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Preliminary Study of Fluidized Bed Combustion to Determine Diffusive and Kinetic Data of Char Pellets from Eucalyptus and Grapevine Additivated with Glycerol

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Kinetic and diffusive data of fluidized combustion of biochars pellets made from eucalyptus with 5 % and 21.4 % (w/w) glycerol additive and grapevine with 5 % (w/w) glycerol additive, were determined. These biomass pellets were pyrolized at 850 ºC in a bed fluidized with N_2. Batches of biochar particles were burned at four bed temperatures, 750, 820, 850 and 900 ºC, at twice the minimum bed fluidization velocity. From the carbon dioxide concentration evolution in the combustion gases, the global combustion resistance was calculated. The combustion of the three biochars was controlled predominantly by diffusion. It was not possible to determine the controlling mechanism of the reaction at 900 ºC, since the addition of glycerol to the biomass weakened the coal in such a way that the fragmentation phenomena started to control the combustion process.

1. Introduction

The utilization of biomass can be carried out through its combustion, and useful thermal energy is released through this process. The combustion efficiency and energy use depends on the type of fuel, the scale and application required and the combustion technology chosen. Due to the varying size of biomass, there are several possible combustion systems, of which grate combustion, fluidized bed combustion, and pulverized combustion are prominent [1].

Grate combustion is the most commonly used technique globally. Biomass is placed on a grate (movable or vibrating) and slowly moves along the furnace as the air supplied by the holes in the grate comes into contact with it, and thus combustion occurs. This combustion system is particularly suitable for coarse and irregularly sized particles, so size restrictions for biomass transport are not a problem. In addition, it is a very flexible system with regard to the type of solid fuel and therefore does not require a large initial investment. The high amount of fly ash due to grid vibration presents itself as the major disadvantage of this system [1].

The fluidized beds are considered one of the best solutions for biomass combustion since they accept a large variability with respect to the quality of the fuel to be used and a fast response to possible load variations [2]. One of its advantages over pulverized combustion is that it allows the combustion of biomass with moisture content higher than 58 % (w/w) [3].

The pulverized combustion method is used for large-scale biomass combustion. Through this process, biomass is finely ground into powder and must be dry. Although these systems have a high yield, the drying and grinding processes require a lot of energy. Since the temperature of pulverized combustion is high, problems such as corrosion, slag formation and NOx emissions can occur. Pulverized combustion biomass is often used in co-firing with coal, so that the chemical properties of coal mitigate the problems created by the high chloride content in biomass [1].

The combustion of biomass, whatever the combustion technique employed, follows a sequence of well-defined steps, starting with the heating of the particles in the burner, followed by the loss of moisture and volatiles, and finally the burning of the carbonaceous residue, also known as coke or coal [4]. In the present study, only the last stage is studied, as it is the most time-consuming stage of the entire combustion process. The fluidized bed burning of solid biomass follows the following steps [5-9]:

a) Diffusion of oxygen from the bubbles into the dense phase;
b) Diffusion of the oxygen in the dense phase to the particle surface;
c) Possible diffusion of oxygen through the porous structure of the particle;
d) Heterogeneous oxidation reaction of carbon at the particle surface.

The rates at which biomass fuels burn depend on several physical and chemical phenomena [10]. Two predominant factors are heat and mass transfer rates and reaction kinetic rates. Particle size dominates the influence heat and mass transfer, with small, fines particles heating up quickly and larger particles heating up more slowly.

Scala et al. [11] attempted to characterize the combined influence of combustion, fragmentation and abrasion wear phenomena in determining the conversion and elutriation rates of fixed carbon. They studied the fluidized bed combustion of a charcoal and found that the conversion occurs mainly through the generation of carbon fines, followed by its combustion within the bed. They also found that the generation of carbon fines is predominantly a result of fragmentation rather than abrasive wear.

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When studying volatilization in non-spherical pine wood particles, Diego et al. [12] found that defining the geometry of the fuel particles was one of the major difficulties in analyzing processes occurring in wood particles. This is due to the irregularity of their shapes. After checking the influence of particle shape through experimental work, they found that wood particles, characterized by an equivalent diameter and a shape factor, can be modeled as spherical particles.

Scala and Chirone [2] explored abrasion between particles of three different biomass types subjected to fluidized bed combustion. They paid special attention to its impact on particle size and on the combustion process and concluded that the fragmentation phenomenon depends on the mechanical characteristics of the fuel particles. They also found that carbon conversion takes place throughout burning with particle size reduction and constant density. The authors stated that part of the carbon conversion results from the generation of fines obtained by fragmentation, and these are subsequently burned, leading to an increase in the combustion rate. Finally, they emphasize the importance of particle shape in correctly evaluating the exposed surface area of the particles.

Jones et al. [13] used demineralized and potassium-doped willow particles to examine the thermal and catalytic behavior of potassium in biomass combustion. With this study, they proved the catalytic behavior of potassium during volatilization and during the burning of willow coal and presented a model to predict potassium release. Fuentes et al. [14], using the same technique of demineralization of fuel particles and subsequent doping, concluded that potassium and phosphorus are important constituents of biomass as they influence the behavior of ash, pyrolysis and combustion of biomass. They also found that the combustion of the charcoals is catalyzed by all metals, especially by potassium. On the other hand, it is strongly inhibited by phosphorus.

In order to study the distribution of biomass in a bubbling fluidized bed, Santos and Goldstein [15] employed a cold bed with transparent walls, and found that the distribution of biomass in the emulsion phase was favored by using particles of higher density and smaller size and also by increasing the surface velocity of the gas. Additionally, they performed fluidized bed combustion tests of the charcoal to determine the burning rate and the combustion control regime.

In the study of the influence of biomass particle shape and size, on the overall conversion rate [16], a model was developed for its prediction, which was experimentally validated with spherical, cylindrical, and disk-shaped particles. Through this experimental work, it was concluded that the influence of shape increases with particle size and that, for fuels whose particles are irregular with diameters above 200-300 µm, approximating them as spherical does not characterize their combustion correctly.

Several studies were carried out on the determination of kinetic and diffusive data of fluidized bed combustion of different biomasses, either of Portuguese origin or from Brazil and Mozambique. Combustion results of commercial and recarbonized chars of nut pine (*Pinus pinea*) and cork oak (*Quercus suber*) were discussed [8, 9]. The influence of the fragmentation phenomenon upon the determination of kinetic and diffusive data on the fluidized bed combustion of chars of nut pine was also considered [17]. In the case of Brazilian biomass, biochars from eight species of wood obtained from the semiarid region of the Brazilian northeast, known as the Cariri Paraibano, were analyzed [18]. This type of study was extended to the fluidized bed combustion of chars made from biomass of Mozambican origin [19]. Following the same procedure, fluidized bed combustion experiments of biochars obtained from woody biomasses from the central region of Portugal, holm oak (*Quercus ilex*), eucalyptus (*Eucalyptus globulus*), maritime pine (*Pinus pinaster*), and cork oak (*Quercus suber*), were also carried out [20]. The importance of particle sphericity and fragmentation on the combustion behavior of these four chars was subsequently discussed [21].

Interest also turned to the study of combustion of pellets made from invasive shrubs and trees, which although being considered harmful vegetable species, should in fact be considered valuable biomass energy resources [22-25]. The influence of mineral ash components in the char ashes upon the kinetic behavior during combustion was also an object of study [26, 27]. More recently studies on the combustion of chars made from pruning wastes of vine plant (*Vitis vinífera*) and kiwi plant (*Actinidia deliciosa*) and also from gorse (*Ulex europaeus*) residues, follows the same trend of some of the previously mentioned works [28-31]. The interest of using crop and forest residues as energy sources, although going back several years, has only been more recently the target of much more scientifically orientated studies [32].

Looking closely to the use of the fluidized bed reactor as an experimental tool, it must be stressed that, the unique combination between an almost uniform combustion temperature and a low rate of pollutants emission makes the fluidized bed combustion of coals, cokes or chars and attractive technology [33] and such combustion depends upon several parameters [34]:

a) Size, porosity and temperature of the burning particle;
b) Size of the bed inert particles;
c) Fluidization velocity;
d) Bed geometry;
e) Bed temperature;
f) Volatiles fraction of the fuel.

During the combustion process, the solid carbonaceous particles undergo a sequence of steps, warm up, drying, pyrolysis with the release of volatile components, followed by the combustion of this gaseous phase and ending with the combustion of the solid carbonaceous residue of the particle. The combustion of the solid pyrolysis residue is the long lasting term of the solid particle combustion and consequently has a major importance on the study of the combustion process [4]. This carbonaceous residual particle can undergo fragmentation due to thermal chock and attrition with the particles composing the dense phase of the fluidized bed, resulting in an increase of the particle porosity with subsequent structural fragility [35].

2. Methodology

2.1. Experimental

An overall scheme of the experimental setup of the laboratory scale fluidized bubbling bed combustor is depicted in Figure 1. The atmospheric bubbling fluidized bed reactor has an internal diameter of 80 mm, and is heated by an electrical resistance of 4 kW, controlled by a PID controller. Two K type thermocouples (ST1 and ST2) measure the bed temperature. The ST1 is connected to the PID controller of the bed heating electrical resistance, while the readings from ST2 are sent to a data acquisition board PD2, installed in a desktop computer. A stainless steel suction probe, located above the bed free surface, is used to collect exhaust combustion gases samples.

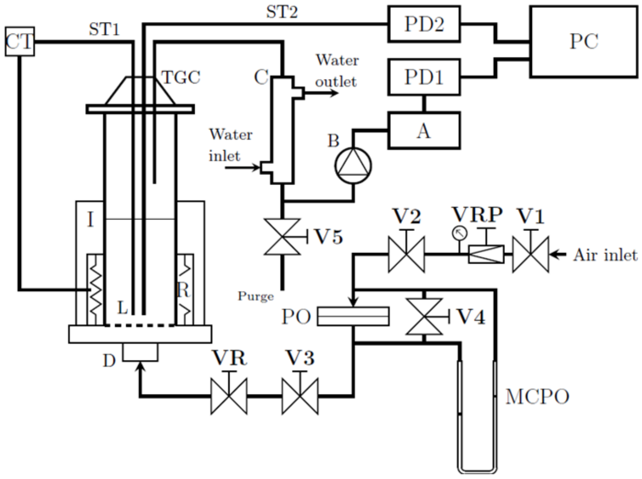


Figure 1. Scheme of the experimental setup

2.2. Biochars production and characterization

The target species of this study are eucalyptus (*Eucalyptus globulus* Labill) and grapevine (*Vitis vinifera*), and both were pelleted and additivated with glycerol at the Thermodynamics and Heat Transfer Laboratory from the Viseu Polytechnic Institute. Both eucalyptus and grapevine are quite common and accessible in Portugal.

The eucalyptus currently occupies about 10 % of the Portuguese territory, making Portugal the country with the largest relative area of eucalyptus plantations worldwide [36]. Consequently, the role of this species throughout the Portuguese economy is remarkable, being the main raw material of one of the most central industrial sectors of the country's economy: the pulp for paper industry [37]. Data from 2017, refer that eucalyptus had a 65 % share in new plantations in Portugal, showing to be, once again, the leading species [38].

Portugal has around 174,000 hectares of vines with protected geographical indication, corresponding to 88 % of the total vineyard produced. Furthermore, in 2015, Portugal was considered the country with the fourth largest area of vines in the European Union, with about 199 thousand hectares [39].

Thus, taking into account the abundance of both species, there is a great pertinence in using them as the target of the present study. Specifically, three samples of pellets were pyrolized consisting of:

a) Eucalyptus additivated with 5 % (m/m) crude glycerol;
b) Eucalyptus with an additive of 21.4 % (w/w) of crude glycerol;
c) Vide additivated with 5 % (w/w) crude glycerol.

In recent research, it is stated that, in the pelleting process, the use of crude glycerol (80 % glycerol, $C_3H_8O_3$, and 20 % water, (w/w)), alcohols or salts [40], can increase the calorific value of pellets and minimize the problem of devaluation of glycerol in the biodiesel industry [41]. Crude glycerol, which, in addition to being a byproduct of biodiesel, is also a byproduct of soap and fatty acid-producing plants, now faces threats to sustainability and reduced market prices due to oversupply resulting from the growing popularity of biodiesel worldwide. In fact, in 2011, more than 65 % of glycerol was produced from biodiesel plants, while fatty acid producing plants had only a 23 % share, thus proving the dynamic expansion of glycerol supply coming from the growing interest in biodiesel production. However, the dynamic growth of its production results in large amounts of waste glycerol, which is a major obstacle to the process profitability [42, 43].

In Portugal, the growth of the biodiesel industry has also generated large amounts of crude glycerol, and in 2017, about 35,591 tons of glycerol were considered as a low-value by-product. The increased production of crude glycerol combined with the difficulty of its purification and reuse is the reason for its price reduction. Thus, the urgency to find an economic and sustainable solution to the overproduction of glycerol is immense [40].

The durability of the pellets is improved with the addition of crude glycerol, as is the energy performance. At the same time, the use of glycerol as a binder also results in a low ash content, low densities and an increased calorific value. On the other hand, glycerol reduces the pellets degree of compaction, acting as a lubricant between the biomass feedstock and the matrix. Glycerol densified pellets have weaker van der Waals forces, producing low bonding forces between adjacent particles. An excessive amount of glycerol can be unfavorable in the sense that it leads to a decrease in bonding properties, hardness, bulk density, and energy density. Tensile strength also tends to decrease by 10 % when the glycerol content increases too much. Therefore, it is established that glycerol should be added between 5 and 10 % (w/w) [44]. The further away from these ideal percentages, the occurrence of deformities will be increased. However, in the present study it was decided also to use an amount of glycerol well above the 10 % limit, in fact 21.4 %, to evaluate the occurrence of anomalies on the performance of the char pellets.

The additivated wood pellets were carbonized in a bed fluidized with N_2 at 850 ºC so that the results of the present study could be compared with previous works [20].

2.3. Characterization of the chars and the corresponding batches

In order to obtain the characterizing parameters of the obtained char particles, proximate analyses of their chemical composition were performed in the Waste Characterization Laboratory, in the Center for Waste Valorization located in Guimarães, Portugal, while the corresponding densities were determined, by mercury pycnometry, at the Chemical Engineering Department, Faculty of Engineering, University of Porto, Portugal. The results are in Tables 1 to 3.

Table 1. Results for the proximate analysis of the char obtained with eucalyptus additivated with 5 % (w/w) of glycerol.

Parameters	Analytical methods	Results
Moisture at 105 ºC (%)	CEN-14774-1	3.0
Volatile mater at 900 ºC (%) D. B.	CEN-15148	6.4
Ashes at 550 ºC (%) D. B.	CEN-14775	11.3
Fixed carbon (%) D.	Calculation	82.3
Density [kg/m^3]	Mercury pycnometry	963.0

Table 2. Results for the immediate analysis of the char obtained with eucalyptus additivated with 21.4 % (w/w) of glycerol.

Parameters	Analytical methods	Results
Moisture at 105 ºC (%)	CEN-14774-1	1.2
Volatile mater at 900 ºC (%) D. B.	CEN-15148	7.8
Ashes at 550 ºC (%) D. B.	CEN-14775	17.2
Fixed carbon (%) D. B.	Calculation	75.0
Density [kg/m^3]	Mercury pycnometry	744.6

Table 3. Results for the immediate analysis of the char obtained with vine additivated with 5 % (w/w) of glycerol.

Parameters	Analytical methods	Results
Moisture at 105 ºC (%)	CEN-14774-1	<0.1
Volatile mater at 900 ºC (%) D. B.	CEN-15148	7.6
Ashes at 550 ºC (%) D. B.	CEN-14775	14.4
Fixed carbon (%) D. B.	Calculation	78.0
Density [kg/m^3]	Mercury pycnometry	888.4

In the experimental combustion tests, the process started with the preparation of the batches of particles to be burned. The char cylindrical particles were selected and categorized by size using a length to diameter (*L*/*D*) ratio. In order to achieve a cylindrical morphology, the tops of the particles were sanded. Taking into account that the diameters of the eucalyptus coal additivated with 5 % and 21.4 % (m/m) glycerol vary between 4 and 5 mm, their lengths were organized into the classes shown in Table 4.

Table 4. Particle dimensions for the three size categories of char from eucalyptus additivated with 5 and 21.4 % (w/w) of glycerol.

L/D	L_{min}	L_{max}
2	9	10
3	13	14
4	18	19

Regarding the particles of the vine coal additivated with 5 % (m/m) glycerol, their diameters vary between 5 and 6 mm. Their lengths were organized into classes according to the values shown in Table 5.

Tests were performed for each char particle category, defined by its composition and size, and for each of the bed selected temperatures, 750 ºC, 820 ºC, 850 ºC, and 900 ºC. The mass of each batch of particles varied between 2 and 3 g, and was measured on a *Sartorius MA* 30 scale, Figure 2. The number of particles composing each batch was also registered. This Figure 2 shows the procedures leading to the accomplishment of a burning experiment.

Table 5. Particle dimensions for the two size categories of char from vine additivated with 5 % (w/w) of glycerol.

L/D	L_{min}	L_{max}
1.5	8	9
3	15	16

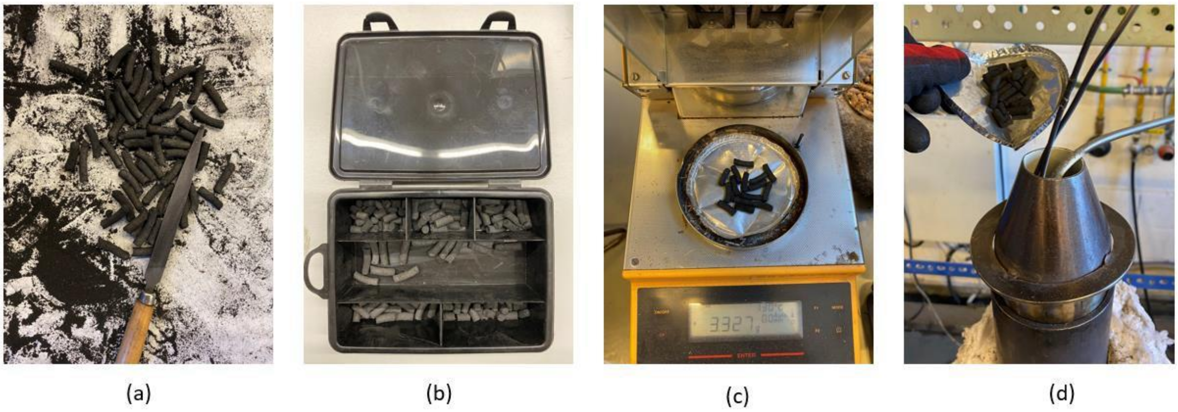


Figure 2. Batch combustion experiments: (a) Batch preparation; (b) Char particles storage according to the corresponding category; (c) Batch weighing; (d) Start of a combustion experiment with batch introduction into the fluidized bed reactor.

In Table 6 are indicated, for each experimental conditions, the fluidized bed temperature, the *L*/*D* ratio for the char particles, the mass of the batch under consideration m_c, the number of char particles composing each batch N_c and the superficial velocity at the bed operating conditions *U*.

2.4. Evolution of the CO_2 in the exhaust gas flow

Figures 3 and 4 present evolutions of the molar concentration of CO_2 in the exhaust gas flow for combustion experiments with char made from eucalyptus additivated with 5 % (w/w) of glycerol. The curve trends are quite similar for all the experiments. In the first instants, after the introduction of the batch of char particles, there is a peak on the CO_2 release rate followed by a continuous concentration declining. Initially, in this declining region, the reduction of concentration is quite smooth, followed by a second part with a stronger concentration reduction, being this reduction stronger for lower *L*/*D* ratios.

Riaza et al. [45] analyzed images of the combustion of individual particles and registered that the first step of the combustion process is the particle heating with consequent drying and release of volatiles, and only after this initial step, the combustion of the solid residues takes place. As propane has been used to simulate the volatiles released from burning coke particles [46, 47], such approach was also followed in this work and volatiles released during the biochar particles combustion were assumed as propane. With this methodology, the carbon balance of the combustion process, obtained through the time integration of the CO_2 concentration in the exhaust gases, was correctly done, and a carbon recuperation close to 100 % was achieved

Table 6. Defining parameters for each combustion experiment.

		Eucalyptus + 5 % (w/w) Glycerol			**Eucalyptus + 21.4 % (w/w) Glycerol**			**Vine + 5 % (w/w) Glycerol**		
T **[ºC]**	***L/D***	m_c **[g]**	N_c **[-]**	***U*** **[mm/s]**	m_c **[g]**	N_c **[-]**	***U*** **[mm/s]**	m_c **[g]**	N_c **[-]**	***U*** **[mm/s]**
	1.5	-	-	-	-	-	-	2.86	25	107.3
	2	2.50	25	107.3	2.26	25	107.3	-	-	-

	3	3.13	20	107.3	3.44	22	107.3	2.89	14	107.3
	4	-	-	-	3.44	16	107.3	-	-	-
	1.5	-	-	-	-	-	-	2.65	25	74,0
	2	2.41	25	111.9	2.19	24	111.9	-	-	-
	3	3.12	20	111.9	3.24	21	111.9	3.13	14	111.9
	4	3.33	15	111.9	3.38	15	111.9	-	-	-
	1.5	-	-	-	-	-	-	2.69	26	76,1
	2	2.39	25	116.6	2.55	28	116.6	-	-	-
	3	3.06	20	116.6	3.00	20	116.6	3.13	14	116.6
	4	3.46	15	116.6	3.41	15	116.6	-	-	-
900	1.5	-	-	-	-	-	-	2.69	25	116.7
	2	2.40	25	116.7	2.45	26	116.7	-	-	-
	3	3.08	20	116.7	3.23	20	116.7	2.91	14	116.7
	4	3.46	15	116.7	3.29	15	116.7	-	-	-

In this situation, the mass fraction of carbon in a given sample of biochar to be burned, is the summation of the fixed carbon and the carbon in the volatiles [31],

$$f_c = f_{cf} + f_{cv} \tag{1}$$

where f_{cf} is the mass fraction of the fixed carbon and f_{cv} is the carbon mass fraction in the volatiles determined by means of,

$$f_{cv} = \frac{3\,M_C}{M_{C3H8}} f_v \tag{2}$$

In equation above M_C and M_{C3H8} are respectively the molecular masses of carbon and propane and f_v is the volatiles mass fraction in the char particles. The calculated values for each type of char are in Table 7.

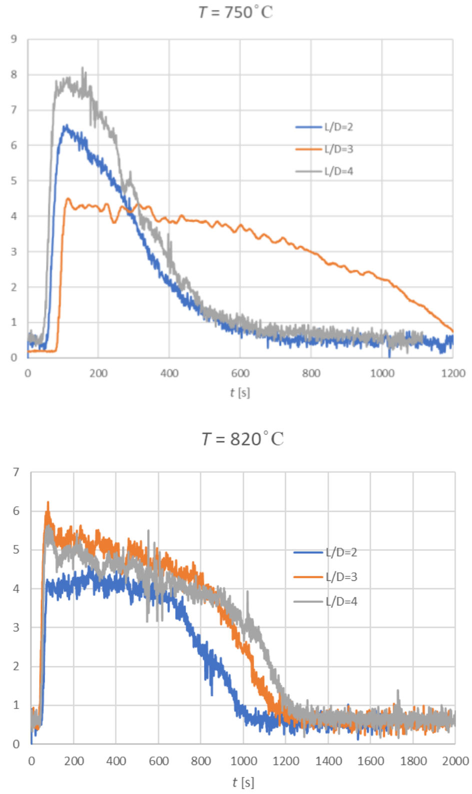


Figure 3. Time evolution of the CO_2 molar fraction obtained in the combustion of batches of char made from eucalyptus additivated with 5 % (w/w) glycerol, at 750 and 820 ºC.

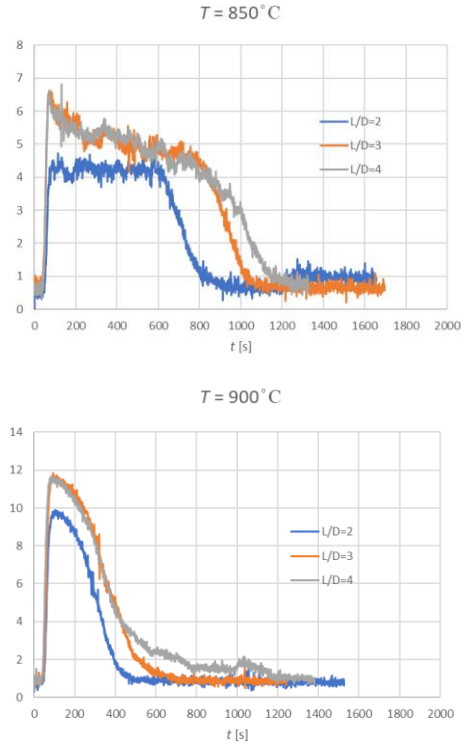
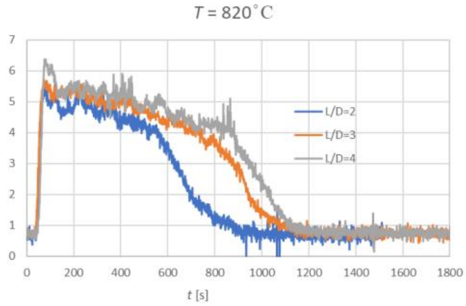


Figure 4. Time evolution of the CO_2 molar fraction obtained in the combustion of batches of char made from eucalyptus additivated with 5 % (w/w) glycerol, at 850 and 900 ºC.

Figure 5 presents evolutions of CO_2 in the exhaust gas flow for combustion experiments with char made from eucalyptus additivated with 21.4 % (w/w) of glycerol, for two bed temperatures, 820 and 900 ºC, while Figure 6 presents equivalent evolutions for char made from grapevine additivated with 5 % (w/w) of glycerol, and the same bed temperatures. These results, were now shown only for two bed temperatures, for the sake of simplicity.



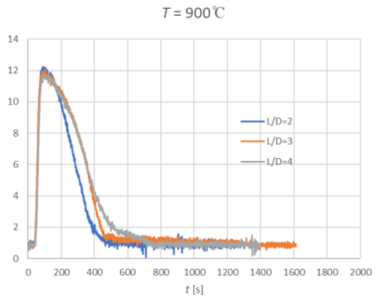


Figure 5. Time evolution of the CO₂ molar fraction obtained in the combustion of batches of char made from eucalyptus additivated with 21.4 % (w/w) glycerol, at 820 and 900 ºC.

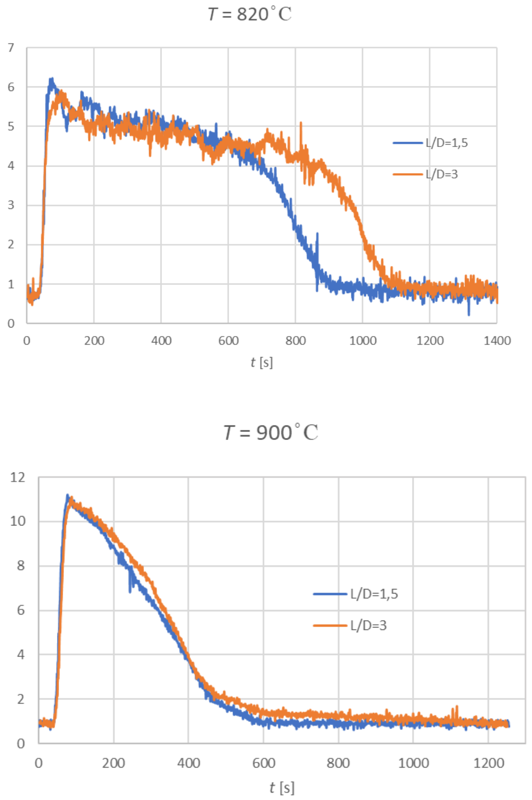


Figure 6. Time evolution of the CO₂ molar fraction obtained in the combustion of batches of char made from grapevine additivated with 5 % (w/w) glycerol, at 820 and 900 ºC.

Table 7. Mass fraction of carbon as fixed carbon and as volatiles.

	Eucalyptus + 5 % (w/w) Glycerol	**Eucalyptus + 21.4 % (w/w) Glycerol**	**Vine + 5 % (w/w) Glycerol**
f_{cv}	5.24 %	6.28 %	6.22 %
f_c	87.54 %	81.38 %	84.22 %

3. Experimental results

3.1. Combustion results

From the integration of the CO₂ versus time curve, and knowing the number of particles composing a batch under combustion, it is possible to determine for each time instant the burned mass fraction of carbon, the particle size and the instantaneous reaction rate and finally the time evolution of the overall resistance to combustion [8, 9, 17, 48]. The evolution of the overall combustion resistance, as a function of the mean diameter of the particles, is calculated using mathematical models developed for the fluidized bed combustion of char particles, assuming that they are spherical. However, this hypothesis normally does not occur and accordingly the combustion data must be analyzed taking the particle non-sphericity into account. In the present study cylindrical particles with different length to diameter ratios *L*/*D*, were considered. The sphericity of the particles must then be taken into consideration, in order to reach a better characterization of the volume and surface area of the particles composing a given batch of char particles.

The corrected spherical diameter of the particle is the product of the diameter of a sphere with the same volume as the particle d_S with the particle sphericity [21],

$$d = \phi_p d_s \tag{3}$$

being ϕ_p, the particle sphericity, given by,

$$\phi_p = \frac{A_s}{A_p} \tag{54}$$

and taking into account the real *L*/D ratio of the particle,

$$\phi_p = \left(\frac{3}{2}\right)\frac{(L/D)^{2/3}}{(L/D)+1} \tag{5}$$

In Table 8 are the corresponding sphericities for all the particles tested.

Table 8. Sphericities of the char particles, function of the *L*/*D* ratio [31].

L/D	ϕ_p
1.5	0.8585
2	0.8320
3	0.7788
4	0.7338

As already referred, there is a similar behavior for the three tested chars, with the curves showing initially a peak of CO₂ release, followed by a decrease phase not very pronounced and ending with a fall that is more pronounced the lower the *L*/*D* ratio. Finally, at the end of each test, the CO₂ concentration remains constant, Figure 7. Thus, it is possible to divide the burning process into two major parts:

a) Heating of the particles and release of volatiles;

b) Burning of the solid carbonaceous residue.

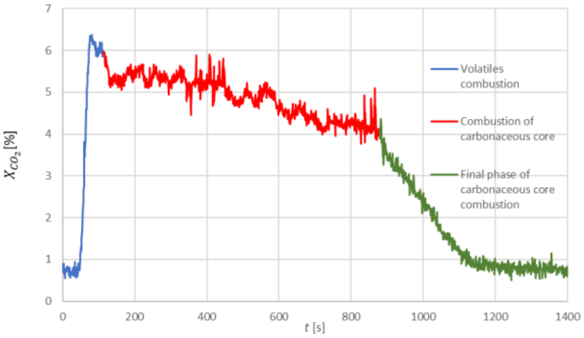


Figure 7. Representation of the temporal evolution of CO₂ dry basis molar fraction, separating the combustion of volatiles from the combustion of carbonaceous core

Taking as an example the test at 820 ºC, for eucalyptus charcoal with 21.4 % (m/m) of glycerol with *L*/D = 4, Figure 7, in blue, shows the evolution of CO₂ concentration during the volatiles release and burning phase. As already mentioned, the peak of CO_2 release is in this phase and the higher the temperature, the higher is this peak of CO_2.

Turning to the combustion of the carbonaceous residue, this phase is divided into two moments. In the first, represented in red in Figure 7, a not very steep decay of the CO_2 concentration can be seen. However, the smaller the particles, the faster the burning process and the higher the reaction rate, resulting in steeper curves. The second moment, presented in green in Figure 7, is characterized by a much sharper drop in CO_2 concentration that can be explained by the fragmentation of the particles, with a consequent increase in the reaction area and speed of combustion. From the overall analysis of all tests, the higher the temperature, the more pronounced is this decay, showing a decrease in kinetic and diffusive resistances in this final stage of carbonaceous waste combustion. From previous works [35] one knows that the temporal evolution of the CO_2 curve is very dependent on fragmentation phenomena that occur with great intensity in the final phase of burning. This causes a large increase in the reaction area, which translates into the aforementioned interpretation of the high drop in kinetic and diffusive resistances at the end of the curve. Any quantification of data in this final part was out of the scope of the present study, which was solely concentrated on the char combustion behavior in the above shown red zone of the CO_2 concentration curve.

Concerning the fluidized bed batch combustion experiments of the carbonaceous particle, it is assumed that the solid particles are spherical (with the above mentioned diameter correction to account for its proper sphericity), and burn at a constant density and reducing size. It was also considered that the particle carbon burns to CO according to $C + ½\ O_2 \rightarrow CO$ and the CO formed burns away from the particle according to $CO + ½\ O_2 \rightarrow CO_2$ [5, 7]. Thus, the oxygen consumption rate at the surface of the particle is then half the carbon consumption rate and the heterogeneous phase reaction that takes place at the surface of the particle is a first order reaction,

$$\dot{N}_{O_2} = \frac{1}{2} R_0 = \pi\ d\ Sh\ D_G \left(C_p - C_s\right) = \frac{1}{2} k_c \pi\ d^{\ 2} C_s \tag{6}$$

where $\dot{N}_{O_2}$ is the molar oxygen flow rate reaching the particle surface, R_0 is the carbon molar consumption rate, *Sh* is the particle Sherwood number, *d* is the diameter of the burning particle, D_G is the oxygen diffusivity in the air, C_p and C_s are respectively the molar concentrations of oxygen in the particulate phase of the bed and at the surface of the burning particle. k_c is the reaction rate constant for the heterogeneous phase reaction occurring at the surface of the char particle. It is possible to write that,

$$R_0 = 2\ \pi\ K\ d^{\ 2} C_p \tag{7}$$

wherein, $1/K$ is the overall combustion resistance [8, 9] for the combustion of batches of carbon particles in a bubbling fluidized bed combustor.

$$\frac{1}{K} = \frac{d}{Sh\ D_G} + \frac{2}{k_c} \tag{8}$$

It is understandable that from the slope of the $1/K$ versus d diffusive information can be gathered through the Sherwood number, while from the intercept the heterogeneous reaction rata constant is determined. More information about the data treatment procedure and the integration of the time evolution of the CO_2 concentration in the exhaust gases flow can be seen elsewhere [8, 9, 17, 21, 48].

3.2. Kinetic and diffusive results

Figure 8 shows a typical evolution of the overall resistance to combustion $1/K$ with the equivalent particle diameter for a combustion experiment of batches of eucalyptus char additivated with 5 % (w/w) glycerol at 850 ºC.

It can be seen that for the three size classes there is a very intense initial decline, which is due to the transient heating regime of the particles and some initial fragmentation of some of them, followed by a perfectly defined downward slope. The line ends abruptly. This is an indication of the absence of final fragmentation of the particles, that is a result of the organization of the particles by classes and similar morphology of the particles. It is thus concluded that the burning time is approximately equal for all particles of each charge and that they therefore disappear simultaneously. The behavior presented in this test was also observed in the study of fluidized bed combustion of char particles made from woods of Mozambican origin [49]. Note that, theoretically, one would expect that the burning resistance of a particle would not vary with the *L*/D ratio. However, as can be seen in Figure 8, the combustion resistance curves are increasingly horizontal with increasing *L/D*.

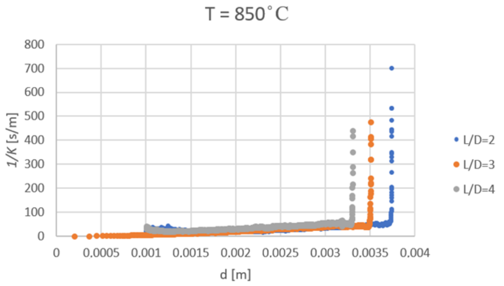


Figure 8. Evolution of the overall resistance to combustion with the equivalent particle diameter for the combustion at 850 ºC, of batches of eucalyptus char additivated with 5 % (w/w) glycerol.

In addition to the type of curves shown in Figure 8, another type of progress was observed and shown in Figure 9. This figure represents the evolution of the overall burning resistance with the diameter, at bed temperature of 820 ºC, for the eucalyptus char with 5% (m/m) of glycerol additive. In this test, it is also noted a drastic decrease in resistance caused by the initial heating and small fragmentation of the char particles. However, at the end of the curve, there is a rise in the combustion resistance motivated by further particle fragmentation, and subsequent elutriation from the fluidized bed in this final part of the combustion. Therefore, the smaller particles burn first and disappear, leading to a reduction in the reaction surface area, with a consequent apparent increase in resistance, forming a U-shaped curve [48, 50].

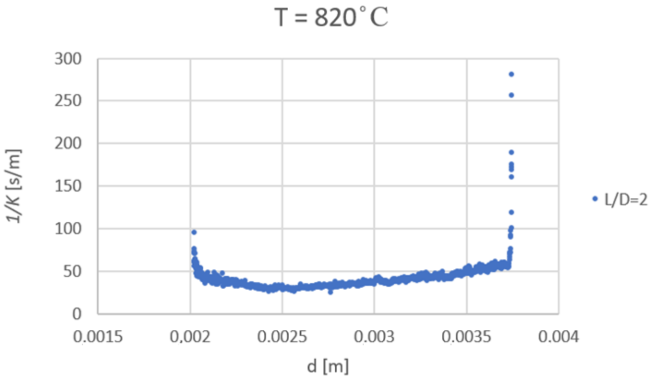


Figure 9. Evolution of the overall resistance to combustion with the equivalent particle diameter for the combustion at 820 ºC of batches of eucalyptus char additivated with 5 % (w/w) glycerol.

Theoretically, the evolution of the global resistance $1/K$ with the diameter should follow a line of positive or zero slope, and in the case of positive slope, where diffusion is of relevant importance, the ordinate at the origin should be greater than or equal to zero. In this last case, the control is purely diffusive. On the other hand, when the slope is zero there is a pure kinetic control. For the temperature of 900 ºC, an anomalous situation occurred for all three char species. As can be seen from the graph in Figure 10, representative of the evolution of the combustion resistance with the diameter, for the vine coal additivated with 5% (m/m) of glycerol, its slope is negative, contrary to what is theoretically correct for unbreakable fuel particles. This situation, is the result of a sequential fragmentation [35], i. e., not only the initial fracture after the introduction of the char particles in the bed, but a continuous fragmentation of the particles leading to an increase in their number and their total area available for the reaction. These events, while being ignored in the data calculation process, result in such unexpected 1/*K* versus *d* trends [35].

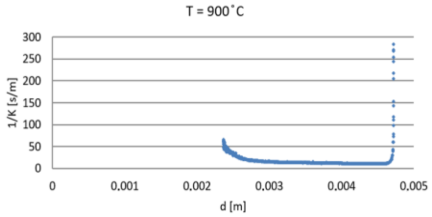


Figure 10. Evolution of the overall combustion resistance with the diameter for the temperature of 900 ºC for the vine coal additivated with 5% (w/w) glycerol

Table 9. Diffusive and kinetic data for eucalyptus char additivated with 5 % (w/w) glycerol.

Bed temperature [ºC]	*L/D*	*Sh*	kc
750	2	0.7837	∞
	3	1.1128	0.0450
820	2	0.5388	∞
	3	0.4674	∞
	4	0.4217	∞
850	2	0.5719	∞
	3	0.4928	∞
	4	0.3892	∞

Table 10. Diffusive and kinetic data for eucalyptus char additivated with 21.4 % (w/w) glycerol.

Bed temperature [ºC]	*L/D*	*Sh*	kc
750	2	0.359	∞
	3	0.678	0.0421
	4	0.237	0.8718
820	2	0.556	∞
	3	0.341	∞
	4	0.312	∞
850	2	0.606	∞
	3	0.474	∞
	4	0.379	∞

Table 11. Diffusive and kinetic data for vine char additivated with 5 % (w/w) glycerol.

Bed temperature [ºC]	*L/D*	*Sh*	kc
750	1.5	0.706	∞
	3	0.456	∞
820	1.5	0.969	∞
	3	0.619	∞
850	1.5	1.348	∞
	3	0.845	∞

It is clear that the addition of glycerol to the biomasses for pellet production has resulted in chars that, above a given temperature, are so fragile that the particle breakdown phenomena control the combustion process. In the tests carried out at 900 ºC, particle fragmentation dominates the burning to such an extent that under the present experimental conditions it was not possible to draw any information about kinetics and diffusion.The diffusive and kinetic data obtained from the experiments carried out at bed temperatures of 750, 820 and 850 ºC are shown in Tables 9, 10 and 11. Through the analysis of these results, it is concluded that the reaction control is mostly diffusive, and for most of the experiments it is purely diffusive. Taking the results obtained for eucalyptus char with 5% (m/m) of glycerol additive and comparing them with those obtained by Pereira and Pinho [20], for eucalyptus char, the Sherwood number values were, in that work, around 0.4 for analogous experimental conditions, i.e., very similar to the current ones, while the k_c

were between 0.2 and 0.3 m/s, and now have infinite values. A note of caution is necessary here, because the eucalyptus char tested by Pereira and Pinho [20] was produced from the tree trunk wood, while in the present case the char was produced from eucalyptus forest clearing waste.

Taking into consideration the results for the vine char additivated with 5 % (m/m) glycerol, and comparing them with those obtained by Mateus et al. [31] for vine char without any additive, similar Sherwood numbers are found while the values of the chemical reaction rate constant k_c, went from values between 0.2 to 3.4 m/s, to infinity, this for bed temperatures between 750 and 850 ºC. Thus, there is a huge increase in reactivity, both of eucalyptus and vine char, due to the use of glycerol as an additive in the manufacture of the pellets. However, contrary to the eucalyptus char, the raw material used in the production of vine char has the same origin.

It is important to underline that, in the case of the char pellets with 21.4 % (m/m) glycerol, the too low *Sh* values indicate a possibly of particle burning not at constant density and decreasing diameter, but at constant diameter and decreasing density or a combination of the two mechanisms [51].

4. Conclusions

The present study was about the determination of kinetic and diffusive data of fluidized combustion of biochar made from three types of pellets: eucalyptus pellets with 5 % and 21.4 % (w/w) glycerol additive and vine pellets with 5 % (w/w) glycerol additive. The three original types of pellets were pyrolized in a bed fluidized with N_2 at 850 ºC, and afterwards the biochars were chemically characterized. With the resulting cylindrical particles of biochar, burning tests were performed at 750, 820, 850 and 900 ºC bed temperatures. The char particles were characterized by their length to diameter ratio in order to guarantee a similar morphology between them.

Considering the diffusive and kinetic data obtained from the experiments carried out at bed temperatures of 750, 820 and 850 ºC, it is clear that the reaction control is mostly diffusive, and for most of the experiments, it is purely diffusive. Besides, there is a huge increase in reactivity, both of eucalyptus and vine char, due to the use of glycerol as an additive in the manufacture of the pellets.

The addition of glycerol to the biomasses for pellet production has resulted in chars that, above a given temperature, are so fragile that the particle breakdown phenomena control the combustion process. For tests carried out at 900 ºC, particle fragmentation dominates the combustion process and it was not possible to draw any information about kinetics and diffusion.

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Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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