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Use of principal component analysis to evaluate thermal properties and combustibility of coffee-pine wood briquettes

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Abstract. The coffee production chain is a potential source of residual biomass inherent to the high productivity that can contribute to the generation of value-added products. The residues from the coffee sector are typically disposed to landfill without treatment causing potential environmental inconveniences. Briquetting presents an alternative process to produce a uniform fuel with high energy density. Briquettes facilitates easy transportation, enables better handling and storage of biomass residues. Properties such as low equilibrium moisture content, high energy density and compressive strength were reported for different coffee-pine wood briquettes treatments. Moreover, understanding of the thermal properties of the briquettes during combustion is crucial to evaluate their final application. This research is the first study that investigates the combustibility properties and kinetic parameters of the thermal decomposition of briquettes from coffee-pine wood using differential and integral thermal analysis under non-isothermal conditions. Multivariate analysis of the collected parameters through principal components analysis (PCA), was implemented to reduce the dimensionality of the data.
The desired profile in the combustibility is directly related to high temperatures and long burning times, thus, the tested briquettes displayed a significant combustibility potential, reporting peak temperatures and burnout times around 600 °C and 27 minutes, respectively. Activation energy kinetic parameter in the range of 12–42 kJ mol^{-1} and average reactivity of 0.14–0.22 min^{-1}, were also found. The results revealed the not thermally hard material to degrade when compared to biomasses typically used for combustion.

Key words: briquette, chemometrics, combustion rate, reactivity, solid biofuels.

GRAPHICAL ABSTRACT

INTRODUCTION

Briquetting is one of the relatively simple technological alternatives that enables an efficient use of different biomass residues. In it, the feedstock material is transformed into blocks of compressed biomass at high pressure (Maradiaga Rodriguez et al., 2017). Biomass briquettes are widely used for any type of thermal application like steam generation in boilers, heating purposes, drying process, food processing industries, brick making units and gasifier systems (Lubwama & Yiga, 2018). The comprehensive understanding of briquettes energy potential is important to the process production, feasibility assessment and to the scaling in industrial applications. The manufacturing process of briquettes is shown in Fig. 1 (Bajwa et al., 2018).

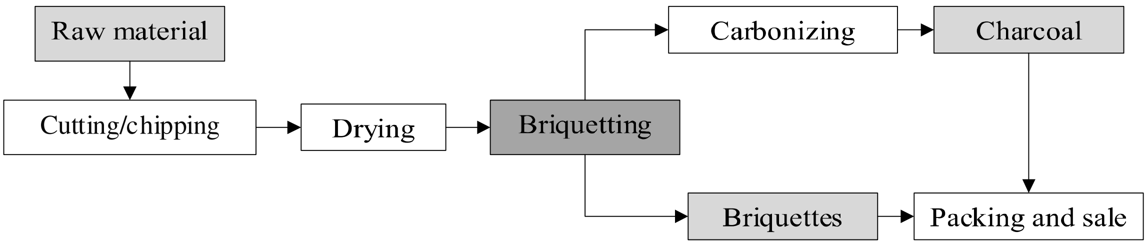

Figure 1. Production of biomass and charcoal briquettes (Bajwa et al., 2018).

Briquettes combustibility

The thermal decomposition of the biomass briquettes is one of the main characteristics to evaluate their energy potential, which is an important parameter for the planning and control of industries that use this type of fuel. As examples, the combustibility analysis is employed for the design of boilers, gasifiers and pyrolysis reactors, as well as in the optimization of thermochemical conditions (Tabarés et al., 2006). Combustibility is directly related to high temperatures and long burning times. Heat and mass transfer limitations, physical and chemical heterogeneity, and systematic errors also influence the combustibility properties of the fuel.

The literature reports significant number of publications about the development of briquettes from agricultural and forestry residues, such: rice husk and coffee husk (Lubwama & Yiga, 2018), sugarcane bagasse (Maradiaga Rodriguez et al., 2017), Madan wood and coconut shell (Kongprasert et al., 2019), sawdust and ground palm kernel shell (Obi, 2015), banana tree waste (Ku Ahmad et al., 2018), corncob and rice husk (Oladeji, 2010), coffee-pine wood (Mendoza Martinez, Sermyagina et al., 2019), guava wood (Ivanova et al., 2018), apricot branches after pruning (Akhmedov et al., 2019), cotton post-harvest trash (Akhmedov et al., 2017), among others, revealing the improvement on the physic-mechanical characteristics of the biomass residues, when compared to the raw material. Despite this, few studies have been done on combustibility properties of briquettes from coffee wood for industrial applications.

The International Coffee Organization (ICO) reported that coffee is one of the most consumed beverages in the world with a production of 9.9 million tons of coffee beans in 2019/2020 worldwide with Brazil as the largest producer and exporter country (ICO, 2021). Coffee production chain generates significant amount of different residues. In Brazil, the high-density coffee plantations produce over 3 million tons of solid residues every year from the 2 million ha of harvested plantation area (Mendoza Martinez, Rocha et al., 2019). Some of the residues come from the cherry and some others from the cultivation after pruning (wood and leaves). Individual residue streams quantification are difficult to estimate due to the differences in the agronomic management practices (Mendoza Martinez et al., 2021). However, an approximate estimation of 31 million tons of coffee wood in Brazil during 2016/2017, was reported by (Mendoza Martinez, Rocha, et al. (2019). In Brazil, the amount of annual available energy from the coffee wood residue is about 49.5 PJ, which reveals its high potential for bioenergy generation (De Oliveira et al., 2013). Nevertheless, the coffee crop residues in Brazil are mostly used for animal feed and bedding, as well as soil fertilizer. In that sense, coffee wood is practically unused as feedstock for briquetting in Brazil or any other energy conversion application.

A previous development research, noted the attractive characteristics of coffee-pine briquettes for application in thermochemical conversion processes, such as low equilibrium moisture content, high energy density, apparent density and compressive strength (Mendoza Martinez, Sermyagina et al., 2019). The produced briquettes also presented a consistent quality with ease of handling, storage and transportation due to their size and regularity of shape. The briquettes were 100% natural, which means that no binder or chemical was required. Pine wood played an important role in the development of the briquettes, since the presence of natural resins in pine composition helps to increase the calorific value (Brito et al., 2008). In addition, the high pine lignin content improves the agglomeration of the particles, since natural lignin acts as a binder during the densification process (Mendoza Martinez, Sermyagina et al., 2019). Pine wood is a significant feedstock for important industries worldwide such pulp and paper mill, which means that the availability of pine residues would not be a limiting factor for the coffee-pine briquettes production.

This study performs a combustibility and kinetic analysis to evaluate the behavior and thermal potential along different combustion stages of coffee-pine wood briquettes for future applications. Multivariate analysis of the collected parameters through principal components analysis (PCA), was implemented to reduce the dimensionality of the data by transforming the original variables into their main components (PCs), which allows to visualize and explain in detail the combustibility properties results. From the experimental procedures, is expected that complete and uniform combustion from the coffee-pine briquettes is achieved as well as high burning efficiency, due to the high energy density, higher heating values and stable quality material characteristics. This information can then be used for modelling purposes, design of tailored equipment, or comparison of combustion behavior with other fuel materials.

MATERIAL AND METHODS

The pine-wood briquettes showed in Fig. 2 corresponded to a previous research developed by Mendoza Martinez, Sermyagina et al. (2019). Coffee wood samples: (i) stems (CS), (ii) primary branches (CPB), and (iii) secondary branches (CSB) from *Coffea arabica* L. and pine sp. wood (PW), were used as a feedstock for the briquettes production. Pinewood was mixed in ratios of 25%, 50% and 75% with stem, primary branch, secondary branch and a mixture of all woody parts (MIX) of coffee shrub. The presence of stems, primary and secondary branches were proportional in the mixture of all woody parts. Composition briquettes of 100% feedstock were also produced. 10 briquettes per treatment were manufactured for a total of 170 samples. The briquettes were produced in a piston-press type of the laboratory scale briquetting machine from Lippel®, model LB 32. The materials were compressed for 4 min at a temperature of 120 °C and pressure of 8.27 MPa with a subsequent cooling for 8 min. Coffee-pine briquettes had cylindrical shape with a fixed diameter of 30 mm and a variable length in the range 25–30 mm.

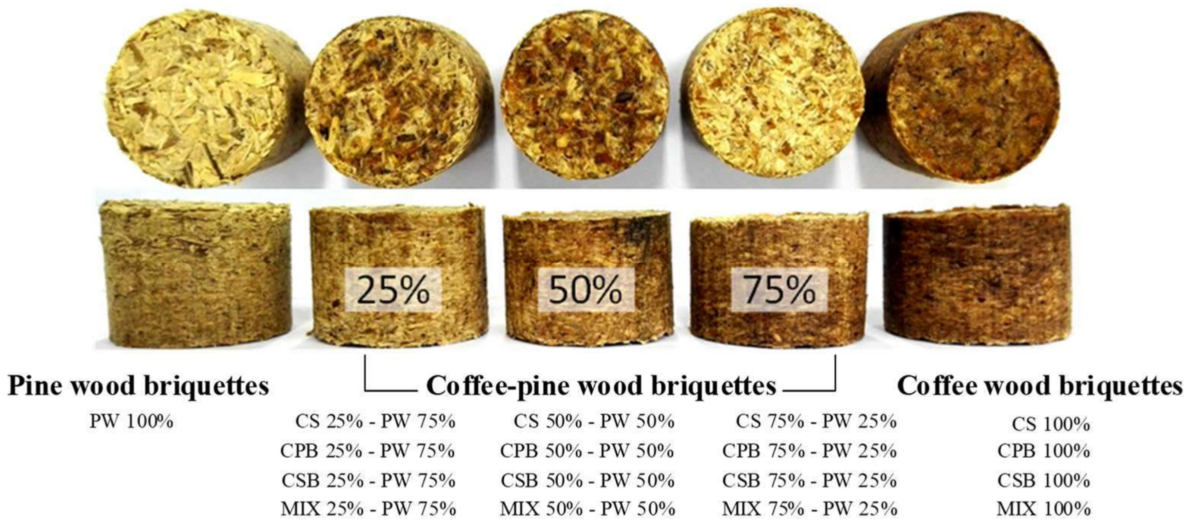

Figure 2. Coffee-pine wood briquettes (top and lateral view). The percentages represent the amount of pine wood in the mixture. PW-pine wood; CS-coffee stems; CPB-coffee primary branches; CSB-coffee secondary branches; MIX-mixture of CS, CPB and CSB.

Some of the biomass quality properties are reported in Table 1. Properties such moisture content, high heating value, ash content, cellulose and lignin are fundamental for biomass utilization, since they are able to influence the conversion process and thermal utilization. Additional briquettes characterization and manufacture information can be found in an available article reported by Mendoza Martinez, Sermyagina et al. (2019).

Table 1. Literature report characterization of feedstocks.

Biomass		Proximate analysis*** (wt%)				HHV*** ($MJ \cdot kg^{-1}$)	Chemical composition (wt%)		
		MC	VM[a]	AC[a]	FC[a]		Holocellulose	Lignin	Extractive
Coffee wood	Stem	11.0	79.8	2.1	18.1	20.1	52.7**	29.6**	10.6**
	Primary branch	8.7	80.7	2.3	17.0	19.8	54.1**	29.8**	13.1**
	Secondary branch	9.3	76.5	4.1	19.4	19.7	50.1**	32.2**	13.9**
Pine wood		12.2	82.5	0.7	16.8	20.7	65.9*	32.3*	1.82*
SD[b]		1.6	2.5	1.4	1.2	0.5	6.9	1.5	4.8

***(Mendoza Martinez, Sermyagina et al., 2019); **(Mendoza Martinez, Rocha et al., 2019); *(Carvalho et al.,. 2015); [a]Dry basis; [b]Standard deviation; MC – Moisture content; VM – Volatile matter; FC – Fixed carbon content; AC – Ash content; HHV– Higher heating value; Holocellulose (hemicelluloses + cellulose).

Experimental set-up

Fig. 3 depicts the combustion system used to evaluate the behavior of the briquettes during combustion (Quirino & Brito, 1991). The device consists of: cylindrical aluminum combustor covered by a combustor bulkhead that protect the equipment of excess of oxygen; laboratory scales with a precision of ± 0.005 g; wooden base for thermal insulation; temperature recorder coupled with a thermocouple, and compensation cables. The briquettes were loaded onto the burner grate using approximately 60 ± 10 g solid mass for every treatment, with two replicates. The ignition occurred by the combustion of 10 g of ethyl alcohol in a crucible located under the grate. The experimental assays were performed at room temperature (~25–28 °C), with selected time of 30 minutes per treatment.

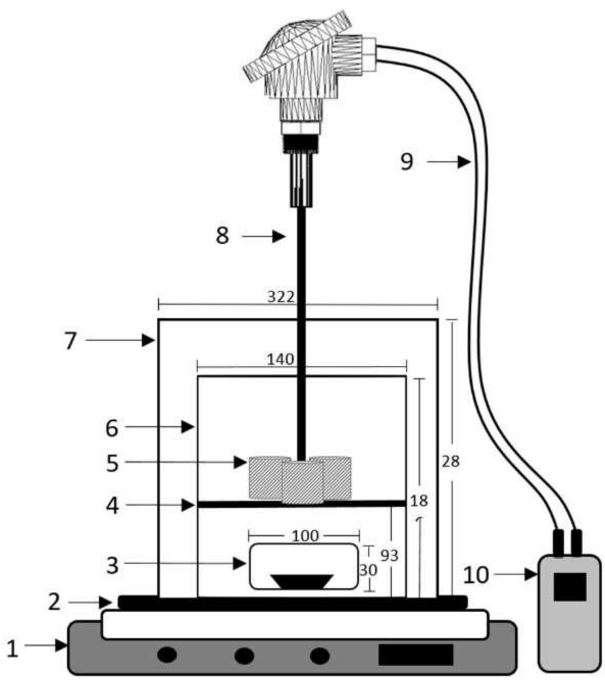

Figure 3. Scheme of the combustion system (dimensions in mm): 1 – digital balance; 2 – wooden base; 3 – ignition chamber; 4 – grate; 5 – briquettes; 6 – combustor; 7 – combustor bulkhead; 8 – thermocouple; 9 – compensation cables; and 10 – temperature recorder.

Mass and temperature variations

The measurements of weight loss and temperature variation during the combustion process were collected with the balance and the thermocouple, respectively. The time required for the complete combustion of the briquette (i.e., immediately before its final residual mass remains constant) was established in 30 minutes. This analysis allowed to determine both the maximum temperature that briquettes can reach during combustion and the percentage of residual mass after burning.

Determination of derivative conversion

For the determination of derivative conversion, the obtained data from weight loss and temperature variation was transformed into the form of the conversion degree, according to Eq. (1) (Vyazovkin &Wight, 1997).

$$\alpha(t) = \frac{m_0 - m(t)}{m_0 - m_f} \tag{1}$$

where $\alpha(t)$ [g·g^{-1}] is the degree of conversion, m_0 [g] the mass at time t_0, $m(t)$ [g] the mass at time t, and m_f [g] the mass at final time (30 minutes).

A numerical differentiation of the transformed conversion data, using the finite difference method, was also applied. Three forms of finite differences: forward, backward and central, were used (Gupta et al., 1980) (Eq. (2)). The first two were applied to estimate the derivative conversion data at the start and end points, respectively. The latter was used to calculate the derivative conversion data for the intermediate points.

$$\left(\frac{d\alpha}{dt}\right)_i = \begin{cases} \dfrac{\alpha_{i+1} - \alpha_i}{t_{i+1} - t_i} & For\ the\ start\ point \\ \dfrac{1}{2}\dfrac{\alpha_i - \alpha_{i-1}}{t_i - t_{i-1}} + \dfrac{1}{2}\dfrac{\alpha_{i+1} - \alpha_i}{t_{i+1} - t_i} & For\ the\ intermediate\ point \\ \dfrac{\alpha_i - \alpha_{i-1}}{t_i - t_{i-1}} & For\ the\ end\ point \end{cases} \tag{2}$$

where α_i and $\left(\frac{d\alpha}{dt}\right)_i$ [g·g^{-1} min^{-1}] are the conversion and derivative conversion of the ith point, respectively.

The fluctuations of the curve were smoothed for further analysis. The LOWESS procedure was then applied to each ith data point (Cai et al., 2018), as shown in Fig. 4.

Numerical differentiation of the transformed data and LOWESS procedure application were used to validate and improves the data quality and help to detect null values, unexpected duplicates, incorrect indexing and outliners. Moreover, the LOWESS process allowed to easily identify patterns and trends from the data in a time series.

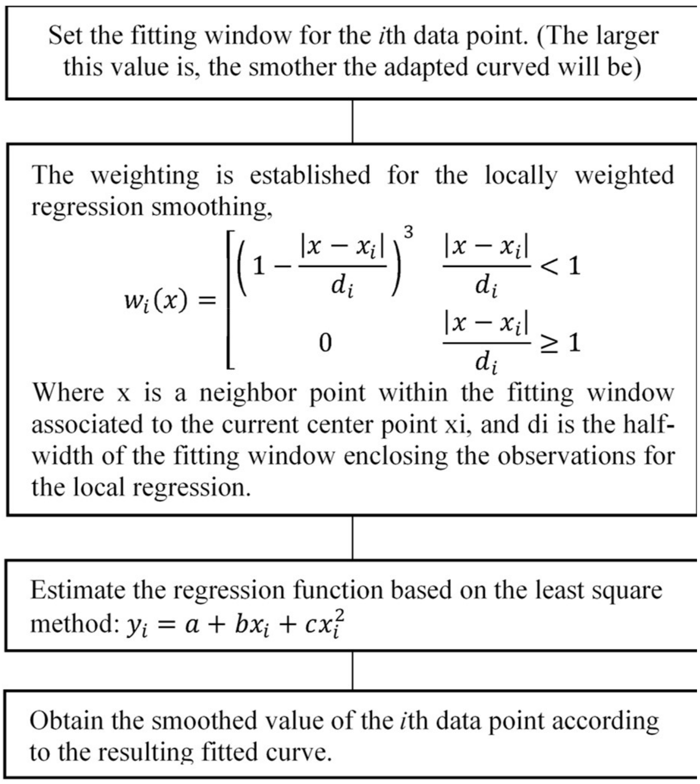

Figure 4. LOWESS procedure for smoothing curve (Cai et al., 2018).

Reaction rate and reactivity

The specific reaction rates were calculated as shown in Eq. (3) (Hart et al., 2001).

$$k = \frac{1}{w} \cdot \frac{dw}{dt} \tag{3}$$

where k [min^{-1}] is the specific reaction rate, w the instantaneous mass [g], and *dw/dt* the mass loss rate [$g \cdot min^{-1}$]. Eq. (3) can be rewritten as in Eq. (4).

$$k = \frac{ln\ (\Delta w)}{\Delta t} \tag{4}$$

The average reactivity, R_a [min^{-1}] can be calculated from the specific reaction rate, k, by splitting the defined range of burnout into a series of discrete intervals as given by Eq. (5) (Tsai &Scaroni, 1987).

$$R_{a,x\%} = \frac{\sum(k \cdot \Delta W)}{\sum \Delta W} \tag{5}$$

where ΔW [g] is the briquette weight loss in a 0.5 minutes time interval.

Kinetic analysis

This section describes the methodology adopted for the kinetic parameter's estimation of coffee-pine wood briquettes combustion. For the isoconversional kinetic calculation, a solid-state reaction is described by the following equation:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \tag{6}$$

where $f(\alpha)$ depends on the reaction mechanism, defined as $f(\alpha) = (1 - \alpha)^n$; n is the order of the reaction, α the degree of conversion defined by Eq. 1, and for k(T) the temperature dependent rate constant that obeys the fundamental Arrhenius rate expression:

$$k(T) = A_r \cdot exp\left(\frac{-E_a}{R \cdot T}\right) \tag{7}$$

where T is the absolute temperature [K], R the universal gas constant [$8.314\ J \cdot mol^{-1} \cdot K^{-1}$], A_r the frequency or pre-exponential factor [min^{-1}], and E_a the activation energy of the reaction [$kJ \cdot mol^{-1}$].

In non-isothermal combustion experiments, the heating rate vary as a function of time (El-Sayed &Mostafa, 2015).

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \cdot \frac{dt}{dT} \tag{8}$$

Where $\frac{dT}{dt} = \beta$ (heating rate [$°C \cdot min^{-1}$]).

Hence, Eq. (6) can be rewritten in the final form as:

$$\frac{d\alpha}{dt} = \beta \cdot \left(\frac{d\alpha}{dT}\right) = A_r \cdot exp\left(\frac{-E_a}{R \cdot T}\right) \cdot\ (1 - \alpha)^n \tag{9}$$

The model can follow either a differential or an integral approach for the data to calculate the kinetic parameters. This study adopted the integral method of Flynn-Wall-Ozawa (FWO) and the differential method described by Boycheva et al. (2013).

The FWO method represents an approach to determining E_a from weight loss and temperature data obtained at several heating rates. The variables given in Eq. (9) may be separated and integrated in logarithm form, using Doyle's approximation for the integral (Ozawa, 1965), the following equation is obtained in the form

$$\log(\beta) = \log\left(\frac{A_r \cdot E_a}{R}\right) - \log(f(\alpha)) - 2.315 - 0.4567\frac{E_a}{R \cdot T} \quad (10)$$

The activation energy can therefore be obtained from a plot of $\log(\beta)$ vs T_i^{-1} for a fixed degree of conversion.

The activation energy can be calculated by the following kinetic equation (Boycheva et al., 2013):

$$\frac{1}{T} = A_r - \left(\frac{R}{E_a}\right) \cdot \ln(\beta) \quad (11)$$

Principal Component Analysis (PCA)

The PCA analysis facilitates visualization, and hence process understanding. In brief, the principal components are the axes of a new coordinate system given by the rotation of the original one. These new directions are defined in order to explain most of the variance in the original data through a smaller number of dimensions (Jolliffe, 2003). The components are linear combinations of the original variables. In this study, the features were combustibility properties measured for all briquette treatments. The original variables were initially standardized (zero mean and unit variance) to avoid the scale problem caused by the discrepant standard deviations among them, to obtain the PCA model using MATLAB R2019a. After obtaining the PCA model, the resulting score (the coordinates of the original data in the new coordinate system) were used for a cluster analysis to evaluate similarities and dissimilarities among the briquettes treatments. Python 3.8.0 was used for the analysis.

RESULTS AND DISCUSSION

Thermal analysis results

Weight loss and temperature variation analysis as well-known as thermal gravimetric analysis (TGA) is the most commonly applied thermo-analytical technique in solid-phase thermal degradation studies (White et al., 2011). This technique can be implement for different purposes, for example, prediction of higher heating values (HHVs) though the thermal mass coefficients of samples composition (Li et al., 2017), determination of less combustible constituents in coals (Shu et al., 2002), combustion, kinetics and thermal behavior of lignocellulosic fuels for energy applications (Mishra & Mohanty, 2018). This article used the combustor instead of TGA analysis as a tool to obtain the weight loss curves along with their derived parameters and the temperature profile during devolatilization of the briquettes. The results are presented in Fig. 5.

The briquettes chemical composition consists principally of cellulose, hemicelluloses, lignin and extractives, which have different thermal behavior during combustion. The chemical composition regarding lignin and holocellulose (hemicelluloses + cellulose) content of the feedstock is tabulated in Table 1. The degradation process of the lignocellulosic briquettes can be divided into three main sections (Janković et al., 2020):

(i) moisture and very light volatiles components removal (< 120 °C). From Fig. 5 (right) a slightly inclined weight loss curve with 10% average weight loss was reported during the first 5–6 minutes of the experiment, due to the appearance of endothermic reaction. The initial moisture content of the briquettes was between 9.5–10.1 wt%

(Mendoza Martinez, Sermyagina et al., 2019), which explains the initial weight reduction percentage. This process ends at around 200°C, with the next region starting.

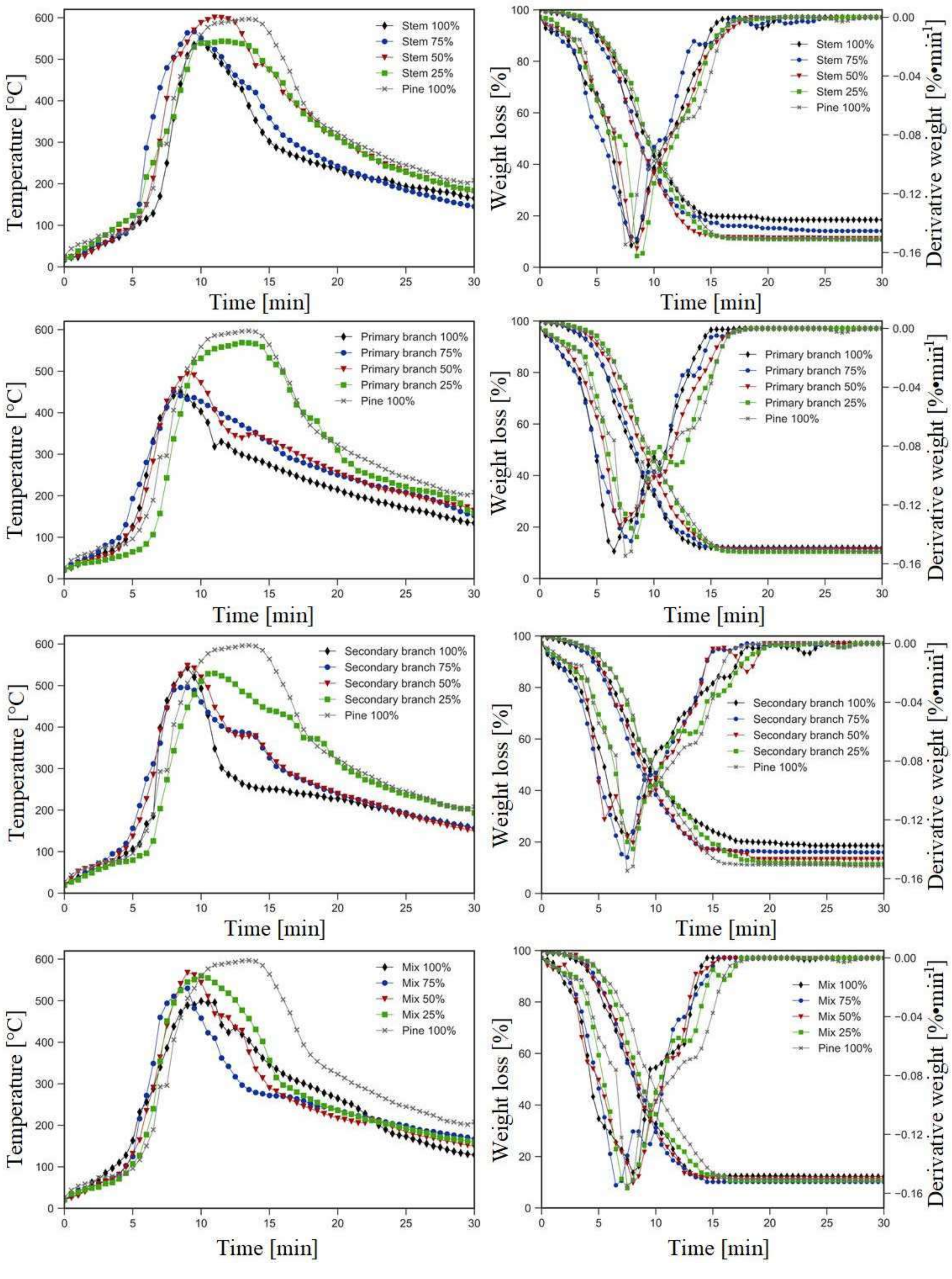

Figure 5. Weight loss along with their derived parameter curves (right) and temperature profile (left) versus time for the coffee-pine wood briquettes.

(ii) degradation of hemicelluloses (220–315 °C), cellulose and lignin decomposition (315–400 °C) and lignin degradation (> 450 °C) (El-Sayed & Mostafa, 2015). The combustion of the briquettes was initiated between 6–7 minutes, where the 75% coffee feedstocks composition reported less time to start combustion. Much of the devolatilization and oxidation occurred in the 6–17 minutes interval, a result of the thermal breaking of bonds in the polymeric structures of the hemicelluloses, cellulose and lignin. This stage is also characterized by the exothermic reactions in which the products are CO_2, water vapor and most importantly the produced heat from exothermic transformation (Janković et al., 2020). On the derivative weight loss curve the times at which maximum rate of weight loss occurred is described by the position of the peaks in the curve. Two distinct peaks were observed in the range of 6–11 minutes, which correspond to the hemicellulose and part of the cellulose degradation, and 11–18 minutes, which correspond to the cellulose and in some of the treatments part of the lignin degradation, this peak was distinctively smaller due to lower values of volatile matter content. 100%, 75% and 50% primary branch and 100% wood mix coffee-pine briquettes did not react more than 500 °C in the combustion, then, no percentage of lignin could have been degraded, in addition, the reaction time was short to complete an entire lignocellulosic decomposition.

(iii) weight loss fraction of material, but in a milder pace till constant profile. Approximately 83–90% of weight loss at the end of the combustion was observed. This stage occurs above 18 minutes and the residual mass content can be related to the content of ash which was present in the tested briquettes. High moisture and ash contents in biomass may cause severe ignition and combustion problems, such as reduction of the burning rate and the heating value of the fuel (Demirbas, 2004). In addition, the low melting point of the ashes may promote fouling and slagging hampering the combustion process.

In general, the behavior of the briquettes, given the same proportion of coffee residues, are quite similar: the weight loss and the highest peaks of temperature occur almost at the same time period. The briquettes solely composed of pine showed the highest temperature, longest burning region and slowest weight losses. The briquettes from the mixture of primary and secondary branches exhibited the lowest temperatures and shortest rapid burning sections. While the briquettes with coffee stem in its composition reached temperatures of 550 °C and 601 °C for 100% and 25% stem, respectively. As expected, briquettes with lower percentages of coffee residues showed higher and longer time range combustion temperatures probably because of lower ash and higher volatile contents in the pinewood (Table 1).

Ignition and peak temperatures are the most important thermal characteristics of a combustion profile (Haykırı-Açma et al., 2001). By the place where the burning profile undergoes a sudden rise, the ignition temperature can be determined, namely 150 °C for 100% stem, 120 °C for 100% primary branch, 117 °C for 100% secondary branch, and 110°C for 100% pine briquettes. The release of volatile matter causes superficial structure modifications in the briquettes with a decrease in the free sites for an oxidative reaction, which promotes the ignition effect (Tognotti et al., 1985). In that sense, the lower ignition temperatures are favorable since they decrease the energy requirement to initiate the combustion process. As for the maximum combustion temperature, it corresponds to the place where the weight loss rate due to combustion is at the maximum level. Fig. 6 registered the peak temperatures of the coffee-pine briquettes.

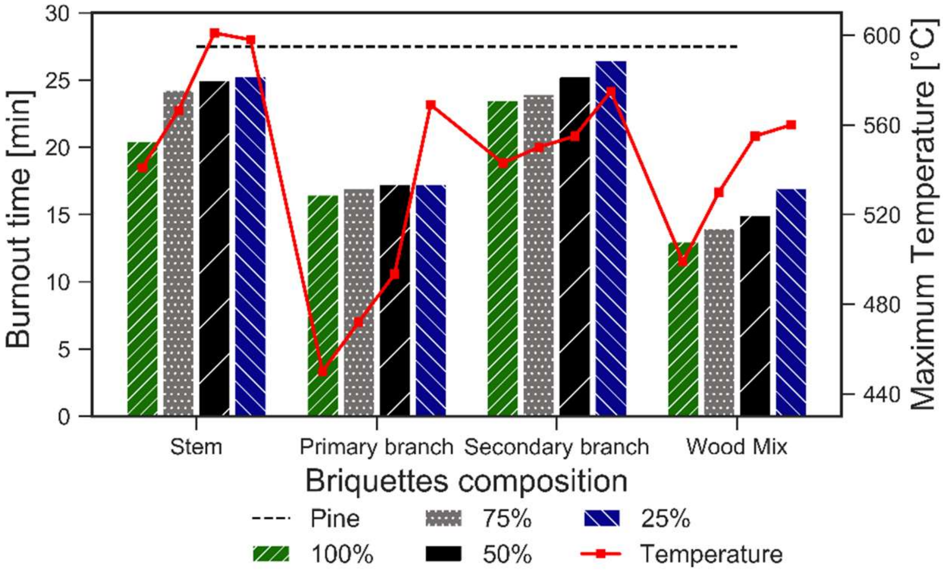

Figure 6. Maximum combustion temperature of the coffee-pine wood briquettes.

Total biomass burnout was also studied in this work based on weight losses, this property includes the heating up, devolatilization and the oxidation time (Li et al., 2016). The burnout occurred at the range of temperature where the rate of weight loss consistently decreases to less than $1\%\cdot min^{-1}$ (El-Sayed & Mostafa, 2015). Fig. 6 also shows that the burnout time of the briquettes increases with an increase in the pine content. For instance, it takes about 27.5 minutes and between 20–25.3, 16.5–17.3, 23.5–26.5 and 13–17 minutes to completely burn a 100% pinewood and steam, primary branch, secondary branch and wood mix present in the briquette composition, respectively. The maximum temperatures reveal that higher temperatures increases the devolatilization and the briquettes burnout process.

The residual mass after the combustion process is composed mainly of inorganic material, originally contained in the fuel. The percentages of residual mass are shown in Fig. 7. The reduction of the residual mass among the treatments is due to the decrease of the coffee residues content in the mixture. Briquettes of 100% secondary branch displayed the highest residual mass percentage, mainly because of the high ash content. They present values approximately 83% higher than pinewood, which reported the lowest ash content.

Nevertheless, high residual mass may also be attributed to the differences in composition and also to the strength of the molecular structure of the coffee residues in comparison to pinewood. The amount of structural polymers (holocellulose (lignin + cellulose) and hemicellulose) and their characteristics differ between softwood (pinewood) and hardwood (coffee wood) materials. Schutyser et al. (2017) reported content in the range of 46–50 wt%, 19–22 wt% and 21–29 wt% of cellulose, hemicellulose and lignin respectively for softwoods, and content in the range of 40–46 wt%, 17–23 wt% and 18–25 wt% of cellulose, hemicellulose and lignin respectively for hardwoods, in accordance of the data found in this study. For instance, the lignin and holocellulose content was 32.3 wt% and 65.9 wt% and between 29.6–32.2 wt% and 50.1–54.1 wt% for pinewood and coffee residues, respectively (Table 1). Lignin is the major plant cell wall component and has the ability to resist thermal degradation due to its chemically complex structure (Cesarino et al., 2013). Consequently, the composition and the bonds that link the macromolecular structure of the briquettes with high content of coffee residues are less resistant to heat.

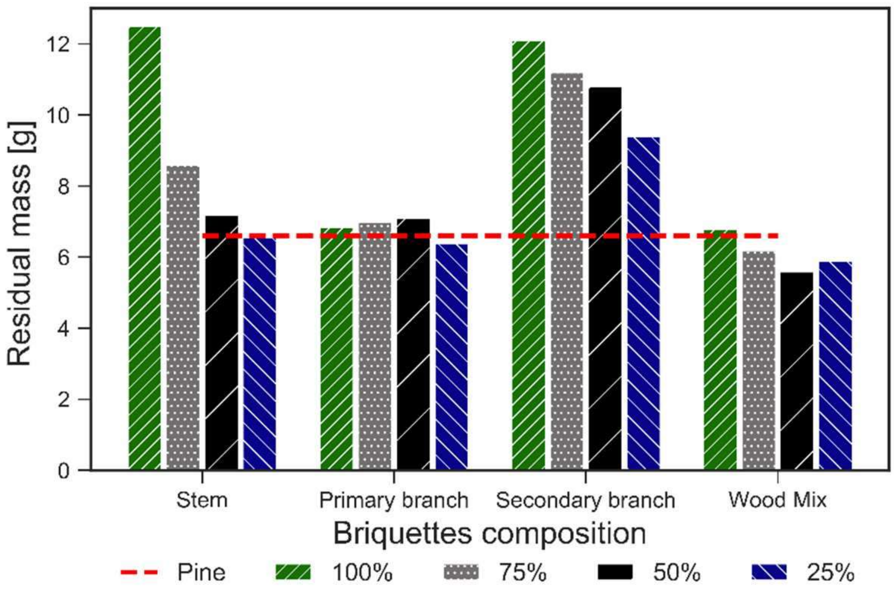

Figure 7. Percentage of the residual mass of the coffee-pine wood briquettes.

Reactivity of coffee-pine briquettes

The average reactivity of the briquettes is illustrated in Fig. 8. It was calculated using the specific reaction rate (k). The k [min^{-1}] property showed a similar behavior as the temperature profile, where a distinctively increase started from approximately 6 minutes and reported k high values in the range of 6–18 minutes. Right after this interval, the k values decrease steadily due to the briquettes burnout, in that way, the combustion reaction rate depends on the velocity gradient of the mass of the unburnt combustible material remaining in the fuel.

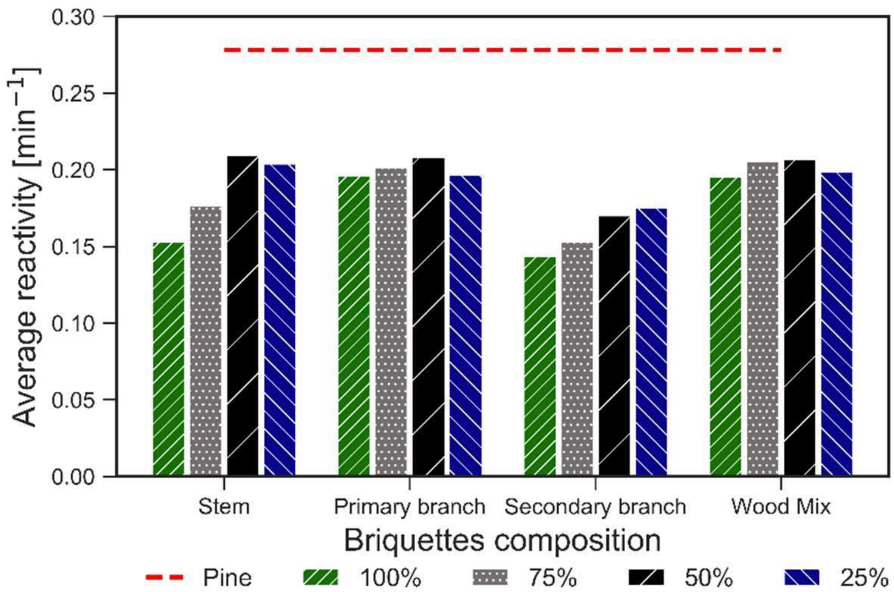

Figure 8. Average reactivity of coffee-pine wood briquettes.

From Fig. 8 it was possible to conclude that, higher amount of coffee residues in the briquettes decrease their reactivities. The reactivity is low because low volatile matter content fuels, which makes the combustion of the fuel difficult (Beamish et al., 1998). Table 1 reports the lowest volatile matter content for coffee stem and secondary branch, and the highest for pinewood, followed by coffee primary branch and wood mix, which explains the difference between coffee residue briquettes and pine wood briquettes. The reactivity difference solely from composition was 45%, 29%, 48% and 30% for stem, primary branch, secondary branch and wood mix regarding to 100% pinewood briquettes, respectively. Only slight differences were observed for the primary branch and wood mix average reactivity behavior. While the stem and the secondary branch show rather low reactivity at mono-combustion, the addition of pinewood improves it significantly. Fuels with lower reactivity levels usually have unburned particles in their ash, which decreases combustion efficiency (Tabarés et al., 2006).

Kinetic model analysis

Thermal analysis provides a useful tool that may support the determination of kinetic parameters of heterogeneous reactions. Parameters such as overall activation energy (E_a) and frequency factor (A_α) provide a quantitative explanation of the thermo-analytical differential curve of the treatments, and enable to predict the process behavior outside of the experimental temperature region (White et al., 2011). The activation energy is considered as the energy threshold that must be reached before the molecules can get close enough to react and form the products. In other words, the molecules with a kinetic energy that overcomes this energy barrier will react (White et al., 2011). The pre-exponential factor represents the vibrational frequency of the activated complex (Vyazovkin, 2006).

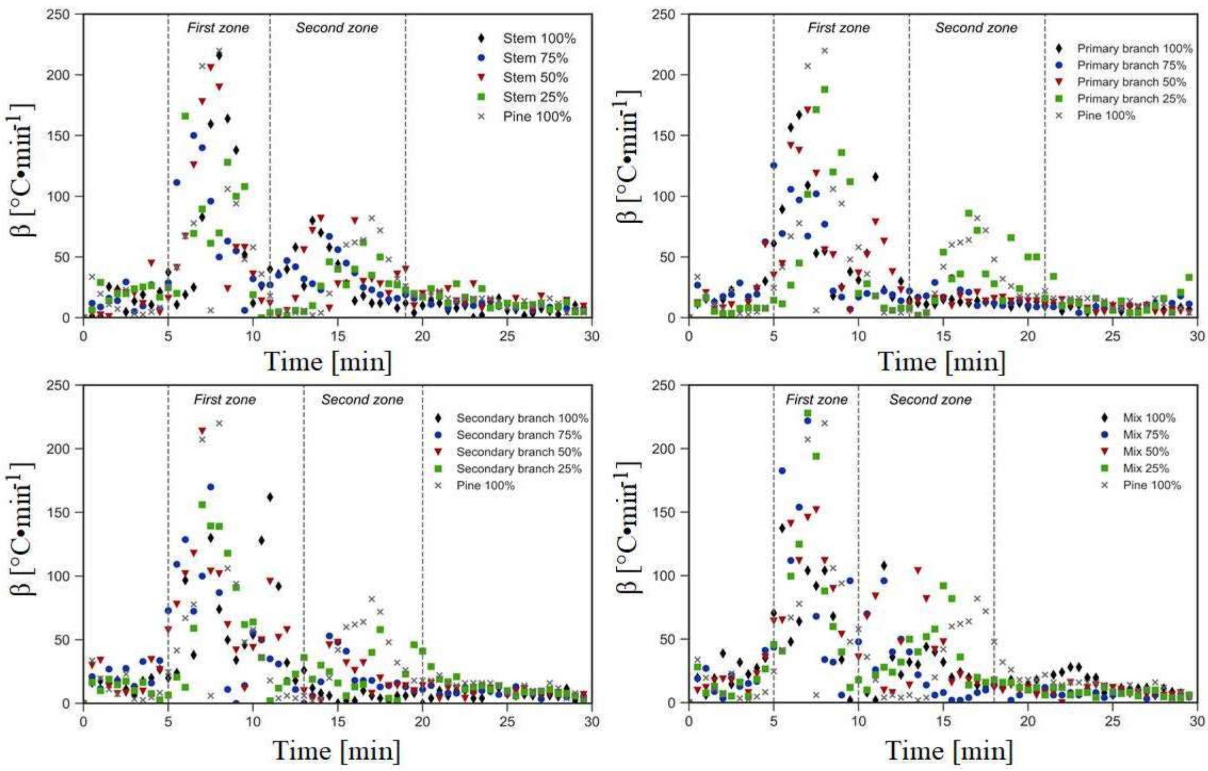

Figure 9. Heating rate during the combustion process of coffee-pine wood briquettes.

To obtain the kinetic parameters of a solid-state reaction, two model-free (differential and integral) non isothermal methods were evaluated. Those methods allow to obtain the value of activation energy from a linear plot, where heating rates are the values presented on the axis. Fig. 9 displayed the heating rates (β) of each treatment, β was estimated by the temperature profiles during coffee-pine briquettes combustion. In Fig. 9 it is possible to observe two distinct zones delimited by 5–11 and 11–19, 5–13 and 13–21, 5–13 and 13–20, 5–10 and 10–19 minutes for stem, primary branch, secondary branch and wood mix briquettes, respectively.

For the kinetic parameters calculation, the thermal profile was divided into zones. The zones reported the higher heating rates intervals during the combustion and corresponded to the maximum weight loss peaks and higher temperatures reported in Fig. 5. Plots of $log(\beta)$ vs T^{-1} and T^{-1} vs $ln(\beta)$ for the FWO method and the model reported by Boycheva et al. (2013), are presented in Figs 10, 11. Best-fit regression lines with the highest value of correlation coefficient are showed in the figures. The kinetic dependence is obtained from the linear fitting of the experimental data, the activation energy values, and the pre-exponential factor, which were calculated from the slope and the intercept of the reported line equation, respectively. Table 2 shows the obtained values for the kinetic parameters.

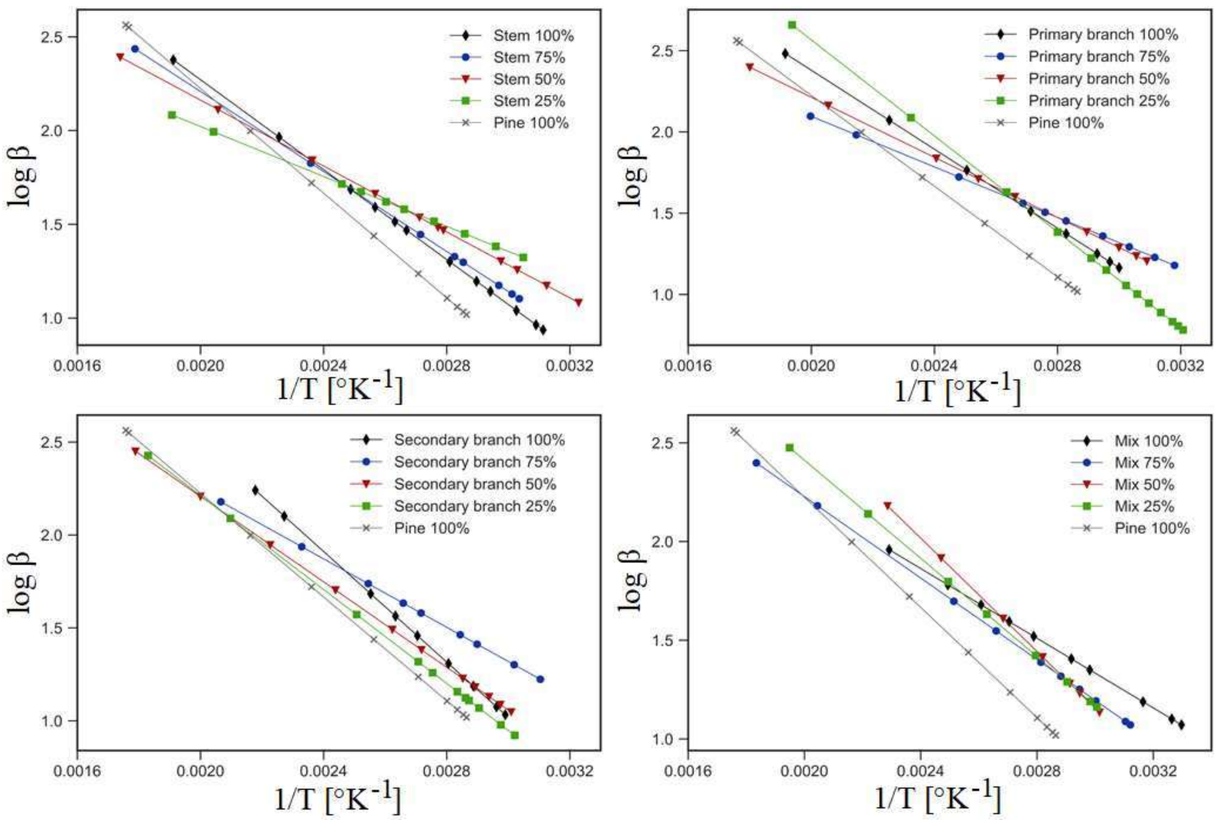

Figure 10. $log(\beta)$ vs T^{-1} of FWO method for coffee-pine wood briquettes.

The calculated activation energies for the studied materials are in the range of 18.5–41.5 kJ mol^{-1}, and 12.1–27.1 kJ mol^{-1} and the pre-exponential factor between 3.3E-03 - 4.28E-03 min^{-1} and 1.0E-02 - 2.7E-01 min^{-1}, for FWO and method reported by Boycheva et al. (2013), respectively. The range of the E_a and A_r values are in accordance with respect to briquettes size. One of the most important factors from the view of combustion kinetics for the briquettes is size (Altun et al., 2004). Hence, small size briquettes as produced in this study will report small E_a and A_r values. To rise the activation energy it is necessary to increase the L/D (length/diameter) ratio of the briquettes considerably (Altun et al., 2004).

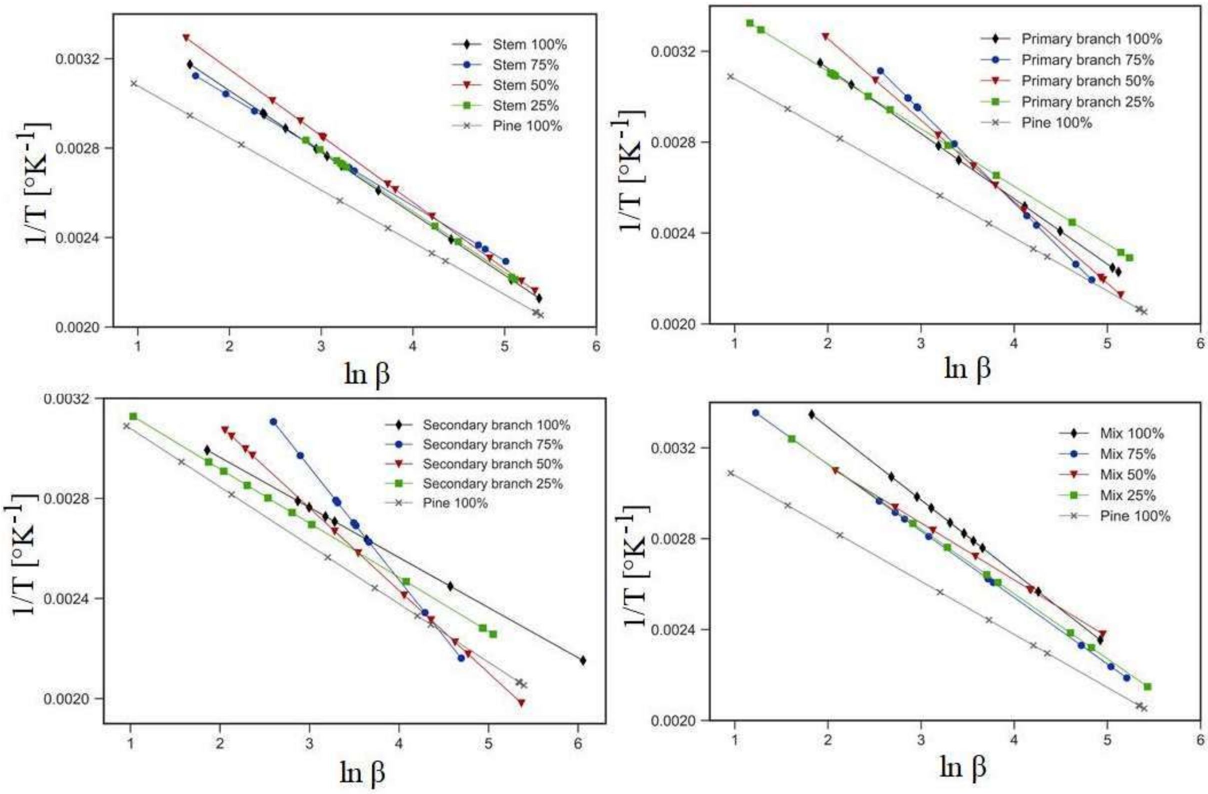

Figure 11. T^{-1} vs $ln(\beta)$ of model reported by Boycheva et al. (2013) for coffee-pine wood briquettes

Table 2. Kinetic parameters of coffee-pine wood briquettes

Biomasses	%	FWO method		Method reported by Boycheva et al. (2013)	
		A_r [min^{-1}]	E_a [$kJ \cdot mol^{-1}$]	A_r[min^{-1}]	E_a [$kJ \cdot mol^{-1}$]
Stem	100	5.8E-02	21.8	3.6E-03	30.2
	75	3.6E-02	19.4	3.5E-03	33.9
	50	2.6E-02	16.0	3.7E-03	27.9
	25	1.0E-02	12.1	3.6E-03	30.4
Primary branch	100	1.4E-01	22.1	3.7E-03	28.9
	75	5.0E-02	14.1	4.2E-03	20.5
	50	7.8E-02	16.8	4.0E-03	23.2
	25	2.7E-01	26.9	3.6E-03	32.8
Secondary branch	100	2.2E-01	27.1	3.4E-03	41.5
	75	6.4E-02	16.8	4.3E-03	18.5
	50	9.7E-02	20.9	3.8E-03	25.2
	25	1.4E-01	23.0	3.4E-03	38.4
Mixture	100	8.4E-02	16.1	3.9E-03	25.9
	75	7.1E-02	18.8	3.7E-03	28.4
	50	2.0E-01	26.1	3.6E-03	33.2
	25	1.7E-01	22.6	3.7E-03	29.1
Pine	100	6.4E-02	25.4	3.3E-03	35.6

The values found for different percentages of pinewood in the mixtures are not following any visible pattern of behavior for all biomass mixtures. However, the presence of pinewood in the mixtures yields higher activation energies and pre-exponential factors through most of the treatments. The results, to some extent, are in agreement with the data obtained by integral and derivate methods and also matched with values calculated by literature report for coal briquettes using similar kinetic models analysis (Altun et al., 2004; Boycheva et al., 2013; Idris et al., 2017). However slightly difference among the results were observed. These variations are probably caused by the difference in both physicochemical composition and metal concentration (Mendoza Martinez, Rocha et al., 2019). The presence of alkali (Na and K) and alkaline earth metals (Mg and Ca) on the feedstock tends to decrease the activation energy.

Principal component and cluster analysis

PCA analysis was used to investigate the effects of the process conditions, given by the briquette treatments over the combustibility properties. All briquette samples were used for a cluster analysis by PCA. The seven autoscaled features used are the residual mass, maximum heating rate, burnout time, activation energy, pre-exponential factor, maximum temperature and average reactivity. The first two principal components (PCs), preserved 44.1% and 29% of the total variance, respectively. In that way, it was feasible to carry out the study using only two PCs rather than seven (given by the original space of properties) dimensions. The analysis of the relationships between treatments and properties in the PC_1-PC_2 plane was performed through the bi-plot graph, as shown in Fig. 12. This graph plots scores (points) and loads (represented by lines) simultaneously. The scores are the coordinates of each point in the original space in the new coordinate system defined by the principal components, and the loads are the weights associated to the original features in a component (each component is a linear combination of the original variables). This way, they can be used to characterize the strength of the original variables in each principal component.

Samples build a relative diverse behavior. Generally, briquettes with high content of pine wood are centered in the cluster represented by squares. From PC1, it can be observed that the largest positive loads are related to the activation energy and the maximum heating rate, equal to 0.46 and 0.41, respectively. On the other hand, the most significant negative loads refer to pre-exponential factor and the average reactivity, equal to -0.44 and -0.27, respectively. Therefore, the greater the value (score) of this first component, the higher the energy consumed for briquette ignition, but higher temperatures and longer burning time will also be reached. Regarding PC2, it can be observed that the most significant negative load (-0.58) refers to average reactivity. In the opposite direction, higher values of residual mass, with loads equal to 0.58, result in more positive PC2. Therefore, the higher the scores of this second component, the more propitious will the briquettes be for ash production and the briquette will produce less energy. It can also be observed that the features that reveal poor briquette combustibility, remain in the upper left quadrant, with positive values for PC1 and PC2, since high residual mass means high tar content and less energy generated. High content of coffee residues in briquettes showed the highest residual mass values in each set of treatments of the same biomass. This indicates that the briquettes with pinewood in its composition are better for combustion.

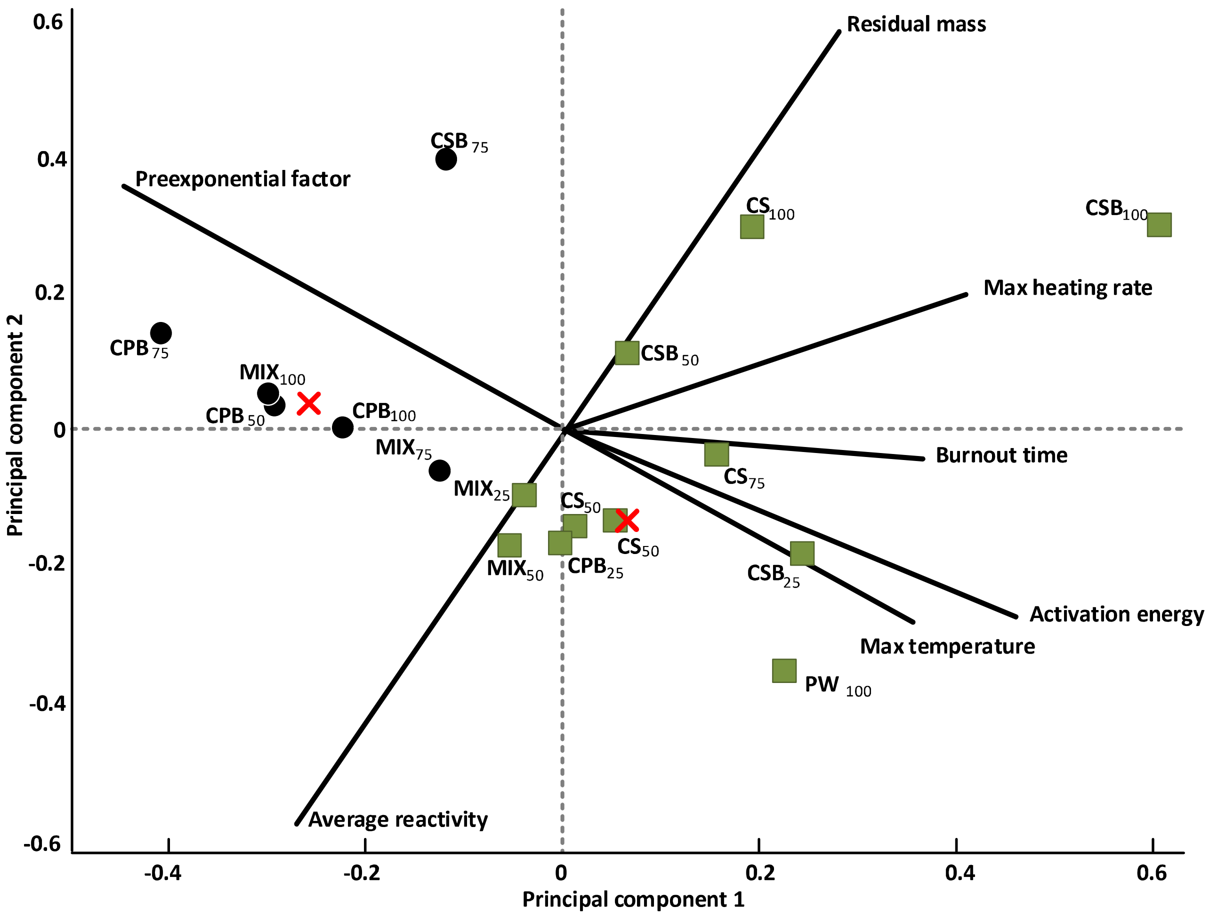

Figure 12. Bi-plot for the PCA analysis of coffee-pine wood briquette treatments. The circle and square symbol denote the clustering groups centered in the X symbol. CS-coffee stems; CPB-coffee primary branches; CSB-coffee secondary branches; MIX-mixture of CS, CPB and CSB; PW-pine wood. Subscript represent the percentage of pinewood in the mixture.

The previous load analysis was then coupled with the scores analysis. Higher pre-exponential values contribute significantly for negative PC1-scores and positive PC2-scores. This condition resides on the upper right quadrant, where briquettes treatments are represented by the cluster (circles). In brief, it means that these treatments yield to combustibility processes that present higher pre-exponential factors. This may be explained by the high molecular collision frequency during the combustion process. It means that the influence of temperature into the reactant molecules is higher for CSB_{75} and CPB_{75} treatments. The relation between the variables that affect the combustibility and the most energy-attractive briquette treatments can be determined.

Other subsets of treatments can be observed. Treatments located in the lower right quadrant are related to higher activation energies and burnout time and can reach higher temperatures. This combination increases the potential of combustibility. Such behavior is given by positive PC1 scores and negative PC2 scores. In this region is possible to observe briquettes with higher content of pinewood in its composition. Other group is given by coffee wood mixture treatment, which presents the highest average reactivity during combustion. The last group is given by the CSB_{100}, CS_{100} and CSB_{50} treatments. It is characterized by positive scores of both PC1 and PC2. This region is strongly associated with the residual mass obtained during the combustion process. The higher quantity of residual mass in these treatments may be explained by the high content of ash in final composition. Therefore, it can be verified that the composition of the briquettes, and more specifically the wood coffee residues, change considerably the combustibility behavior. The briquettes centered in the cluster represented with squares, displayed the highest combustibility potential, once they provide significant peak temperatures and burn out times.

CONCLUSIONS

Coffee wood from varied parts of the shrub mixed with pinewood were used to produce coffee-pine wood briquettes. The combustibility analysis of the produced briquettes was evaluated in this work. It was possible to observed by means of the mass loss and temperature behavior, small difference between the sample's combustibility properties, acknowledge that all produced briquettes are an alternative solution to maximize the thermochemical properties of coffee-pine-based biomass residues. However, coffee-pine briquettes composed of coffee stem and secondary branch displayed the highest combustibility potential, given their peak temperatures over 550 °C and burnout times over 20 minutes. Properties such as high volatiles matter (82.5 wt%) and low ash content (0.7 wt%) in pinewood favor the combustion process and the energy potential of the briquettes. The kinetic analysis provided useful parameters for optimization of the combustion of the briquettes improving the burning stage in domestic and industrial applications. The presence of coffee wood in the mixture, yields to higher values of activation energy and pre-exponential factor in relation to 100% pine wood briquette. Lastly, the PCA analysis made the similarity and dissimilarity analysis among the briquette treatments easier favoring the selection of those most energy attractive, which again point the coffee-pine briquettes composed of coffee stem and secondary branch. PCA chemometric technique presents a great potential for a better understanding of combustion processes in general, and more specifically with respect to the use of coffee residues wood in briquettes should be more explored, due to its high energetic potential.

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