. The relative abundance of individual biopolymers (cellulose, hemicellulose and lignin) in CGR was determined by the sulfuric acid hydrolysis method [20].

2.3. *Pyrolysis tests*

The pyrolysis tests were performed in the same TGA previously mentioned, at atmospheric pressure. The CGR sample (around 15 mg) was deposited in an alumina crucible with a circular base and total volume of 150 μl . In this work, all the experiments were performed under non-isothermal conditions at 500 $^{\circ}\text{C}$ and different heating rates (HR), 5–100 $^{\circ}\text{C}/\text{min}$, with a nitrogen flow rate of 100 ml/min.

A zeolite to CGR ratio of 1:1 (g/g) was selected for the catalytic experiment, in which the Beta zeolite layer was deposited over the CGR sample in the crucible.

2.4. *Kinetic models*

The one-step global model assumes that the devolatilization phenomena proceeds as a single reaction.



where *Volatiles* represents the sum of the gas and bio-oil, and *char* is the remaining unreacted solid. The fundamental rate of transformation from solid-state to volatiles is generally described by the following expression:

$$\frac{dX}{dt} = k(T)f(X) \quad (2)$$

where X is the degree of conversion of the fuel, t is the reaction time, $k(T)$ is the reaction rate constant, and $f(X)$ is a function that represents the reaction model.

The degree of conversion, X , is calculated as its relative weight loss as follows:

$$X = \frac{m_0 - m_t}{m_0 - m_f} \quad (3)$$

where m_0 , m_t and m_f represents the initial mass, the mass at time t , and the final residual mass of the sample, respectively.

The reaction rate constant, k , is temperature dependent, and it obeys the fundamental Arrhenius rate expression:

$$k = A \cdot e^{\frac{-E_a}{RT}} \quad (4)$$

where A is the pre-exponential factor (min^{-1}), E_a is the apparent activation energy (kJ/mol), T is the absolute temperature (K) and R is the gas constant (8.314 J/mol·K).

Non-isothermal method employs a heating rate (β), normally linear, to raise the temperature. A linear heating program follows:

$$T = T_0 + \beta t \quad (5)$$

$$\beta = \frac{dT}{dt} \quad (6)$$

where T_0 is the starting temperature, β the constant heating rate (K/min), and T the temperature at time t . Then, substituting equations (4) and (6) in equation (2) gives:

$$\frac{dX}{dT} = \frac{A}{\beta} \cdot e^{\frac{-E_a}{RT}} f(X) \quad (7)$$

Equation (7) represents the differential form of the non-isothermal rate law.

Kinetics analysis is conventionally expected to produce a suitable kinetic description of the process in terms of the reaction model and the Arrhenius parameters. These three components, $f(X)$, E_a , and A , are sometimes called the “kinetic triplet”. There are many methods for analysing solid-state kinetic data [21]. These methods can be classified according to the experimental conditions and the mathematical analysis implemented. The mathematical approaches employed can be divided into model-fitting and isoconversional (model-free) methods. However, as discussed in the introduction section, in this work only the isoconversional model-free dynamic methods were used to calculate the kinetic parameters for the CGR pyrolysis, which require a set of experimental tests at different heating rates. These methods are the Kissinger, Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) methods. The advantages of the model-free analysis are: its simplicity, and the avoidance of errors associated to choices of a kinetic model [18].

2.5. Model-free methods

Kissinger method

This method allows for the kinetic parameters of a solid-state reaction without prior knowledge of the reaction mechanism. Kissinger [22] developed a model-free non-isothermal method where E_a does not need to be calculated for each conversion value in order to evaluate kinetic parameters. The method equation is represented as follows:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{A \cdot R}{E_a}\right) - \frac{E_a}{RT_m} \quad (8)$$

According to Kissinger, in the differential thermogravimetric curve (DTG), the temperature at which the peak weight loss velocity (in %/min) occurs for a given heating rate is determined by both A and E_a . Then, changing the heating rate the peak temperature will change. Hence, plotting $\ln(\beta/T_m^2)$ versus $1/T_m$, should give a straight line of slope $-E_a/R$.

Flynn-Wall-Ozawa method (FWO)

The *FWO* method [23,24] is one of the most commonly accepted methods for the computation of kinetic parameters. It allows for the apparent activation energy to be obtained for each degree of conversion from the equation:

$$\ln(\beta) = \ln\left(\frac{A_X \cdot E_{aX}}{R \cdot g(X)}\right) - 5.331 - 1.052 \frac{E_{aX}}{R \cdot T_X} \quad (9)$$

where E_{aX} is the apparent activation energy for a fix degree of conversion X , and is calculated from the slope of the straight line obtained by plotting logarithm of heating rates, $\ln\beta$, versus $1/T_X$, where T_X is the reaction temperature at which this grade of conversion X is reached.

Kissinger-Akahira-Sunose method (KAS)

The *KAS* method [22,25] is an integral isoconversional technique based on the following expression:

$$\ln\left(\frac{\beta}{T_X^2}\right) = \ln\left(\frac{A_X \cdot R}{E_{aX} \cdot g(X)}\right) - \frac{E_{aX}}{R \cdot T_X} \quad (10)$$

where E_{aX} is the apparent activation energy for a fix degree of conversion X , and is calculated from the slope of the straight line obtained by plotting $\ln(\beta/T_X^2)$, versus $1/T_X$, where T_X is the reaction temperature at which this grade of conversion X is reached.

3. Results and discussion

3.1. Biomass analysis

Table 1 summarizes the proximate and ultimate analysis, as well as composition in terms of key biopolymers (hemicellulose, cellulose and lignin) of CGR. The pre-dried sample still showed 5 wt% of moisture because this material rapidly adsorbs moisture during transfer and storage. The table also shows that CGR contains more carbon and less oxygen (and therefore lower O/C ratio ≈ 0.66) than woody biomass and agricultural residues (O/C $\approx 0.8-1.2$) [26]. Such behaviour is attributed to the higher lignin contents in CGR, which reaches 40.6 wt% (whose O/C ratio $\approx 0.4 - 0.5$), while hemicellulose and cellulose account for 36.6 and 10.6 wt%, respectively. This composition is rather similar to that reviewed by Obruca et al. [27] in terms of holocellulose biopolymers but with larger content of lignin. Consequently, the high heating value (HHV) of CGR, 23.4 MJ/kg, is higher than that of most biomass (17-20 MJ/kg) [26]. However, ultimate analysis also showed that CGR contains more nitrogen (2.3 wt%) than other more commonly used lignocellulosic biomass (0.1-1.0 wt%) due to high protein and caffeine content [4].

3.2. CGR thermochemical decomposition (TGA)

Fig. 1 shows both the conversion curves as weight loss in wt% (A), and their first derivative curves with time (DTG) as wt%/min (B) of the thermochemical decomposition of CGR as a function of reaction temperature under nitrogen atmosphere at 500 °C and at five heating rates (HR): 5 – 100 °C/min. The conversion curves at all heating rates indicate that mass loss of CGR mainly occurred at temperatures ranging from 250 to 500 °C. The conversion curves shift to the right with increasing heating rate as can be observed in Fig. 1(A), which implies higher values of initial decomposition temperature (see Table 2). However, this representation of the conversion data makes it difficult to identify the changes in the slope at different temperatures and reaction rates for the thermal decomposition of the three biopolymers contained in CGR. Therefore, the DTG curves, as shown in Fig. 1(B) were derived from the TG data, showing a first large peak with two

remarkable shoulders corresponding to the well-established order of biopolymers decomposition: hemicellulose, cellulose and lignin [28–30]. As the figure shows, the peak with the subsequent shoulders can be clearly distinguished for all the heating rates, with the exception of 100 °C/min. Although the identification of the maximum degradation rate of lignin in biomass is not commonly reported in the literature, as it usually overlaps with the cellulose decomposition peak [13,31,32], in the case of CGR it was possible, due to the large difference in cellulose and lignin contents, ≈ 11 and 42 wt%, respectively. Based on this initial observation it might be suggested that a more efficient staged pyrolysis process of these materials could be carried out to preferentially obtaining products of decomposition of individual biomass constituents separately when heating the material to different temperatures in stages.

On the other hand, it is evident from the results that increasing the heating rate from 5 to 100 °C/min resulted in a progressive rise in the total volatile matter released at 500 °C from 72.2 to 75.1 wt%, respectively as summarized in Table 2. This behaviour agrees with the theory that heating rate has an influence on the secondary reactions of the primary pyrolysis vapours. So, lower heating rates result in longer residence times of volatiles inside biomass particles and the reactor, favouring secondary reactions such as cracking, re-polymerization and re-condensation, which eventually lead to the char formation [13,17,33–35]. This is normally observed when comparing slow pyrolysis with fast/flash pyrolysis according to the product goal for the pyrolysis process; i.e., biochar production (for slow pyrolysis: 0.1-2 °C/s) or bio-oil production for fast (10-200 °C/s) and flash pyrolysis (>1000 °C/s) [36]. However, it is interesting to see this effect even in the heating rate range still corresponding to slow (5-50 °C/min) or at best intermediate (100 °C/min) pyrolysis here studied because it could be used to modulate the reaction to the desired products.

Fig. 2(A) depicts the temperatures of maximum decomposition rate of CGR biopolymers during pyrolysis as a function of the heating rate. Here it can be observed that these peak temperatures logarithmically depend on the heating rate for the three biopolymers; which implies that at low heating rates the mass transfer limitations are more important than at high heating rates, at which the maximum decomposition rate for the different biopolymers occurs at similar temperatures.

On the other hand, Fig. 2(B) shows that the maximum decomposition rate increased linearly with heating rate for all biopolymers in CGR. In addition, the observed difference in the slope of these lines suggests that the heating rate affected diverse biopolymers differently; thus, the more reactive the material (hemicellulose > cellulose > lignin) the higher the slope. As lignin is the most stable and complex of biopolymers comprising biomass, its amount is assumed to be the main rate limiting factor in the thermochemical decomposition process of CGR.

Fig. 3 shows the TG-MS spectrum of the evolved gas species during the pyrolysis of CGR at 500 °C and 15 °C/min heating rate versus reaction time. This technique is the only one to simultaneously measure in real time the thermal decomposition and the gas product distribution of a very small sample. DTG curve and temperature profile are also plotted to show which gaseous compounds were evolved at each stage of the pyrolysis and at which temperatures. Water is the principal component, and it has two origins. Firstly, the physically adsorbed water, which is desorbed at ≈ 90 °C; and secondly reaction water, produced at 250 – 400 °C, with a maximum production at 314 °C, originated from various dehydration reactions of the original CGR biopolymers and/or dehydration of the primary and secondary pyrolysis vapours from the removal of hydroxyl groups ($-OH$) overlapping with the main CGR degradation regime [37]. Fig. 4 displays the gases evolution trends at all the heating rates versus the reaction temperature. In this figure are also two water

peaks regardless the heating rate, 5 – 50 °C/min; though both peaks merged as a consequence of the fast heating at high heating rate. The other main gases, whose evolution also coincides with CGR decomposition rate profile are CO and CO₂. On the one hand, CO is mostly produced from the removal of carbonyl groups from biopolymers. While CO₂ is originated from decarboxylation of –COOH and O–Acetyl groups from the original biopolymers, principally the hemicellulose. But also these oxygenates are originated from primary and secondary vapours; generated in the same range of temperatures, with maximum production shifted to a slightly higher temperature 330 °C. These three oxygen containing gases seem to originate from the thermal degradation of the three biopolymers that constitute the CGR (hemicellulose, cellulose and lignin), which is visible on the DTG curve. Moreover, this is also demonstrated by the two small shoulders to the right from the main peak of these evolved gases.

The removal of methoxyl groups (–O–CH₃) from the lignocellulosic structure is associated with the CH₄ production during pyrolysis. CH₄ is released from the biomass structure as a consequence of multi-step reactions, so the removal of methoxyl substituents of the hemicellulose and lignin and the conversion of the alkyl chain of the lignin are attributed to the CH₄ evolution during biomass pyrolysis [38–41]. The release of (C₁–C₂) and H₂ is mainly due to the instability of intermediate condensable species produced during primary degradation. Thus, as temperature increased, the C–C and C–H bonds break to form free radicals, which are recombined into small molecular compounds like light hydrocarbons C₂H₄ and C₂H₆, while H₂ was mainly produced from the breaking of C–H bonds. These species are evolved to a much lower extent, which might be related to the aromatization or the char structure during the secondary pyrolysis [13]. Fig. 4 also shows that the first appearance of the different gaseous species are shifted to lower reaction temperatures as the heating rate was raised.

Fig. 5 displays the evolution with reaction time of the main evolved gases during a very preliminary catalytic pyrolysis test performed at 500 °C and 15 °C/min by placing a Beta zeolite layer over the CGR sample in the TGA crucible for comparison with its non-catalytic performance. In this figure can be appreciated that the progression of the oxygenated species, H₂O, CO and CO₂, during the catalytic test matched relatively well with that obtained without catalyst at temperatures below 400 °C, from which their production started to be slightly higher, especially CO. This means that the Beta zeolite employed herein shows certain deoxygenation activity for the pyrolysis primary vapors, but not much. However, is in the light hydrocarbons development where most significant differences are observed, reflecting a severe cracking activity of this zeolite over the pyrolysis primary and secondary vapours with temperature peaks around 475 – 500 °C [42]. On the one hand, the production of CH₄ and H₂ deviated from the non-catalytic behaviour above 405 °C, whilst the production of the C₂ hydrocarbons significantly increased from 330 to 500 °C, with peak productions of C₂H₄ and C₂H₆ at 470 and 485 °C, respectively. The utilisation of this type of catalyst would significantly increase the heating value of the gas fraction due to its higher hydrocarbons content.

3.3. Kinetic analysis

The TGA experimental data were analyzed in order to obtain the kinetic parameters using three model-free methods. To avoid any influence of the physically bound moisture desorption from CGR sample, the conversion (in wt%) was calculated from the experimental data collected at temperatures between 150 and 500 °C, corresponding to the active pyrolysis stage where hemicellulose, cellulose and lignin decomposition occurs. Figs. S1(A – C) show the plots corresponding to the Kissinger, FWO and KAS models, respectively, used to calculate the kinetic parameters of the dynamic degradation of the biopolymers in CGR according to equations described in Section 2.3. Data in Fig.

S1(A) were used to calculate the A and E_a according to the Kissinger method. This method has the disadvantage that these parameters are calculated just from the temperature that corresponds to the highest weight loss rate (DTG_{max}). So, it means that this method should be employed simply for those samples showing a single DTG peak. In the case of CGR, these parameters would purely correspond to the hemicellulose degradation, which is the most reactive biopolymer in this biomass, in terms of degradation rate as shown in Fig. 2, disregarding the role of the other two biopolymers. However, the FWO and KAS methods calculate the kinetic parameters based on values of conversion from 5 to 90 wt%, with a 5 wt% step as shown in **Figs. S1(B – C)**, which implies that the kinetic parameters for the individual biopolymers that comprise CGR may be estimated. These lines from linear fit at different conversion levels have fairly high linear correlation coefficients, > 0.995 (as summarized in **Table S1**), suggesting that the values of E_a and A satisfy accuracy requirements. This can be observed in **Fig. 6**, where the calculated apparent E_a is plotted as a function of the conversion level for FWO and KAS methods in comparison with that constant value obtained with Kissinger method. Here, it can be seen that E_a increases with temperature and conversion level. This is characteristic of processes with different reaction mechanisms. Even when each of the biopolymers that constitutes the CGR (hemicellulose, cellulose and lignin) has its own apparent activation energy, its thermal decomposition proceeds via a very complex set of competitive and concurrent reactions, due to the synergistic effects between its biopolymers. However, an approximate estimation of the E_a of these components can be assessed from the average values of different steps shown in **Fig. 6**. Thus, hemicellulose, cellulose and lignin would present values of 213, 240 and 265 kJ/mol, respectively according to FWO method; while 215, 242 and 268 kJ/mol, respectively for the KAS method as is summarized in **Table S1**.

The results show that the values estimated for the decomposition of hemicellulose are very close to those obtained for CGR using the Kissinger method (212 kJ/mol), which is in concordance as this method uses the maximum decomposition rate to calculate the kinetic parameters. When the conversion increases further than 80 wt%, the apparent activation energy increased sharply from 273 kJ/mol to 347 kJ/mol for FWO, and from 276 kJ/mol to 353 kJ/mol for KAS method as shown in Table S1, which could be due to the re-polymerization and re-condensation reactions leading to char formation. Then, taking into account all the steps in the pyrolysis process of the coffee ground residues, the apparent activation energy for the whole process was estimated as 244 and 241 kJ/mol for KAS and FWO methods, respectively. These E_a results are in correspondence with thermostability sequence analysis of these three CGR biopolymer components (hemicellulose, cellulose and lignin) [43]. Therefore, the lignin content would be the main controlling factor in biomass pyrolysis in industrial processes [44]. In this way, these kind of model-free isoconversional dynamic methods have been shown as a very useful tools to assess the kinetic parameters of CGR, as they can provide E_a values to be applied in models for designing reactors for its utilisation as fuel. Furthermore, due to the ability to obtain kinetic parameters for decomposition of individual biopolymers, the data could be used for designing a more efficient staged pyrolysis process allowing preferential recovery of decomposition products of individual biopolymers separately. Such process would enable more efficient production of high-value chemicals from biomass.

Conclusions

In this work, the utilisation of coffee ground residues, a lignocellulosic residue whose worldwide production is continuously increasing, has been explored for its pyrolysis application through the calculation of its kinetics parameters and those for its biopolymers constituents by thermogravimetric analysis. For that purpose, a thermogravimetric

analyser coupled to a mass spectrometer (TG-MS) for the online detection of the evolved gases were employed to perform the pyrolysis tests at different heating rates (5 – 100 °C/min) and at maximum temperature of 500 °C. The results show that the heating rate significantly affected the thermal decomposition of coffee ground residues during pyrolysis. The maximum decomposition rate increased linearly with the heating rate; but also, the more reactive the material (hemicellulose > cellulose > lignin) the higher the slope.

Main gases produced during the pyrolysis of CGR were oxygen containing species, and were evolved between 250 and 425 °C, with H₂O being the most important (from the removal of hydroxyl groups –OH), followed by CO (from decarbonylation reactions) and CO₂ (from decarboxylation reactions) of parent biopolymers and primary and secondary vapours. The use of the Beta zeolite had only negligible effect on deoxygenation reactions, however it significantly promoted cracking reactions of pyrolysis primary and secondary vapours giving rise to a significant increase of light hydrocarbons formation (C₁-C₂) with the subsequent improvement in the heating value of the pyrolysis gas.

Kinetic parameters of the pyrolysis process were determined using isoconversional methods. While with the Kissinger method a single value for the apparent activation energy was obtained (212 kJ/mol), which correspond to the hemicellulose decomposition (as the most reactive component in this biomass), KAS and FWO methods showed that the E_a increases with the conversion level, revealing a complex set of competitive and concurrent reactions. The average value for the E_a of the hemicellulose, cellulose and lignin from these two methods were equal to 214, 241 and 266 kJ/mol, respectively. Whereas the apparent activation energy for the whole pyrolysis process would increase up to 242 kJ/mol. The use of model-free isoconversional dynamic methods proved to be valuable to assess the kinetic parameters of CGR. The E_a values for pyrolysis of CGR are

important input parameters for modelling and design of reactors and their optimisation for production of biochar, fuels or high added-value chemicals.

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Highlights

- Maximum decomposition rate of each biopolymer increased linearly with heating rate.
- Maximum biopolymers reactivity decreased in the order of: hemicellulose > cellulose > lignin.
- MS evolution of oxygenates (H₂O, CO and CO₂) overlaps with main CGR degradation regime (250 – 425 °C).
- Catalytic pyrolysis improved deoxygenation only negligibly but importantly enhanced vapours cracking.
- KAS and FWO kinetic methods satisfactorily gave rise to E_a values of CGR individual biopolymers.

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11 **Title:**
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13 **Thermochemical decomposition of coffee ground residues: a kinetic study**
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62 **Thermochemical decomposition of coffee ground residues: a kinetic study**
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82 **Abstract**
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84 A thermogravimetric analyser coupled to a mass spectrometer, for evolved gas analysis,
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86 were employed to perform pyrolysis tests at heating rates (5 – 100 °C/min) and at
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88 maximum temperature of 500 °C to determine kinetic parameters of thermochemical
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90 decomposition of the biopolymers comprising coffee ground residues. During the
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92 pyrolysis process, the maximum decomposition rate of each biomass component
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94 increased linearly with the heating rate used. The slope increased with the biopolymer
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96 reactivity in the following sequence: hemicellulose > cellulose > lignin. Accordingly,
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98 kinetic parameters for any of these individual biopolymers in CGR were estimated using
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100 the model-free isoconversional dynamic methods: Kissinger–Akahira–Sunose (KAS) and
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102 Flynn–Wall–Ozawa (FWO) models. The average value for the apparent activation energy
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104 of the individual biopolymers (hemicellulose, cellulose and lignin) in CGR calculated by
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106 KAS and FWO methods: were estimated as 214, 241 and 266 kJ/mol, respectively; whilst
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108 for the CGR as a whole it was 242 kJ/mol. The two model-free isoconversional dynamic
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110 methods have been shown to be useful tools for assessment of biomass pyrolysis kinetic
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112 parameters, as they can provide E_a values for use in reactor design models.
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121 **Keywords:** coffee ground residues; kinetics; isoconversional methods; apparent
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123 activation energy
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126 127 **1. Introduction**

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129 The depletion of fossil fuel reserves and the environmental problems derived from their
130 utilization have made necessary the use of alternative fuels. Biomass is a clean and
131 renewable energy source leading to environmental, technical and economic benefits.
132 Residues from agricultural production and processing industries are readily available in
133 large quantities. Coffee is the second most traded commodity in the world after oil, and
134 one of the most widely consumed beverages in the world [1]. Moreover, the residues
135 derived from its production are steadily increasing in proportion to the coffee
136 consumption growth [1–3]. Coffee silverskin and spent coffee grounds are the main
137 coffee industry residues [4]. The latter is a residue with fine particle size, high humidity
138 (≈ 80 wt%), organic load and acidity, obtained during the treatment of raw coffee powder
139 with hot water or steam for the instant coffee preparation. Therefore, this residue is
140 generated in large amounts, with a worldwide annual generation of 8 million tons [3]. On
141 an average one ton of green coffee generates about 650 kg of spent coffee ground and
142 about 2 kg of wet spent coffee ground are generated per kg of soluble coffee produced
143 [5]. Coffee grounds are disposed as household waste that may be incinerated and/or
144 moved to landfill [4]. Some alternative applications for coffee ground residues are their
145 utilisation to produce compost [6], deodorizer or adsorbents [7,8], as well as source of
146 renewable energy [9,10]. In this latter regard, the pyrolysis is a thermochemical
147 conversion process that, depending on the reaction conditions, can be used to transform
148 biomass directly into liquid, solid or gaseous biofuels [11]. However, pyrolysis is also the
149 first stage of other thermochemical processes, such as combustion and gasification. In
150 this respect, a systematic understanding of pyrolysis kinetics is a key factor for the
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180 assessment of feasibility, design, and scale-up of such biomass conversion processes for
181 energy applications [12]. Thermogravimetric analysis (TGA) is the most commonly used
182 technique to study the solid-phase thermal decomposition reactions [13]. Although it
183 typically operates in a different form in comparison to a real reactor (pyrolyzer, gasifier
184 or combustor), it provides an understanding of thermal degradation processes occurring
185 during the fuel conversion. In addition, as this study is focused on slow pyrolysis
186 conversion of coffee grounds to solid and gaseous products, the conditions in the TGA
187 represented real reactor conditions much more realistically that would be the case for
188 processes deploying high heating rates, such as fast pyrolysis and gasification.

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190 The thermal decomposition of biomass proceeds via a very complex set of competitive
191 and concurrent reactions and thus, the exact mechanism for biomass pyrolysis remains
192 unknown. Each step likely has its own single apparent activation energy, and thus the use
193 of an average, global apparent activation energy to define the kinetics of such processes
194 could be interpreted as an inadequate simplification at best [14]. Furthermore, the DTG
195 curves from these models may hide the true multi-stage character of pyrolytic reactions
196 under a single peak [15].

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198 During the second half of the 20th century several novel methods for determining
199 Arrhenius parameters based on a single parameter emerged. These so-called “model-free”
200 methods are founded on an isoconversional basis, wherein the degree of conversion, X ,
201 for a reaction was assumed to be constant and therefore the reaction rate, k , depended
202 exclusively on the reaction temperature, T . By allowing apparent activation energy (E_a)
203 to be calculated a priori, these approaches eliminate the need to initially hypothesize a
204 form and rate order for the kinetic equation. Hence, isoconversional methods do not
205 require previous knowledge of the reaction mechanism for biomass thermal degradation.
206 Another advantage of such approaches is that the systematic error resulting from the
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237 kinetic analysis during the estimation of the Arrhenius parameters is eliminated [16].

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241 Isoconversional models can follow either a differential or an integral approach to the
242 treatment of TGA data. So, they are considered as a helpful solution for truly determining
243 apparent activation energy [13].
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247 Therefore, the main objective of this study was to determine the kinetic parameters for
248 the slow pyrolysis of coffee ground residues (CGR) and its individual biopolymer
249 components (cellulose, hemicellulose and lignin) employing isoconversional model-free
250 dynamic methods: Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO),
251 due to the advantages they offer in determining Arrhenius equation parameters without
252 the need to make choices regarding kinetic models to be used [17].
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260 During pyrolysis, due to the poor thermal conductivity of biomass, a temperature gradient
261 is normally developed through the biomass sample between the external surface and the
262 internal part. This gradient may be assumed to be proportional to the particle size, and
263 decreases with reducing heating rate to the point that both, the external surface and the
264 internal part of the biomass particles attains same temperature at a certain reaction time
265 when appropriate time is given for heating [18]. Therefore, a defined particle size range
266 was selected in this study to avoid the effect of the particle size on the determination of
267 kinetic parameters under dynamic conditions of different heating rates.
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277 The peak decomposition rates of biopolymers constituting the CGR and associated
278 temperatures during pyrolysis process were evaluated. This was achieved by
279 thermogravimetric analysis utilising different heating rates under inert (N₂) atmosphere.
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283 The obtained data and models provide important basis for design and operation of slow
284 pyrolysis or estaged pyrolysis systems using coffee ground residues for production of
285 biochar and chemicals.
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291 **2. Materials and methods**

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298 2.1. *Materials*
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300 The biomass employed in this study was coffee ground residue (CGR), collected from
301 local canteen at the University, ensuring that one type of beans was used. As the pre-dried
302 CGR still contained ≈ 15 wt% of moisture, the material was air dried for 24 hours at 105
303 °C in a laboratory oven before further use. To avoid the effect of the particle size on the
304 kinetic parameters determination, the CGR was crushed and sieved to collect particles in
305 the range of 250 – 500 μm .
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313 2.2. *Analytical techniques*
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315 The proximate analysis was determined according to European standards: moisture
316 content (UNE-EN 14774-1:2010), ash content (UNE-EN 14775:2010), volatile matter
317 (UNE-EN 15148:2010) and fixed carbon (determined by difference). A
318 thermogravimetric analyzer, TGA (Mettler-Toledo TGA/DSC1) equipped with automatic
319 sample handling was employed to assess the volatile matter and the ash contents of the
320 coffee ground residue. This is a well established thermoanalytical technique for thermal
321 degradation studies of solid materials, such as biomass pyrolysis [13].
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329 A mass spectrometer, MS (HIDEN Analytical HPR-20) coupled to the TGA was
330 employed for evolved gas analysis during the pyrolysis experiments. The ultimate
331 analysis of feedstock and was carried out in a micro-elemental analyzer (Thermo
332 Scientific) in order to determine content of C, H, N, S and O (by difference). The higher
333 heating value (HHV) of CGR was calculated using the formula developed by Channiwala
334 and Parikh [19]. The relative abundance of individual biopolymers (cellulose,
335 hemicellulose and lignin) in CGR was determined by the sulfuric acid hydrolysis method
336 [20].
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347 2.3. *Pyrolysis tests*
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349 The pyrolysis tests were performed in the same TGA previously mentioned, at
350 atmospheric pressure. The CGR sample (around 15 mg) was deposited in an alumina
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357 crucible with a circular base and total volume of 150 μl . In this work, all the experiments
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359 were performed under non-isothermal conditions at different heating rates (HR), 5–
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361 100°C/min, with a nitrogen flow rate of 100 ml/min.
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363 2.4. Kinetic models

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365 The one-step global model assumes that the devolatilization phenomena proceeds as a
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367 single reaction.
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371 where *Volatiles* represents the sum of the gas and bio-oil, and *char* is the remaining
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373 unreacted solid. The fundamental rate of transformation from solid-state to volatiles is
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375 generally described by the following expression:
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$$378 \frac{dX}{dt} = k(T)f(X) \quad (2)$$

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380 where X is the degree of conversion of the fuel, t is the reaction time, $k(T)$ is the reaction
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382 rate constant, and $f(X)$ is a function that represents the reaction model.
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386 The degree of conversion, X , is calculated as its relative weight loss as follows:
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$$388 X = \frac{m_0 - m_t}{m_0 - m_f} \quad (3)$$

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390 where m_0 , m_t and m_f represents the initial mass, the mass at time t , and the final residual
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392 mass of the sample, respectively.
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396 The reaction rate constant, k , is temperature dependent, and it obeys the fundamental
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398 Arrhenius rate expression:
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$$400 k = A \cdot e^{\frac{-E_a}{RT}} \quad (4)$$

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402 where A is the pre-exponential factor (min^{-1}), E_a is the apparent activation energy
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404 (kJ/mol), T is the absolute temperature (K) and R is the gas constant (8.314 J/mol·K).
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408 Non-isothermal method employs a heating rate (β), normally linear, to raise the
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410 temperature. A linear heating program follows:
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$$T = T_0 + \beta t \quad (5)$$

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$$\beta = \frac{dT}{dt} \quad (6)$$

422 where T_0 is the starting temperature, β the constant heating rate (K/min), and T the
423 temperature at time t . Then, substituting equations (4) and (6) in equation (2) gives:
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$$\frac{dX}{dT} = \frac{A}{\beta} \cdot e^{\frac{-E_a}{RT}} f(X) \quad (7)$$

429 Equation (7) represents the differential form of the non-isothermal rate law.
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431 Kinetics analysis is conventionally expected to produce a suitable kinetic description of
432 the process in terms of the reaction model and the Arrhenius parameters. These three
433 components, $f(X)$, E_a , and A , are sometimes called the “kinetic triplet”. There are many
434 methods for analysing solid-state kinetic data [21]. These methods can be classified
435 according to the experimental conditions and the mathematical analysis implemented.
436 The mathematical approaches employed can be divided into model-fitting and
437 isoconversional (model-free) methods. However, as discussed in the introduction section,
438 in this work only the isoconversional model-free dynamic methods were used to calculate
439 the kinetic parameters for the CGR pyrolysis, which require a set of experimental tests at
440 different heating rates. These methods are the Kissinger, Kissinger-Akahira-Sunose
441 (KAS) and Flynn-Wall-Ozawa (FWO) methods. The advantages of the model-free
442 analysis are: its simplicity, and the avoidance of errors associated to choices of a kinetic
443 model [17].
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459 2.5. Model-free methods

460 *Kissinger method*

461 This method allows for the kinetic parameters of a solid-state reaction without prior
462 knowledge of the reaction mechanism. Kissinger [22] developed a model-free non-
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isothermal method where E_a does not need to be calculated for each conversion value in order to evaluate kinetic parameters. The method equation is represented as follows:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{A \cdot R}{E_a}\right) - \frac{E_a}{RT_m} \quad (8)$$

According to Kissinger, in the differential thermogravimetric curve (DTG), the temperature at which the peak weight loss velocity (in %/min) occurs for a given heating rate is determined by both A and E_a . Then, changing the heating rate the peak temperature will change. Hence, plotting $\ln(\beta/T_m^2)$ versus $1/T_m$, should give a straight line of slope $-E_a/R$.

Flynn-Wall-Ozawa method (FWO)

The *FWO* method [23,24] is one of the most commonly accepted methods for the computation of kinetic parameters. It allows for the apparent activation energy to be obtained for each degree of conversion from the equation:

$$\ln(\beta) = \ln\left(\frac{A_X \cdot E_{a_X}}{R \cdot g(X)}\right) - 5.331 - 1.052 \frac{E_{a_X}}{R \cdot T_X} \quad (9)$$

where E_{a_X} is the apparent activation energy for a fix degree of conversion X , and is calculated from the slope of the straight line obtained by plotting logarithm of heating rates, $\ln\beta$, versus $1/T_X$, where T_X is the reaction temperature at which this grade of conversion X is reached.

Kissinger-Akahira-Sunose method (KAS)

The *KAS* method [22,25] is an integral isoconversional technique based on the following expression:

$$\ln\left(\frac{\beta}{T_X^2}\right) = \ln\left(\frac{A_X \cdot R}{E_{a_X} \cdot g(X)}\right) - \frac{E_{a_X}}{R \cdot T_X} \quad (10)$$

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533
534 where E_{ax} is the apparent activation energy for a fix degree of conversion X , and is
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536 calculated from the slope of the straight line obtained by plotting $\ln(\beta/T_X^2)$, versus $1/T_X$,
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538 where T_X is the reaction temperature at which this grade of conversion X is reached.
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541 **3. Results and discussion**

542 *3.1. Biomass analysis*

543
544 Table 1 summarizes the proximate and ultimate analysis, as well as composition in terms
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546 of key biopolymers (hemicellulose, cellulose and lignin) of CGR. The pre-dried sample
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548 still showed 5 wt% of moisture because this material rapidly adsorbs moisture during
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550 transfer and storage. The table also shows that CGR contains more carbon and less oxygen
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552 (and therefore lower O/C ratio ≈ 0.66) than woody biomass and agricultural residues (O/C
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554 $\approx 0.8-1.2$) [26]. Such behaviour is attributed to the higher lignin contents in CGR, which
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556 reaches 40.6 wt% (whose O/C ratio $\approx 0.4 - 0.5$), while hemicellulose and cellulose
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558 account for 36.6 and 10.6 wt%, respectively. This composition is rather similar to that
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560 reviewed by Obruca et al. [27] in terms of holocellulose biopolymers but with larger
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562 content of lignin. Consequently, the high heating value (HHV) of CGR, 23.4 MJ/kg, is
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564 higher than that of most biomass (17-20 MJ/kg) [26]. However, ultimate analysis also
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566 showed that CGR contains more nitrogen (2.3 wt%) than other more commonly used
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568 lignocellulosic biomass (0.1-1.0 wt%) due to high protein and caffeine content [4].
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571 *3.2. CGR thermochemical decomposition (TGA)*

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573 Fig. 1 shows both the conversion curves as weight loss in wt% (A), and their first
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575 derivative curves with time (DTG) as wt%/min (B) of the thermochemical decomposition
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577 of CGR as a function of reaction temperature under nitrogen atmosphere at 500 °C and at
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579 five heating rates (HR): 5 – 100 °C/min. The conversion curves at all heating rates indicate
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581 that mass loss of CGR mainly occurred at temperatures ranging from 250 to 500 °C. The
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583 conversion curves shift to the right with increasing heating rate as can be observed in Fig.
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593 1(A), which implies higher values of initial decomposition temperature (see Table 2).
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595 However, this representation of the conversion data makes it difficult to identify the
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597 changes in the slope at different temperatures and reaction rates for the thermal
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599 decomposition of the three biopolymers contained in CGR. Therefore, the DTG curves,
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601 as shown in Fig. 1(B) were derived from the TG data, clearly showing three conversion
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603 peaks corresponding to the well established order of biopolymers decomposition:
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605 hemicellulose, cellulose and lignin [28–30]. As the figure shows, the three peaks can be
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607 clearly distinguished for all the heating rates, with the exception of 100 °C/min. Although
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609 the identification of the maximum degradation rate of lignin in biomass is not commonly
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611 reported in the literature, as it usually overlaps with the cellulose decomposition peak
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613 [13,31,32], in the case of CGR it was possible, due to the large difference in cellulose and
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615 lignin contents, \approx 11 and 42 wt%, respectively. Based on this initial observation it might
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617 be suggested that a more efficient staged pyrolysis process of these materials could be
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619 carried out to preferentially obtaining products of decomposition of individual biomass
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621 constituents separately when heating the material to different temperatures in stages.
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623 On the other hand, it is evident from the results that increasing the heating rate from 5 to
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625 100 °C/min resulted in a progressive rise in the total volatile matter released at 500 °C
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627 from 72.2 to 75.1 wt%, respectively as summarized in Table 2. This behaviour agrees
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629 with the theory that heating rate has an influence on the secondary reactions of the primary
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631 pyrolysis vapours. So, lower heating rates result in longer residence times of volatiles
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633 inside biomass particles and the reactor, favouring secondary reactions such as cracking,
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635 re-polymerization and re-condensation, which eventually lead to the char formation
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637 [13,18,33–35]. This is normally observed when comparing slow pyrolysis with fast/flash
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639 pyrolysis according to the product goal for the pyrolysis process; i.e., biochar production
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641 (for slow pyrolysis: 0.1-2 °C/s) or bio-oil production for fast (10-200 °C/s) and flash
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652 pyrolysis (>1000 °C/s) [36]. However, it is interesting to see this effect even in the heating
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654 rate range still corresponding to slow (5-50 °C/min) or at best intermediate (100 °C/min)
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656 pyrolysis here studied because it could be used to modulate the reaction to the desire
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658 products.
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661 Fig. 2(A) depicts the temperatures of maximum decomposition rate of CGR biopolymers
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663 during pyrolysis as a function of the heating rate. Here it can be observed that these peak
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665 temperatures logarithmically depend on the heating rate for the three biopolymers; which
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667 implies that at low heating rates the mass transfer limitations are more important than at
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669 high heating rates, at which the maximum decomposition rate for the different biopolymers
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671 occurs at similar temperatures.
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674 On the other hand, Fig. 2(B) shows that the maximum decomposition rate increased
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676 linearly with heating rate for all biopolymers in CGR. In addition, the observed
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678 difference in the slope of these lines suggests that the heating rate affected diverse
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680 biopolymers differently; thus, the more reactive the material (hemicellulose > cellulose >
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682 lignin) the higher the slope. As lignin is the most stable and complex of biopolymers
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684 comprising biomass, its amount is assumed to be the main rate limiting factor in the
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686 thermochemical decomposition process of CGR.
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689 Fig. 3 shows the MS spectrum of the evolved gas species during the pyrolysis of CGR at
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691 500 °C and 15 °C/min heating rate versus reaction time. DTG curve and temperature
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693 profile are also plotted to show which gaseous compounds were evolved at each stage of
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695 the pyrolysis and at which temperatures. Water is the principal component, and it has two
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697 origins. Firstly, the physically adsorbed water, which is desorbed at ≈ 90 °C; and secondly
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699 reaction water, produced at 250 – 400 °C, with a maximum production at 314 °C,
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701 originated from various dehydration reactions of the original CGR biopolymers and/or
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703 dehydration of the primary and secondary pyrolysis vapours [37]. The other main gases
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711 are CO and CO₂ produced from decarbonylation and decarboxylation reactions of same
712 original biopolymers and primary and secondary vapours, respectively; generated in the
713 same range of temperatures, with maximum production shifted to a slightly higher
714 temperature 330 °C. These three oxygen containing gases seem to originate from the
715 thermal degradation of the three biopolymers that constitute the CGR (hemicellulose,
716 cellulose and lignin), which is visible on the DTG curve. Moreover, this is also
717 demonstrated by the two small shoulders to the right from the main peak of these evolved
718 gases. In addition, H₂ and light hydrocarbons (C₁-C₂) are evolved to a much lower extent,
719 with two small peaks appearing at 330 and 480 °C, which might be related to the
720 aromatization or the char structure during the secondary pyrolysis [13]. These gas
721 evolution trends apply to all the heating rates investigated in this study.

734 3.3. Kinetic analysis

735
736 The TGA experimental data were analyzed in order to obtain the kinetic parameters using
737 three model-free methods. To avoid any influence of the physically bound moisture
738 desorption from CGR sample, the conversion (in wt%) was calculated from the
739 experimental data collected at temperatures between 150 and 500 °C, corresponding to
740 the active pyrolysis stage where hemicellulose, cellulose and lignin decomposition
741 occurs. Figs. 4(A – C) show the plots corresponding to the Kissinger, FWO and KAS
742 models, respectively, used to calculate the kinetic parameters of the dynamic degradation
743 of the biopolymers in CGR according to equations described in Section 2.3. Data in Fig.
744 4(A) were used to calculate the A and E_a according to the Kissinger method. This method
745 has the disadvantage that these parameters are calculated just from the temperature that
746 corresponds to the highest weight loss rate (DTG_{max}). So, it means that this method should
747 be employed simply for those samples showing a single DTG peak. In the case of CGR,
748 these parameters would purely correspond to the hemicellulose degradation, which is the
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770 most reactive biopolymer in this biomass, in terms of degradation rate as shown in Fig.
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772 2, disregarding the role of the other two biopolymers. However, the FWO and KAS
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774 methods calculate the kinetic parameters based on values of conversion from 5 to 90 wt%,
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776 with a 5 wt% step as shown in Figs. 4(B – C), which implies that the kinetic parameters
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778 for the individual biopolymers that comprise CGR may be estimated. These lines from
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781 linear fit at different conversion levels have fairly high linear correlation coefficients, >
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783 0.995 (as summarized in Table 3), suggesting that the values of E_a and A satisfy accuracy
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785 requirements. This can be observed in Fig. 5, where the calculated apparent E_a is plotted
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787 as a function of the conversion level for FWO and KAS methods in comparison with that
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789 constant value obtained with Kissinger method. Here, it can be seen that E_a increases with
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791 temperature and conversion level. This is characteristic of processes with different
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793 reaction mechanisms. Even when each of the biopolymers that constitutes the CGR
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795 (hemicellulose, cellulose and lignin) has its own apparent activation energy, its thermal
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797 decomposition proceeds via a very complex set of competitive and concurrent reactions,
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799 due to the synergistic effects between its biopolymers. However, an approximate
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801 estimation of the E_a of these components can be assessed from the average values of
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803 different steps shown in Fig. 5. Thus, hemicellulose, cellulose and lignin would present
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805 values of 213, 240 and 265 kJ/mol, respectively according to FWO method; while 215,
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807 242 and 268 kJ/mol, respectively for the KAS method as is summarized in Table 3.

810 The results show that the values estimated for the decomposition of hemicellulose are
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812 very close to those obtained for CGR using the Kissinger method (212 kJ/mol), which is
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814 in concordance as this method uses the maximum decomposition rate to calculate the
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816 kinetic parameters. When the conversion increases further than 80 wt%, the apparent
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818 activation energy increased sharply from 273 kJ/mol to 347 kJ/mol for FWO, and from
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820 276 kJ/mol to 353 kJ/mol for KAS method as shown in Table 3, which could be due to
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829 the re-polymerization and re-condensation reactions leading to char formation. Then,
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831 taking into account all the steps in the pyrolysis process of the coffee ground residues, the
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833 apparent activation energy for the whole process was estimated as 244 and 241 kJ/mol
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835 for KAS and FWO methods, respectively. These E_a results are in correspondence with
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837 thermostability sequence analysis of these three CGR biopolymer components
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839 (hemicellulose, cellulose and lignin) [38]. Therefore, the lignin content would be the main
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841 controlling factor in biomass pyrolysis in industrial processes [39]. In this way, these kind
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843 of model-free isoconversional dynamic methods have been shown as useful tools to assess
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845 the kinetic parameters of CGR, as they can provide E_a values to be applied in models for
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847 designing reactors for its utilisation as fuel. Furthermore, due to the ability to obtain
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849 kinetic parameters for decomposition of individual biopolymers, the data could be used
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851 for designing a more efficient staged pyrolysis process allowing preferential recovery of
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853 decomposition products of individual biopolymers separately. Such process would enable
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855 more efficient production of high-value chemicals from biomass.
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860 **Conclusions**

861
862 In this work, the kinetic parameters of the thermochemical decomposition of biopolymer
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864 components of coffee ground residues were estimated by thermogravimetric analysis. For
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866 that purpose, a thermogravimetric analyser coupled to a mass spectrometer for the
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868 detection of the evolved gases were employed to perform the pyrolysis tests at different
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870 heating rates (5 – 100 °C/min) and at maximum temperature of 500 °C. The results shoed
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872 that the heating rate significantly affected the thermal decomposition of coffee ground
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874 residues during pyrolysis. The maximum decomposition rate increased linearly with the
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876 heating rate; but also, the more reactive the material (hemicellulose > cellulose > lignin)
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878 the higher the slope.
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888 Main gases produced during the pyrolysis of coffee ground residues were oxygen
889 containing species, and were evolved between 250 and 425 °C, with H₂O being the most
890 important, followed by CO (from decarbonylation reactions) and CO₂ (from
891 decarboxylation reactions) of parent biopolymers and primary and secondary vapours.
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896 Kinetic parameters of the pyrolysis process were determined using isoconversional
897 methods (Kissinger, KAS and FWO). The apparent activation energy (212 kJ/mol)
898 obtained from the Kissinger method would simply correspond to that of the hemicellulose
899 biopolymer in coffee residues, as the most reactive component in this biomass. However
900 with the other two methods, KAS and FWO, the apparent activation energy and pre-
901 exponential factors increase with the conversion level, revealing a complex set of
902 competitive and concurrent reactions. The apparent activation energy estimated for the
903 major constituents of coffee ground residues with the two isoconversional dynamic
904 methods, FWO and KAS, were rather similar as shown in Fig. 5 and summarized in Table
905 3. The average value for the E_a of the hemicellulose, cellulose and lignin from these two
906 methods were equal to 214, 241 and 266 kJ/mol, respectively. Whereas the apparent
907 activation energy for the whole pyrolysis process would increase up to 242 kJ/mol using
908 the same methods. Thus, these kind of model-free isoconversional dynamic methods
909 have been demonstrated to be valuable tools to assess the kinetic parameters of CGR, as
910 they can provide E_a values to be applied in models for designing reactors for its utilisation
911 as fuel; but also, for a more efficient staged pyrolysis process.
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Figures

Figure Captions

Fig. 1. TG (A) and DTG (B) curves of the thermal decomposition of coffee ground residues (CGR) under N₂ atmosphere at 500 °C and at different heating rates (5 – 100 °C/min).

Fig. 2. Temperature of maximum DTG (A) and DTG_{max} values (B) corresponding to the peaks associated to the thermochemical decomposition of three biopolymers (hemicellulose, cellulose and lignin) of coffee ground residues (CGR) under N₂ atmosphere at 500 °C and at different heating rates (5 – 100 °C/min).

Fig. 3. Conversion and DTG curves, and evolved gaseous species (MS signal) versus reaction time during the pyrolysis of coffee ground residues (CGR) under N₂ atmosphere at 500 °C (heating rate: 15 °C/min).

Fig. 4. Evolution of the gaseous species (MS signal) versus reaction time during the pyrolysis of coffee ground residues (CGR) under N₂ atmosphere at 500 °C and different heating rates.

Fig. 5. Evolution of the gaseous species (MS signal) versus reaction time during the non-catalytic (red) and catalytic (blue) pyrolysis of coffee ground residues (CGR) under N₂ atmosphere at 500 °C (heating rate: 15 °C/min).

Fig. 6. Calculated apparent activation energy for pyrolysis of coffee ground residues (CGR) by the Kissinger, FWO and KAS kinetic methods for heating rates of between 5 and 50 °C/min.

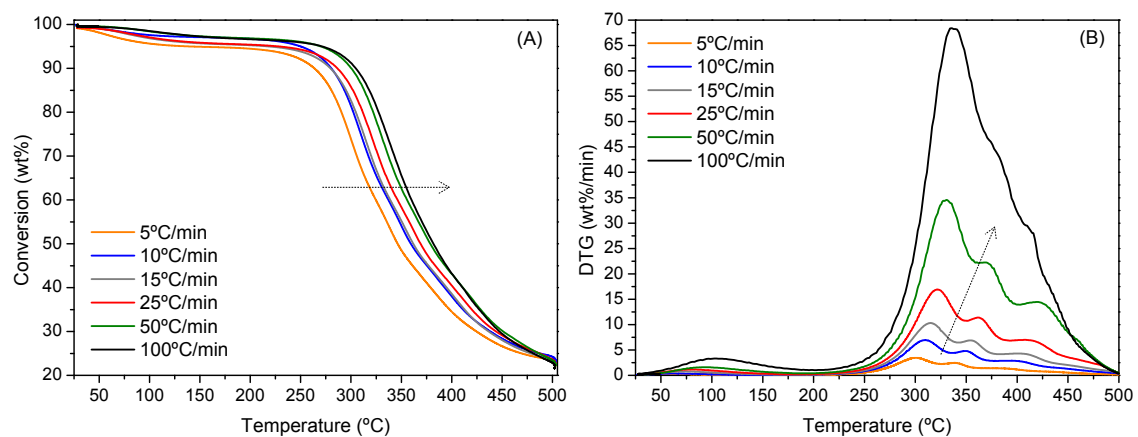


Fig. 1. TG (A) and DTG (B) curves of the thermal decomposition of coffee ground residues (CGR) under N₂ atmosphere at 500 °C and at different heating rates (5 – 100 °C/min).

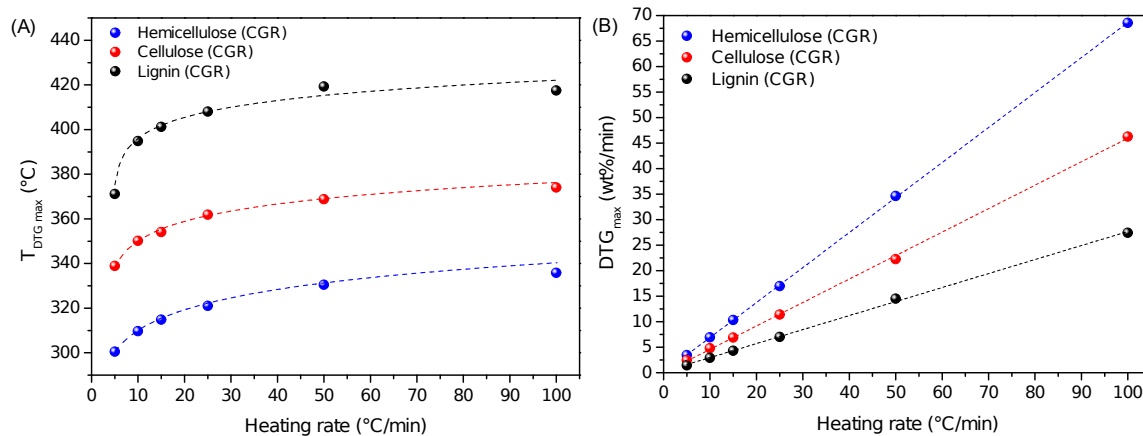


Fig. 2. Temperature of maximum DTG (A) and DTG_{max} values (B) corresponding to the peaks associated to the thermochemical decomposition of three biopolymers (hemicellulose, cellulose and lignin) of coffee ground residues (CGR) under N_2 atmosphere at 500 °C and at different heating rates (5 – 100 °C/min).

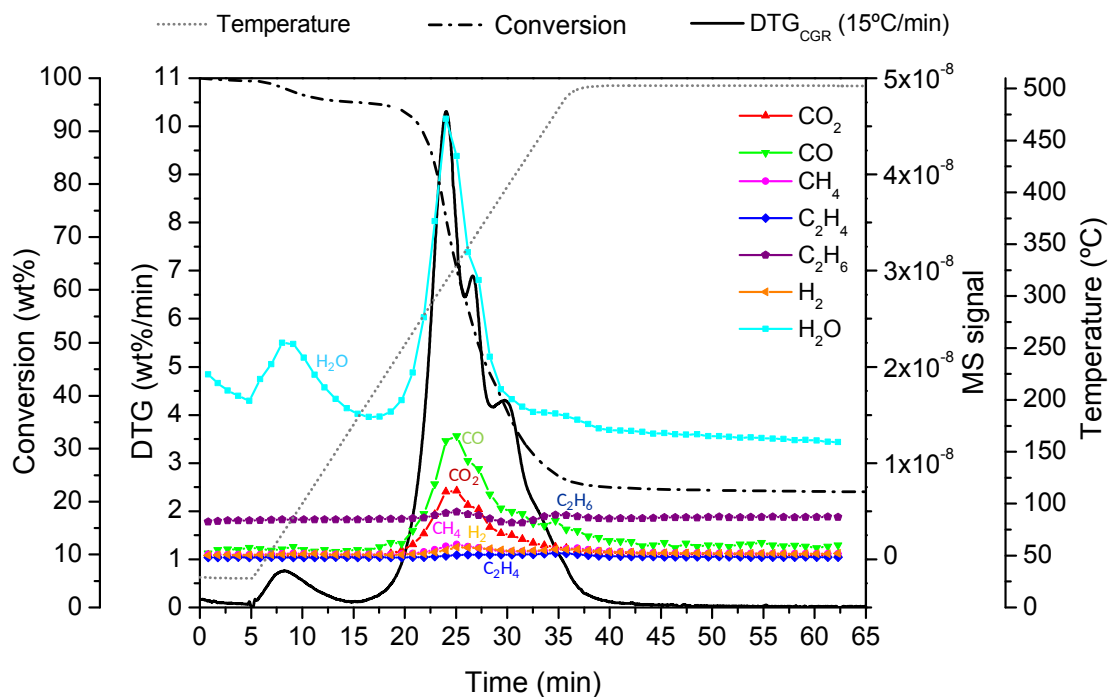


Fig. 3. Conversion and DTG curves, and evolved gaseous species (MS signal) versus reaction time during the pyrolysis of coffee ground residues (CGR) under N₂ atmosphere at 500 °C (heating rate: 15 °C/min).

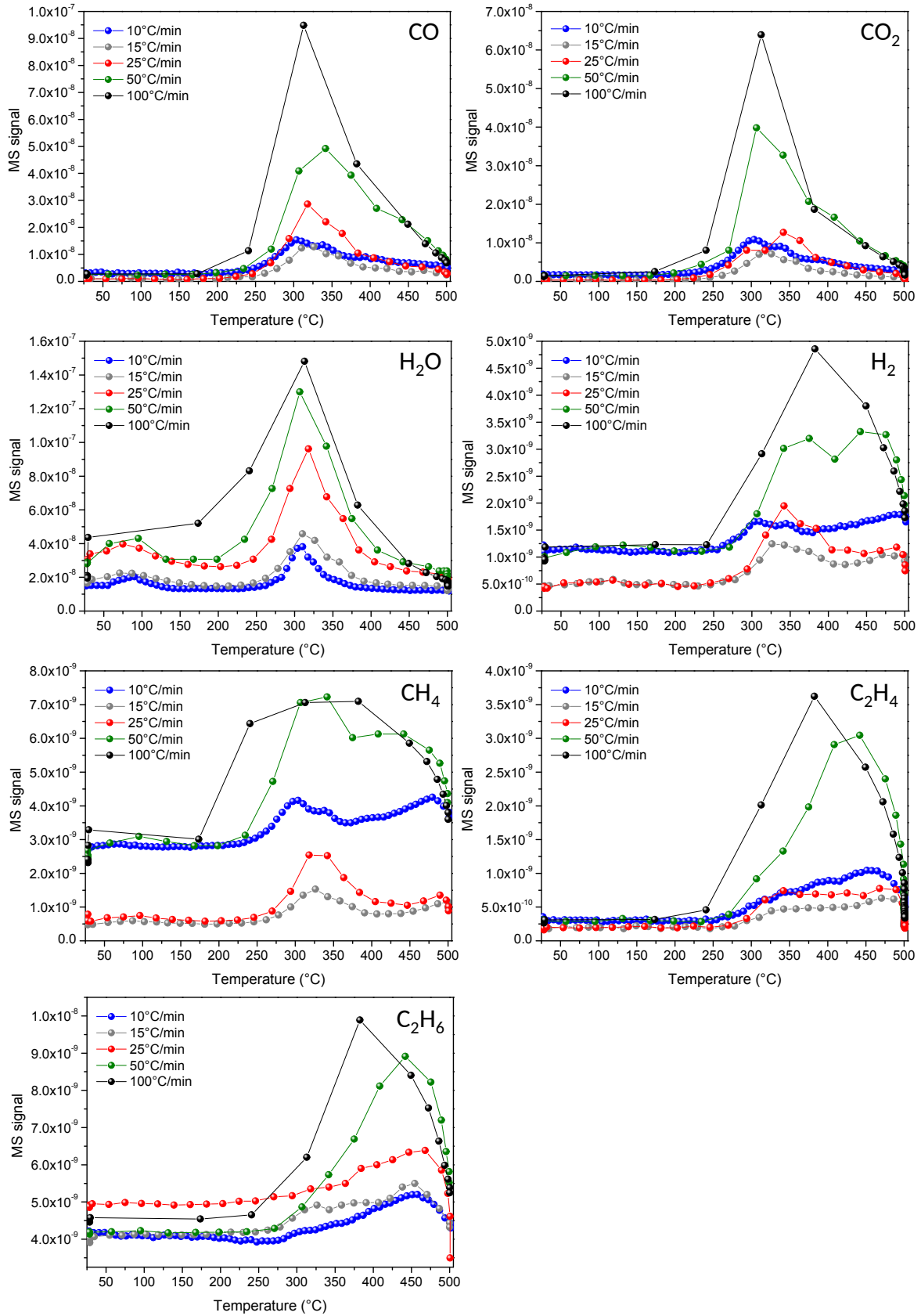


Fig. 4. Evolution of the gaseous species (MS signal) versus reaction temperature during the pyrolysis of coffee ground residues (CGR) under N₂ atmosphere at 500 °C and different heating rates.

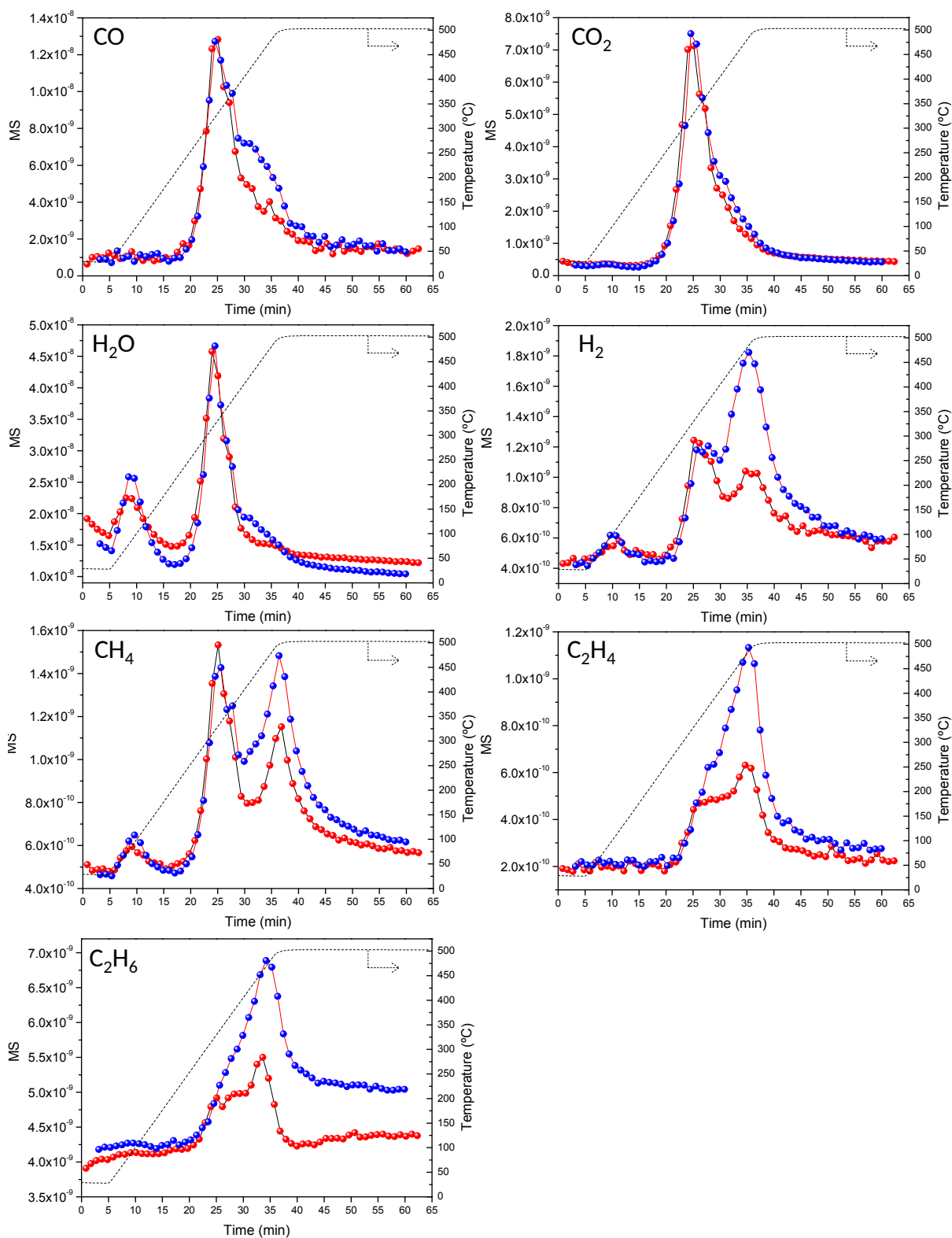


Fig. 5. Evolution of the gaseous species (MS signal) versus reaction time during the non-catalytic (red) and catalytic (blue) pyrolysis of coffee ground residues (CGR) under N₂ atmosphere at 500 °C (heating rate: 15 °C/min).

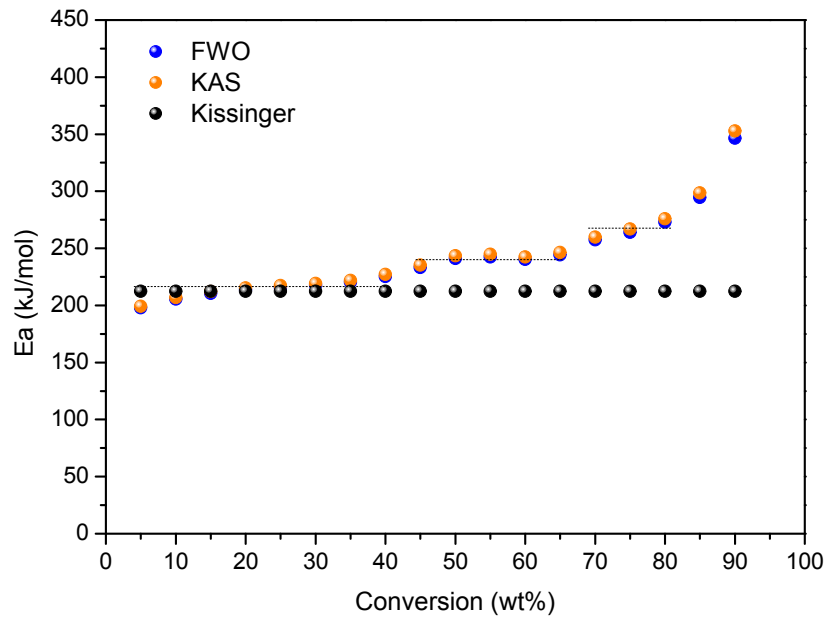


Fig. 6. Calculated apparent activation energy for pyrolysis of coffee ground residues (CGR) by the Kissinger, FWO and KAS kinetic methods for heating rates of between 5 and 50 °C/min.

SUPPORTING INFORMATION

Thermochemical decomposition of coffee ground residues by TG-MS: a kinetic study

Javier Feroso, Ondřej Mašek

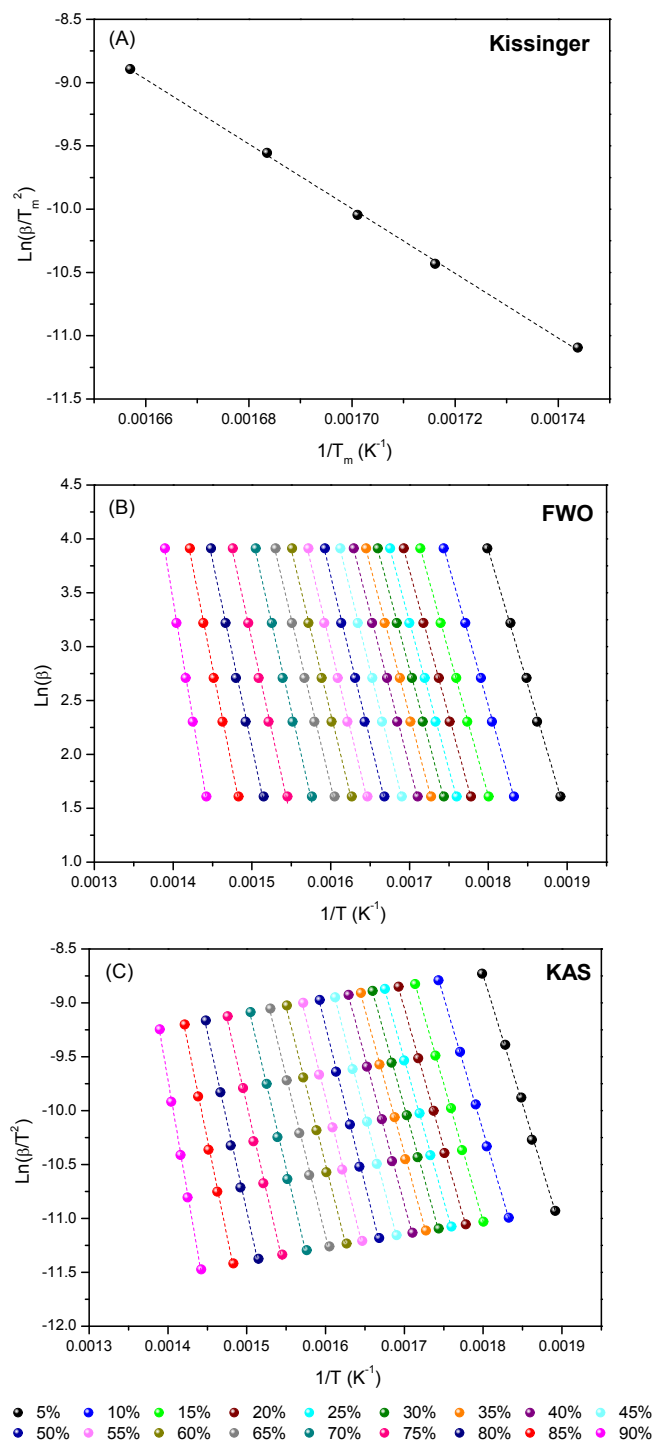


Fig. S1. Plots of the Kissinger (A), FWO (B) and KAS (C) kinetic methods of CGR thermal decomposition from 150 to 500 °C at different heating rates (5 – 50 °C/min) to the calculation of the apparent activation energy (E_a). Conversion values of between 5 and 90 wt% were used for FWO and KAS methods.

Table S1. Kinetic parameters of coffee ground residues (CGR) obtained from the Kissinger, KAS and FWO models

Conversion (wt%)	KAS			FWO		
	E_a (kJ mol ⁻¹)	A (min ⁻¹)	R ²	E_a (kJ mol ⁻¹)	A (min ⁻¹)	R ²
5	199.1	2.02E+19	0.9988	197.8	1.59E+19	0.9990
10	206.9	2.66E+19	0.9997	205.5	2.07E+19	0.9997
15	212.0	3.59E+19	0.9997	210.6	2.75E+19	0.9997
20	215.2	3.91E+19	0.9996	213.7	2.98E+19	0.9996
25	217.4	3.86E+19	0.9996	215.9	2.95E+19	0.9996
30	219.3	3.67E+19	0.9995	217.7	2.81E+19	0.9996
35	221.9	4.10E+19	0.9995	220.3	3.12E+19	0.9995
40	227.0	7.47E+19	0.9994	225.2	5.54E+19	0.9995
45	235.3	2.35E+20	0.9991	233.2	1.66E+20	0.9992
50	243.5	2.02E+19	0.9984	241.1	4.39E+20	0.9985
55	244.8	2.02E+19	0.9975	242.5	2.98E+20	0.9976
60	242.4	2.02E+19	0.9974	240.4	1.06E+20	0.9976
65	246.3	1.62E+20	0.9975	244.2	1.15E+20	0.9977
70	259.9	9.15E+20	0.9962	257.3	6.09E+20	0.9964
75	266.8	1.24E+21	0.9952	264.1	8.13E+20	0.9955
80	275.9	2.44E+21	0.9963	272.9	1.56E+21	0.9966
85	298.5	2.02E+19	0.9982	294.6	2.90E+22	0.9983
90	352.9	2.02E+19	0.9988	346.6	7.05E+25	0.9989
Estimated average values						
CGR	243.6	3.00E+20		241.3	3.92E+24	
Hemicellulose	214.8	3.91E+19		213.3	2.98E+19	
Cellulose	242.4	9.15E+19		240.3	2.25E+20	
Lignin	267.5	1.53E+21		264.8	9.94E+20	
KISSINGER	212.4	8.48E+18				

Table 1. Proximate, ultimate and biopolymers analyses of dry coffee ground residues

Analysis	Coffee ground residues (CGR)
Moisture (wt%)	5.0
Proximate analysis, db (wt%)	
Ash	0.9
Volatile Matter	76.4
Fixed Carbon	22.7
Ultimate analysis, db (wt%)	
C	53.9
H	7.1
N	2.3
O	35.8
HHV (MJ kg _{db} ⁻¹)	23.4
Cellulose	10.6
Hemicellulose	36.6
Lignin	40.6
Others*	12.2

db: dry basis

* Organic extractives unidentified compounds and ash determined by difference

Table 2. Decomposition characteristic of coffee ground residues (CGR) at different heating rates

Heating rate ($^{\circ}\text{C min}^{-1}$)	T_i ($^{\circ}\text{C}$)	$T_{DTG_{\max}}$ ($^{\circ}\text{C}$)	DTG_{\max} ($\text{wt}\% \text{ min}^{-1}$)	$X_{\max, 500^{\circ}\text{C}}$ ($\text{wt}\%$)
5	173	300	3.5	72.2
10	180	310	6.9	72.9
15	200	315	10.3	73.6
25	216	321	16.9	73.7
50	225	330	34.6	74.6
100	237	336	68.5	75.1