

EFFECTS OF POTASSIUM AND CALCIUM ON THE COMBUSTION BEHAVIOUR OF BIOMASS

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ABSTRACT

The main objective of this work is to evaluate the effects of potassium (K) and calcium (Ca) on the combustion behaviour of biomass at low and high heating rates. The biomass used was grape pomace, sieved in the size range of 200-250 μm . With the pre-treatments of demineralization and impregnation, a total of 12 different samples were obtained: raw, demineralized and impregnated grape pomace with 0.1, 0.5, 0.82, 3 and 6 wt.% of K, and 0.1, 0.5, 1.08, 3 and 6 wt.% of Ca. Firstly, to identify the individual role of K and Ca, the biomass samples were pyrolyzed in a N_2 atmosphere and oxidized in air using a thermogravimetric analyser (TGA). In general, the combustion process was promoted with increasing K concentration, whereas Ca did not significantly influence this process. The high heating rate tests were performed in a McKenna burner at two different operating conditions. A CMOS high-speed camera was used to record the ignition and the volatiles combustion events. The results obtained showed that K impregnation led to a decrease in the ignition delay time as the concentration of K increased, while Ca impregnation did not have a significant impact on the ignition delay time. Both impregnation pre-treatments decreased the volatiles combustion time as the concentration of K or Ca increased. Finally, the impregnation with K and Ca had a more significant impact on the volatiles combustion time than on the ignition delay time.

Keywords:

Potassium, calcium, thermogravimetric analysis, single particle, ignition delay time, volatile combustion time.

INTRODUCTION

Biomass is a CO₂-neutral energy source that can play a key role in global energy production, in pulverized suspended combustion systems [1]. However, its diverse composition may be the origin of critical issues in industrial applications. These issues are generally associated with the low heating value, the high content of moisture and ash composition of the biomass [2–4]. A critical fraction of the biomass composition is its ash content that can have a significant impact on the whole combustion process. Potassium (K) and calcium (Ca) are two main alkali and alkaline earth metals present in the ash content and they can exist in biomass as inorganic salts, minerals or be organically bounded [5,6]. In addition to their contribution to the well-known problems of ash deposition and corrosion in boilers and

furnaces, which may reduce their conversion efficiency, the K and Ca can also have a catalytic effect on the thermochemical conversion processes of biomass.

Most of the studies focusing on ash behaviour during combustion are related to the final stages of combustion [7–9], with little attention being given to the early stages of combustion, namely ignition and volatiles combustion. Previous studies on the catalytic effects of K and Ca on biomass conversion were usually performed using thermogravimetric analysers (TGA) mostly focusing on pyrolysis [10–12] and gasification [13–15]. These studies revealed that K catalyse both pyrolysis and gasification processes, whereas Ca has little or no impact during pyrolysis, but shows catalytic behaviour in gasification processes.

Fuentes et al. [11] studied the effect of K and Ca on the biomass combustion stages using TGA. The authors observed that K catalysed both the volatiles release and the char oxidation stages by shifting the DTG characteristic peaks of these stages to lower temperatures, whereas Ca catalysed only the char combustion stage, but to a lesser extent than K.

There have been very few attempts to study the ignition behaviour of single particle biomass fuels [16–18], and studies focusing on the effect of the biomass composition on particle ignition are rather scarce. Mason et al. [17] studied the duration of the combustion stages of three biomass fuels (pine, eucalyptus and willow) on a Meker burner, observing a tendency for the ignition delay time to be higher for the solid fuels with higher moisture content. Simões et al. [18] studied the ignition behaviour of five biomass fuels (wheat straw, kiwi branches, vine branches, sycamore branches and pine bark) using an optical flat flame McKenna burner, and concluded that, for temperatures of 1500 and 1650 K, particle shape plays a more important role than the biomass composition on the ignition mode, and that the biomass composition has a higher impact on the ignition delay time for temperatures of 1500 and 1650 K than for temperatures of 1700 and 1800 K. Jones et al. [19] studied the effect of K on the combustion stages of static single particles in a Meker burner and of moving particles of biomass in a flat flame burner, simulating conditions typically encountered in pulverized combustion. The results showed a catalytic effect of K through the reduction of the devolatilization and char oxidation times.

In this context, the aim of this work is to investigate the impact of the presence and concentration of K and Ca on the devolatilization and char oxidation characteristics of biomass fuels, taking as reference point, grape pomace biomass. Grape pomace was demineralized and subsequently doped with different concentrations of K and Ca, making a total of 12 different samples. The work was then divided in two

main parts depending on the type of experiments done which in turn are closely related to the heating rates applied. In a first part, the impact of K and Ca on the pyrolysis and combustion behaviour of biomass at low heating rates, using thermogravimetric analysis (TGA), is examined in order to understand the processes and reactions involved during devolatilization and char oxidation.

With the aim of extending the study to conditions closer to those of practical applications, raw, demineralized and impregnated biomass particles were fed, as single particles, to a confined laminar flow of combustion products produced by a McKenna flat flame burner, submitting the particles to high heating rates of around 10^5 K/s. First, the biomass particles were tested under two distinct temperature conditions to evaluate the effect of the presence of K and Ca on the ignition delay time. Subsequently, one of the conditions was chosen to evaluate the effects of the presence of those elements on the volatiles combustion time.

MATERIALS AND METHODS

Sample preparation

The fuel used was grape pomace, which is a residue formed during the wine production, constituted essentially by skins and seeds. The particle size used in this work ranged from 200-250 μm . Table 1 shows the properties of this biomass residue.

To prepare the different samples, the raw grape pomace was firstly demineralized by a nitric acid leaching procedure in order to remove the inorganic elements present [15]. In particular, 30 g of raw biomass were placed in a flask with 500 ml of ion-exchanged water. The pH of the dissolution was adjusted to 2 using HNO_3 and stirred for 1 h at 60 °C. Subsequently, the biomass was filtered and washed thoroughly with 200 ml of ion-exchanged water. The filtering-washing procedure was repeated 4 times. Finally, the biomass was dried at 105 °C. The complete procedure was repeated twice.

Afterwards, the demineralized biomass was impregnated with different concentrations of either K (using potassium oxalate monohydrate as reactant) or Ca (using calcium oxalate monohydrate as reactant).

Table 1. Properties of raw grape pomace biomass.

Parameter	Value
<i>Proximate analysis (wt.%, as received)</i>	
Volatiles	48.4
Fixed carbon	18.6
Moisture	30.2
Ash	2.8
<i>Ultimate analysis (wt.%, dry ash free)</i>	
Carbon	51.1
Hydrogen	6.7
Nitrogen	1.9
Sulphur	0.2
Oxygen	40.1
<i>Heating value (MJ/kg)</i>	
High	21.2
Low	19.8
<i>Ash analysis (wt.%, dry basis)</i>	
SiO ₂	5.5
Al ₂ O ₃	1.0
Fe ₂ O ₃	1.2
CaO	37.8
SO ₃	1.7
MgO	7.2
P ₂ O ₅	19.7
K ₂ O	24.7
Na ₂ O	0.4
Other Oxides	0.8

The wet impregnation procedure consists of adding different amounts of K or Ca reactant to 11 ml of ion-exchange water and their subsequent mixture with 5 g of demineralized biomass. The resultant impregnated biomass samples were dried at 105 °C, and stored at ambient conditions. The specific K and Ca reactant amounts were selected to cover a wide and realistic

range of K and Ca concentration in different biomass residues [20]. Thus, A total of 12 different samples were obtained, specifically, raw grape pomace, demineralized grape pomace and impregnated grape pomace with 0.1, 0.5, 0.82 (equal to the K concentration in the raw biomass), 3 and 6 wt.% of K, and 0.1, 0.5, 1.08 (equal to the Ca concentration in the raw biomass), 3 and 6 wt.% of Ca.

Thermogravimetry setup

The evaluation of the combustion behaviour of biomass is based on the measurement of the mass change in a sample as a function of the temperature and time at a constant heating rate of 10 K/min from room temperature up to 1275 K in either nitrogen or air, using a Netzsch STA F1 Jupiter thermogravimetric analyser. The experiments were performed at atmospheric pressure using alumina crucibles and 5 mg of each biomass sample. The initial sample mass and heating rate used in these tests were chosen based on previous studies addressing the pyrolysis and combustion behaviour of different biomass residues in TGA experiments [21]. Prior to the experiments, for each experimental condition (i.e. air atmosphere or N₂ atmosphere), a calibration curve was made to avoid possible fluctuations caused by the apparatus that could influence the measurements.

To determine the uncertainty in the experimental procedure, the experiments were repeated at least three times. In addition, to disregard the possible influence of the biomass size distribution on the TGA results, the samples were sieved into the 200-250 µm size interval and, subsequently, subjected to the pyrolysis and combustion tests. The similitude of results is high, indicating a good repeatability of the procedure and a low effect of the biomass size distribution of the samples under the conditions of the present work.

Ignition Setup

Figure 1 shows the schematic of the experimental setup. It consists of McKenna flat flame burner, a biomass feeding unit, a gas feeding system, and an image acquisition system. The McKenna flat flame burner consists of a stainless-steel cylinder containing a water-cooled bronze porous sintered matrix of 60 mm diameter with a central hole of 1.55 mm internal diameter.

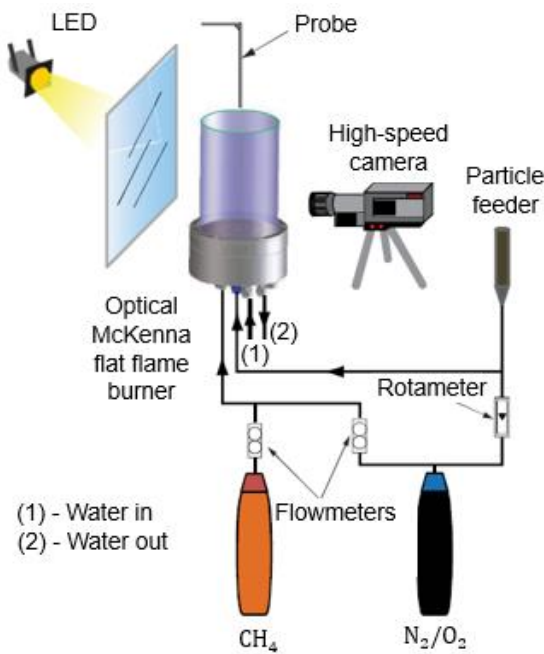


Figure 1. Schematic of the experimental setup.

The flat flame is created above the sintered matrix by a premixed mixture of primary air flow and methane flow supplied to the burner by the gas feeding system. Two mass flowmeters are used to control the flow rates. Furthermore, to cool the sintered matrix, water is supplied through copper tubes. A high-grade fused quartz with an internal diameter of 70 mm, a height of 500 mm and a thickness of 2 mm, is used in order to confine the combustion products flow, and prevent the entrainment of ambient air while providing optical access. The biomass feeding unit includes a 10 ml syringe where the biomass particles are stored, a fine mesh, and a rotameter to regulate the transport air flow.

The biomass particles are added to the transport air stream by gravitational force and injected upward through the central hole of the burner. The fine mesh placed inside the syringe ensured a low feeding rate of particles allowing the recording of single particle videos.

The image acquisition system includes a CMOS high-speed camera Optronis CamRecord CR600x2, equipped with a lens AF Micro-Nikkor 60 mm f/2.8D and a teleconverter Kenko TelePlus MC7 AF 2.0X DGX to increase the focal length of the lens used. Additionally, the image acquisition system includes a diffuse led backlight to create the shadow projection of the particles. In order to align the position of the camera, a target with millimeter marks was used for calibration before and after each experimental session. The axis of the camera was aligned perpendicularly with the axis of the burner so that the camera could record images of the particles since their injection. Table 2 lists the main camera settings used. A detailed description of the experimental setup used can be found elsewhere.

Table 2. Main camera settings.

Parameter	Setting
FPS	2300
Resolution [pix]	200x752

Test conditions

Two different operating conditions were used in this work named here conditions T1 and T2. These conditions were established by varying the thermal input while maintaining constant the excess air coefficient, which made possible to obtain a mean temperature difference of approximately 200 K along the working zone. Also, during the experiments the transport air flow rate was maintained very low (0.11 dm³/min), which was the lowest flow rate tested that guaranteed single particle feeding. Table 3 lists the burner operating conditions used in this work.

The mean gas temperature measurements were obtained by using 76 μm diameter fine wire platinum/platinum: 13% rhodium (type-R) thermocouples and the mean O_2 concentration measurements were obtained with the aid of a water-cooled probe and a paramagnetic analyzer. Each measurement was repeated three times.

Table 3. Burner operating conditions.

Parameter	T1	T2
Thermal input [kW]	0.9	1.8
Methane flow [dm^3/min]	1.5	3.2
Primary air flow [dm^3/min]	19.2	40.5
Transport air flow [dm^3/min]	0.11	
Excess air coefficient λ	1.3	
Mean gas temperature [K]	1575	1775
Mean O_2 concentration [dry vol.%]	5.4	5.2

Figure 2 shows the mean gas temperature and the mean O_2 concentration profiles for the test conditions used, along with the repeatability bars. Figure 2 also includes the gas temperature profiles corrected for radiation losses using the method described in Simões et al. [18].

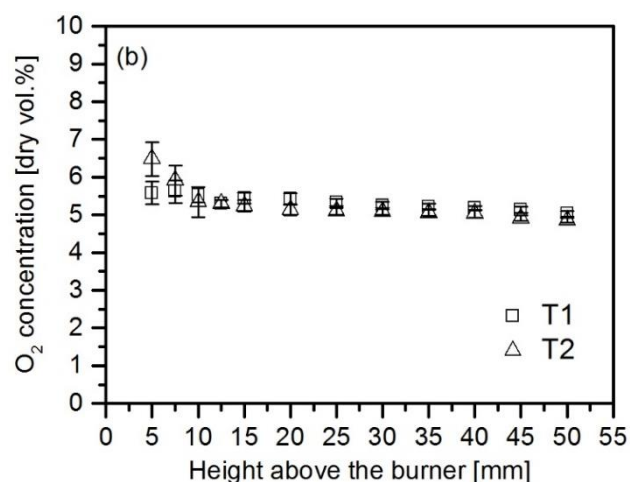
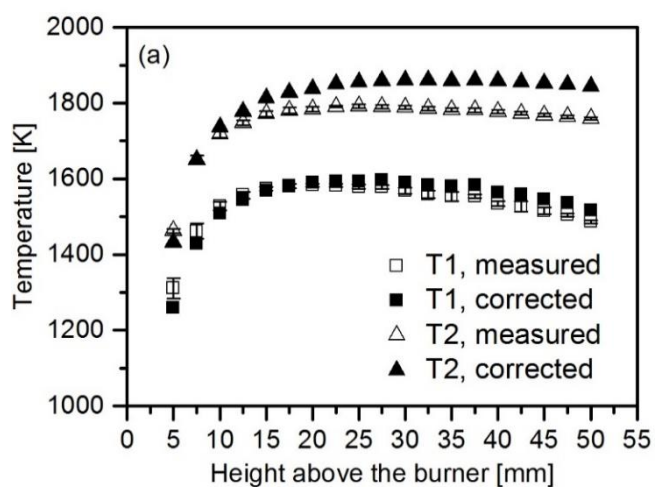


Figure 2. Mean gas temperature (a) and mean O_2 concentration (b) profiles for the operating conditions used.

Post processing of data

The images collected with the high-speed camera were examined in order to calculate the ignition delay time and the volatiles combustion time, using a method based on a previously developed by Simões et al. [18]. Capturing the visible light from the particles has been proved to be a good indicator of ignition despite soot and char emissions being included in the visible light captured [22,23]. Single particles burned almost exclusively in sequential form (97% of the samples), i.e., volatiles combustion followed by char combustion, which allowed measuring the duration of the volatiles combustion. The post-processing of the normalized signal consists in a filtering process that removes noise by smoothing the curve. Subsequently, an ignition criterion is used to find the frame in which the maximum pixel intensity is closest to the intensity defined by the ignition criterion. Volatiles combustion starts at the ignition point and ends at the local minimum. In this work, the filtering process was improved to allow for a better signal-to-noise ratio and a reduction of the ignition criterion from 15% to 5% of the maximum luminosity intensity. The filtering process consists mainly on three steps: a noise attenuation step, a translation step, and a normalization step. In the noise

attenuation step, a robust local regression was applied to the light signal using weighted linear least squares and a second order polynomial regression. This method was chosen due to its simplicity and flexibility. A detailed description of the smoothing procedure can be found elsewhere [24]. The translation step consisted on the removal of the background noise from the original signal and the normalization step normalized the scale of the signal to the maximum pixel intensity found in each recorded set of frames for a single particle.

Figure 3 shows a typical example of the statistical convergence of the ignition delay time and volatiles combustion time for one biomass sample. In the case of the ignition delay time, a minimum of 50 single particle ignition events for each biomass sample were analysed, in order to identify the number of ignition events necessary to have statistical convergence. In the case of the volatiles combustion time, a minimum of 30 single particle events were analysed for each biomass sample.

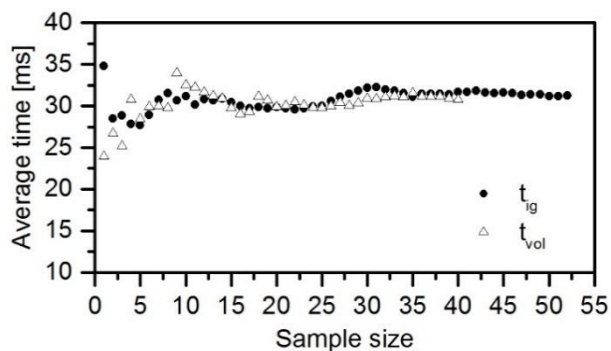


Figure 3. Example of the statistical convergence of the ignition delay time and volatiles combustion time.

RESULTS

Thermogravimetry analysis

Results for both pyrolysis and combustion of grape pomace samples, in TGA, were obtained, however, the general biomass pyrolysis profile did not show significant differences by increasing the K or Ca content in biomass, thus the pyrolysis results will not be considered in this analysis.

Figure 4 shows the conversion, X , and the conversion rate, dX/dt , as a function of the temperature of the raw grape pomace and the demineralized grape pomace during the combustion process.

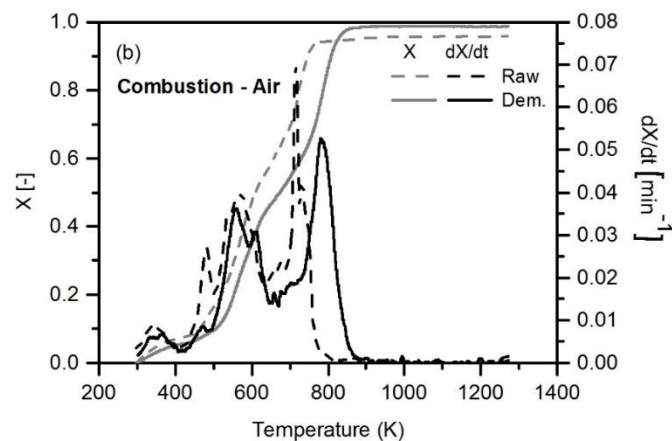


Figure 1. Combustion with air of raw and demineralized grape pomace up to 1275 K at 10 K/min in TGA.

After the first peak of the rate curve at 350 K, that corresponds to the water release, the first two peaks occur at similar temperatures in both demineralized and raw grape pomace curves. However, a third peak, which is very intense and stronger than the other peaks associated with the char oxidation, occurs at different temperatures for the two samples. In the combustion rate curve of the demineralized sample, the hemicellulose peak decreased when compared with the raw sample meaning that the demineralization pre-treatment affects the hemicellulose peak. Also, the char oxidation peak decreased its intensity and was shifted to higher temperatures when the biomass was demineralized, reinforcing the catalytic effect of metals on char combustion.

Figure 5 shows the rate of mass loss for the demineralized grape pomace and all the K and Ca doped biomass samples considered in this work during their combustion in TGA. From this figure, it is possible to infer the main devolatilization peak is not significantly affected by the K and Ca content of the biomass. However, K and Ca play a different role on the char oxidation process. In general, the K content of biomass

influences the char oxidation process by changing the temperature of its occurrence as well as its mass loss rate, whereas Ca does not significantly influence this process. The char oxidation peak temperature is progressively shifted to lower temperatures and its intensity increased as the K content of biomass is increased. It's important to note that it is not only the char oxidation peak that is shifted to lower temperatures as the K content increases. The initial and final temperatures of this stage also decrease, meaning that the whole char oxidation process is occurring at lower temperatures, as the K content in biomass increases.

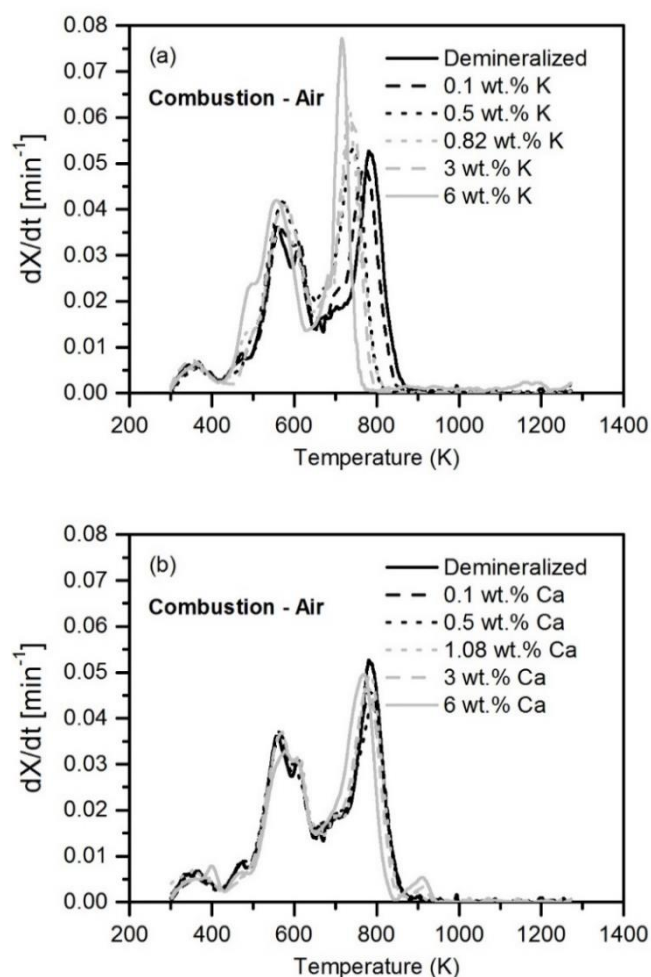


Figure 5. Combustion profiles of demineralized grape pomace and grape pomace doped with different concentrations of K (a) and Ca (b).

Early stage combustion of single particles

Early stage combustion process

Figure 6 shows typical signal intensity curves of the combustion process of single particles as a function of time, and Figure 7 shows images of selected events marked in Figure 6. Taking the K impregnated samples as an example, the original and filtered signal intensity curves are shown for a single particle of samples with 0.1 and 6 wt.% of K impregnated.

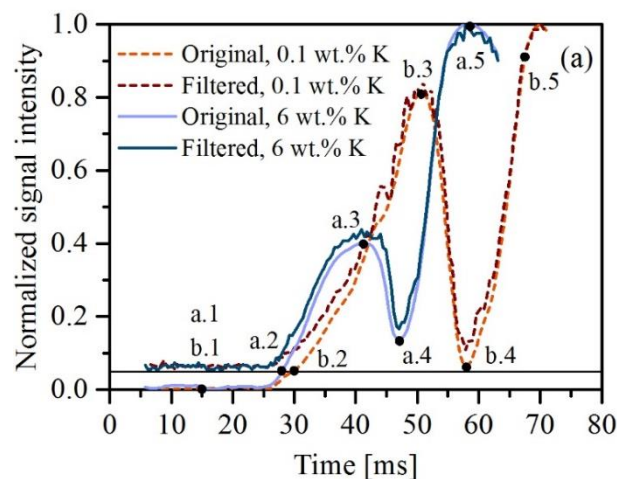


Figure 6. Signal intensity curves of K impregnated samples

Each curve in Figure 6 presents similar characteristics for each phase of the combustion process varying only on the signal intensity and the characteristic time of each event. Taking the signal curves (original and filtered) of 0.1 wt.% K as an example, the signal intensity increases when ignition occurs (a.2). Subsequently, the signal intensity continues to increase due to the light captured from the volatiles flame around the particle until a local maximum is reached (a.3). Then, the signal intensity decreases until a local minimum is reached corresponding to a transition from the volatiles combustion to the char oxidation phase (a.4). In the char oxidation phase the particle surface glows brightly with a rapid increasing of the signal intensity (a.5).

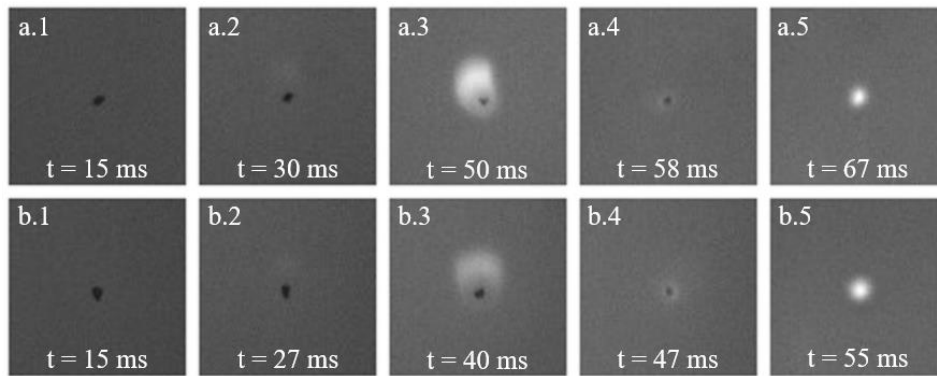


Figure 7. Images of selected events marked in Figure 6.

Ignition delay time

Figure 8 shows the ignition delay time as a function of the K and Ca concentrations for both operating conditions T1 and T2. Figure 8a) shows that the impact of the K on the ignition delay time. Two distinct regions can be observed: region I and II. In region I the ignition delay time decreases with the increase of the K concentration and an asymptote is reached around 1 wt.% of K, regardless of the operating condition. This asymptote remains until 3 wt.% of K, beyond which the ignition delay time decreases again (region II) for both operating conditions. Finally, the ignition delay time for the biomass sample with 0.82 wt.% (same K concentration as the raw sample) is very close to the ignition delay time of the raw sample of grape pomace for operating conditions T1 and T2.

Figure 8b) shows that the effect of the Ca on the ignition delay time differs from the effect of the K, although two regions can also be observed. In region I there is an increase of the ignition delay time from the sample with zero concentration of Ca until the sample with a Ca concentration similar to that in the raw biomass (1.08 wt.% in this case), regardless of the operating condition. The subsequent data points (3 and 6 wt.%) registered a decrease in the ignition delay time from the previous ones (region II) for operating conditions T1 and T2. Finally, the biomass sample with the same Ca concentration as the raw sample presents differences of 15% and 27% on the ignition delay times when

compared with the raw grape pomace sample, for the operating conditions T1 and T2, respectively.

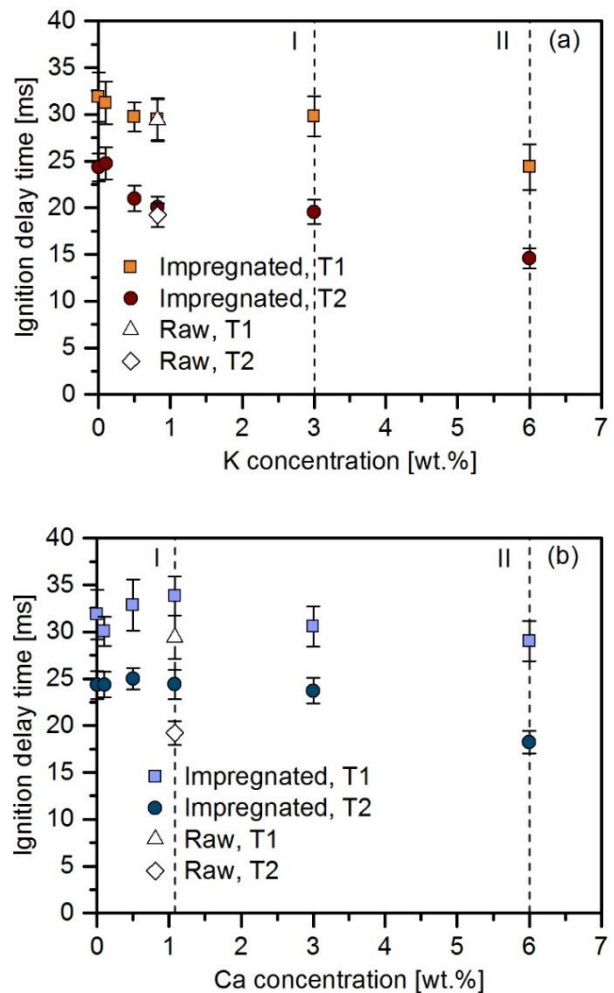


Figure 8. Ignition delay time as a function of the (a) K and (b) Ca concentration.

Volatiles combustion time

Figure 9 shows the volatiles combustion times as a function of the K and Ca concentrations for the operating condition T1. The figure reveals that the volatiles combustion time is much higher for the demineralized grape pomace sample than for the raw sample, with a difference of 24%, which means that the volatiles combustion time is strongly affected by the demineralization process.

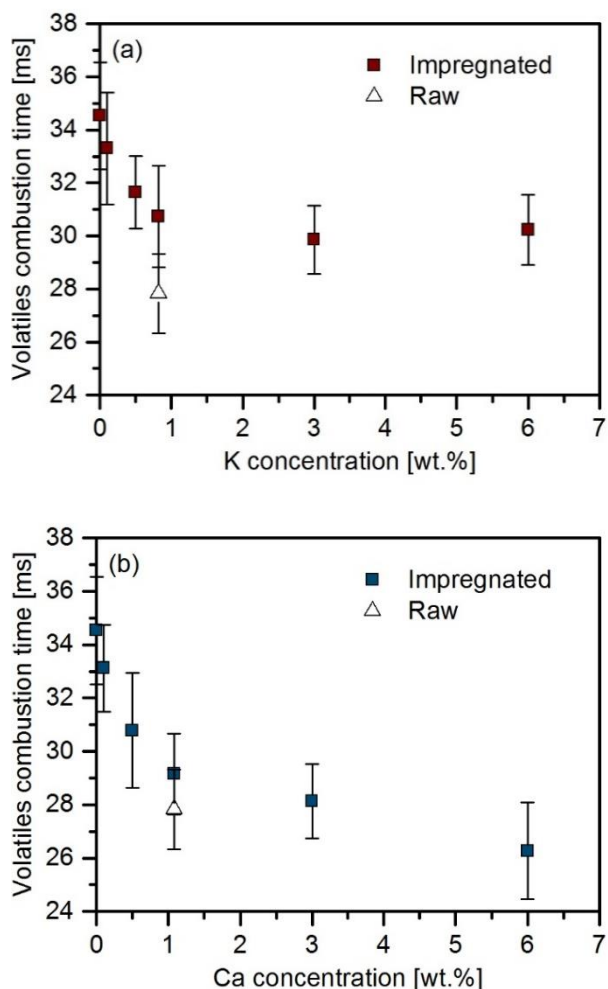


Figure 9. Volatiles combustion times as a function of the (a) K and (b) Ca concentration for the operating condition T1.

Figure 9a) shows that the volatiles combustion time rapidly decreases as the concentration of impregnated K in the biomass samples increases up to a K concentration of 0.82 wt.%, beyond which it remains constant up to 6 wt.% of K. Nonetheless, it is important

to note that the volatiles combustion time for the raw sample is lower than that observed for all samples with K impregnated. Figure 9b) shows that the evolution of the volatiles combustion time with the concentration of Ca impregnated in the biomass samples is similar to that of Figure 9a). As the impregnated Ca concentration increases the volatiles combustion time rapidly decreases until 1.08%, but in this case the asymptote is not reached up to a concentration of Ca of 6 wt.%.

CONCLUSIONS

In this work, the effects of K and Ca on the combustion behaviour of biomass were firstly examined at low heating rates, using thermogravimetric analysis, in order to understand the processes and reactions involved during devolatilization and char oxidation and which of these stages is more affected by the presence of K or Ca. Afterwards, a flat flame McKenna burner was used to determine the effect of K and Ca on the ignition delay time and volatiles combustion time of single particles of pre-treated biomass samples, at high heating rates, with the aim of extending the study to conditions closer to those of practical applications. Considering the effect of demineralisation, the thermogravimetric analysis showed that the demineralization decreased the hemicellulose peak and shifted the combustion rate profile to higher temperatures revealing that the mineral matter affects the combustion process. The results at high heating rates reveal that both the ignition delay time and the volatiles combustion time of single particles increased with the demineralization process, revealing a catalytic effect of the presence of the minerals on the early stages of the combustion process.

Considering the effect of the impregnated K concentration, the thermogravimetric analysis showed that by increasing the K concentration in the biomass, the devolatilization peak slightly increased whereas the char oxidation peak clearly increased. Additionally, the

combustion rate profile was shifted to lower temperatures. The results at high heating rates reveal that both the ignition delay time and the volatiles combustion time of single particles decreased as the K concentration increased. However, this decrease was more significant on the volatiles combustion time than on the ignition delay time, showing that K has a more pronounced impact on the volatiles combustion stage. Considering the effect of the impregnated Ca concentration, the thermogravimetric analysis showed that increasing Ca concentration in the biomass had no significant influence on the combustion rate profile. The results at high heating rates reveal that the ignition delay time first increased and then decreased as the Ca concentration increased. Impregnated Ca, also had an impact on the volatiles combustion by decreasing its duration as the concentrations of impregnated Ca increased. Again, as in the case of K impregnation, the impact of Ca impregnation was more prominent in the volatile combustion time than on the ignition delay time.

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