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Article

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Determination of kinetic data through the fluidized bed combustion of chars made from vine and kiwi pruning wastes

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Abstract

This work concerns a preliminary study of the combustion of chars made from two different biomass species, vine and kiwi pruning wastes. The study was performed in a fluidized bed combustor, operating in a bubbling bed regime.

The pellets were manufactured in a different installation, Viseu Polytechnic Institute, transported and, then carbonized in fixed bed batches at 900 °C in a nitrogen atmosphere, in site, to obtain char. To acquire complete information on the combustion behavior, different sizes of char particles were subsequently burned in a bubbling fluidized bed and, through the measurement and subsequent analysis of the time progression of the CO₂ in the flue gases, the evolution of the overall combustion resistance was obtained, and information on the combustion control was gathered. The evaluation of the relative importance of the kinetic and diffusive phenomena on the reaction was quantified, and it was observed that for the chars tested, the combustion was kinetically controlled. Applying the Arrhenius law to the kinetic data for each char, the corresponding pre-exponential factors and activation energies were obtained.

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Keywords: Biomass; Pruning waste; Combustion; Fluidized bed

1. Introduction

Several studies have been carried out by the present research team, on the determination of kinetic and diffusive data of fluidized bed combustion of different biomasses, either from Portugal or from Brazil and Africa. In Rangel and Pinho [1,2] combustion results of commercial and recarbonized chars of nut pine (*Pinus pinea*) and cork oak (*Quercus suber*) were reported. Rangel and Pinho [3] studied the influence of the fragmentation phenomenon upon the determination of kinetic and diffusive reactions on the fluidized bed combustion of nut pine (*Pinus pinea*) chars,

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and Ramos et al. [4] investigated the chars obtained from eight species of wood from the semiarid region of the Brazilian northeast, known as the Cariri Paraibano. Later, Pereira and Pinho [5] studied the chars obtained from woody biomasses from the central region of Portugal, *Quercus ilex* (holm oak), *Eucalyptus globulus* (eucalyptus), *Pinus pinaster* (maritime pine), and *Quercus suber* (cork oak), and the importance of particle sphericity and fragmentation on the behavior of these four chars was presented in [6]. In addition, Tomé et al. [7] studied the fluidized bed combustion of chars made from biomasses of Mozambican origin, and Pereira and Pinho [8] and Marques et al. [9] analyzed the influence of mineral ash components in the char ashes upon the kinetic behavior during combustion.

The present preliminary study on the combustion of chars made from pruning wastes of vine plant (*Vitis vinifera*), and kiwi plant (*Actinidia deliciosa*), follows the same trend of the previously works done by the research team. It evaluates the kinetic and diffusive data from the fluidized bed combustion of these chars carried out in a laboratory scale bubbling fluidized bed combustor. The mechanism controlling the combustion process was determined accordingly. To do that, pellets were fabricated from the original biomasses and were then carbonized in fixed bed batches at 900 °C, under a nitrogen flow. The main properties of the obtained chars are presented in Table 1.

Table 1. Proximate analysis and density of the vine and kiwi chars.

Parameters (dry basis)	Analytical methods	Vine	Kiwi
Moisture at 105 °C [% w/w]	EN 1860-2	0.5	0.6
Volatile mater at 900 °C [% w/w]	EN 1860-2	24.4	21
Ashes at 710 °C [% w/w]	EN 1860-2	9.5	11.9
Fixed carbon [% w/w]	Calculation	66.1	67.1
Density [kg/m ³]	Mercury picnometry	789.7	820.7

The char particles were then burned in small batches in a laboratory scale bubbling fluidized bed reactor. Different sizes of char particles were tested, at four different bed temperatures, 750, 820, 850 and 900 °C. The char particles composing a batch to burn were chosen one by one in order to guarantee its size closeness.

All batches were weighted in a *Sartorius MA 30* balance, the number of particles on each batch was quantified, and consequently the average particle diameter was calculated. The mass of each batch of particles was in the 2 to 3 g range, while the initial mean particle diameter was in the 6 to 9 mm range. The fluidization velocity was between 1.5 and 1.6 times the minimum fluidization velocity.

The vine and the kiwi are vegetable species very common in Portugal. The country has the fourth largest winegrowing area of vine plant, *Vitis vinifera*, in Europe (around 199,000 ha) and has about 174,000 ha of protected winegrowing nomination, i.e., about 80% of the cultivated vine growing [10]. In the kiwi case, *Actinidia deliciosa*, the cultivated area is above 2800 ha and Portugal is the fourth large European kiwi producer, behind Italy, France and Greece, with an annual production of 35,000 tons in 2017 [11].

2. Experimental setup

The laboratory scale fluidized bed combustor is shown in Fig. 1. It has a small bubbling fluidized bed reactor made with a refractory steel pipe with 80.0 mm internal diameter, externally heated by a 4.2 kW electrical resistance controlled by a proportional differential integral temperature controller. The bed is made of quartz sand particles with an average diameter of 283 µm, obtained through sieving and separation through two consecutive sieves of 250 µm and 315 µm size.

The bed was fed with fluidizing air whose flow was previously measured through an orifice plate flow meter, which was connected to a differential pressure transducer. The sampled exhaust combustion gases were cooled in a condenser and afterwards sent to an *ADC infrared gas analyzer, model MGA-3000 Series Multi Gas Analyzer*. During each combustion experiment, the carbon dioxide concentration in the exhaust gases was measured. The analyzer was connected to a data acquisition system installed in a desktop computer. Readings of the fluidized air mass flow rate, as well as the bubbling bed temperature were also sent to the data acquisition system, which was controlled by the *DasyLab* software.

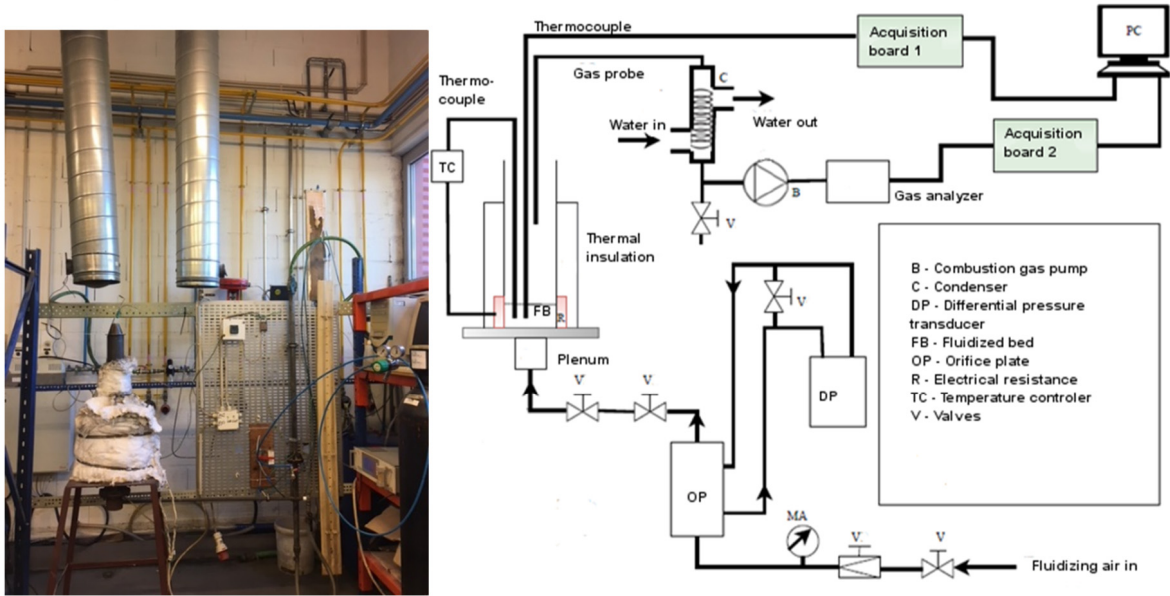


Fig. 1. Picture and scheme of the experimental setup.

3. Experimental results

According to the combustion models for the batch combustion of carbon particles in bubbling fluidized beds [2,5], from the time evolution of the carbon dioxide concentration in the combustor exhaust flow, the overall combustion resistance can be easily obtained. This overall combustion resistance is theoretically composed by two terms, a kinetic term and a diffusive term,

$$\frac{1}{K} = \frac{2}{k_c} + \frac{d}{Sh D_G} \quad (1)$$

$1/K$ is the overall combustion resistance [s/m], k_c is the heterogeneous phase carbon to CO oxidation reaction [m/s], Sh is the burning particle Sherwood number [-] and D_G is the oxygen diffusivity [m^2/s]. Fig. 2 shows the evolution of $1/K$ versus the particle diameter d [m], on the left plot for vine char at 750°C , and on the right plot for kiwi char at 900°C . Further treatment of the $1/K$ versus d curves was carried out in the 30 to 70% burned mass fraction ratio interval, to avoid initial and final combustion transient periods.

From Eq. (1) it is clear that the $1/K$ versus d plot should be a straight line, with a $d/(Sh D_G)$ slope and a $2/k_c$ intercept. This occurs in the plots of Fig. 2, except during the initial and the final parts of the combustion process, where transient phenomena [2] explain the abnormalities. However, considering only data in the 30 to 70% burned mass fraction, for all tested bed combustion temperatures, it can be concluded for both biomass types that the combustion is kinetically controlled, as the $1/K$ versus d plots result in horizontal straight lines. In these plots, the corresponding legends show the mass and the number of char particles of each batch.

For the determination of the reaction rate constant dependency upon the burning particle temperature T_p [K], an energy balance was made, because assuming that the particle was burning at the bed temperature T_b [K] would lead to erroneous results. The resulting equation [12] is,

$$\dot{m}_c \Delta h + \dot{m}_c c_{pg} (T_p - T_b) \frac{\exp\left(-\frac{\dot{m}_c c_{pg}}{2\pi d k_{tg}}\right)}{1 - \exp\left(-\frac{\dot{m}_c c_{pg}}{2\pi d k_{tg}}\right)} + \varepsilon_p \pi d^2 \sigma (T_p^4 - T_b^4) = 0 \quad (2)$$

In the above equation, c_{pg} is the constant pressure specific heat of the gas around the burning particle [J/(kg K)], d is the instantaneous diameter of the burning particle, k_{tg} is the thermal conductivity of the gas [W/(m K)] around the particle, \dot{m}_c is the particle burning rate [kg/s], T_b is the bed temperature [K], T_p is the surface temperature of

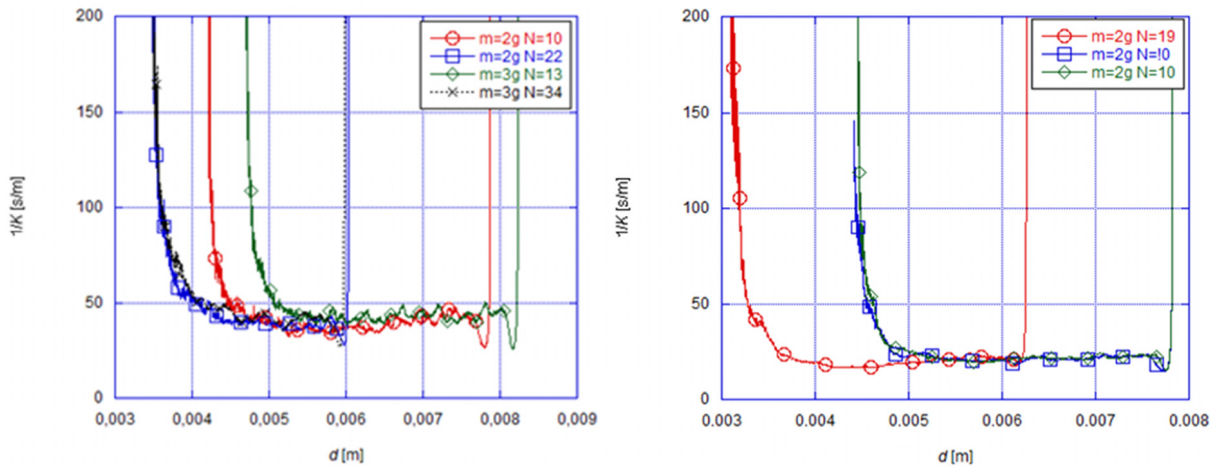


Fig. 2. Evolution of the overall combustion resistance for the vine char burning at 750 °C, left, and kiwi char burning at 900 °C, right. For each plot, the legends indicate the mass and the number of particles composing the batch.

the burning particle [K], ε_p is the emissivity of the burning particle [–], Δh is the heat of combustion of C to CO [J/kg] and σ is the Stefan–Boltzeman constant [W/(m² K⁴)]. The particle-burning rate is determined through [2],

$$\dot{m}_C = 2M_C \pi d^2 K C_p \quad (3)$$

where C_p is the molar concentration of oxygen in the particulate phase of the fluidized bed [mol/m³] and M_C is the molecular mass of carbon [kg/mol].

From the experimental data, the following Arrhenius equations were obtained. For the vine char,

$$k_c = 51.15 \exp \left[-61.77 / (\bar{R}T) \right] \quad (4)$$

while for the kiwi char,

$$k_c = 61.76 \exp \left[-61.08 / (\bar{R}T) \right] \quad (5)$$

The obtained activation energies, 61.77 and 61.08 [kJ/mol], are typical for woody chars, but the pre-exponential factors are very low, thus explaining the kinetically controlled combustion. This is understandable due to the high ash content of the chars under study, Table 1. In the Eqs. (4) and (5) \bar{R} is the universal gas constant [J/(mol K)].

4. Conclusion

In this preliminary study on the bubbling fluidized bed combustion of chars made from vine and kiwi pruning wastes, it was found that the combustion was kinetically controlled. The activation energy values, 61.77 kJ/mol for the vine char and 61.08 kJ/mol for the kiwi char, are of the order of magnitude of values obtained in several other studies, albeit on the lower side of the value range already obtained by the team for other chars [2,5]. They are however coherent with other studies. For example, Janse et al. [13] have a large set of data collected from the literature from different authors and refer activation energies from 84.9 to 160 kJ/mol for several types of wood chars. Adánez et al. [14] using a modified Arrhenius equation got values in the 55 to 63 kJ/mol range for pine and eucalyptus chars, i.e., very similar to the present ones.

The important conclusion to stress here is the very low pre-exponential factors, justified by the high ash content of the chars, see Table 1, thus coherent with the kinetically controlled combustion. The present work is in line with the interest of agro-forestry residues as an energy source, and how the study of combustion problems arising from some of the ash components of these biomasses [15], is becoming an important request for the understanding of the phenomena occurring inside the reaction zone.

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