Role of Potassium and Calcium on the Combustion Characteristics of Biomass Obtained from Thermogravimetric Experiments

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Supporting Information

ABSTRACT: This work focuses on the combustion behavior of raw and demineralized grape pomace and grape pomace doped with 0.1, 0.5, 0.82 (equal to the K concentration in the raw biomass), 3, and 6 wt % K and 0.1, 0.5, 1.08 (equal to the Ca concentration in the raw biomass), 3, and 6 wt % Ca. To identify the individual role of calcium and potassium, the biomass samples were either pyrolyzed in a N2 atmosphere or oxidized in air in a thermogravimetric analyzer (TGA) during non-isothermal runs at 10 K/min from room temperature to a maximum temperature of 1275 K. In all of the cases, the biomass pyrolysis process shows one main stage associated with the volatile matter release. This process is not significantly affected by the mineral content of biomass nor the presence of high K and Ca contents. During combustion in air, the biomass samples show two main distinct stages that are associated with the volatile matter release and the char oxidation. Whereas the main devolatilization stage is not significantly affected by the mineral content of the biomass, the char oxidation stage is shifted to higher temperatures for the demineralized biomass. Potassium and calcium play a different role on the char oxidation process. In general, char oxidation is promoted with increasing the K content, whereas Ca does not significantly influences this process. The TGA results were also used to determine the kinetic parameters of the pyrolysis and combustion processes of biomass in the presence of K and Ca.

1. INTRODUCTION

The use of biomass in combustion has increased over the last few decades because it is considered as a renewable and CO2-neutral energy source. However, despite the growing development of different technologies for the thermochemical conversion of biomass, there are still issues, such as preparation of biomass and/or ash-related matters during and after combustion, that hinder the clean and efficient utilization of biomass in energy applications.1 In particular, the presence of metals, even in small quantities, may affect the overall combustion process and the formation of pollutants.2

The pyrolysis of solid fuels produces volatiles and char, which, in turn, result from both the direct primary decomposition of the solid fuel and the secondary reactions of volatile condensable organic products.3 During combustion, the decomposition of the organic structures of biomass is accompanied by the release of its mineral constituents. Once released, the metals can be transported in the combustion gas as either solid particles or vapor species,1 depending upon the given element considered. Although the mineral content depends upon the type of biomass (e.g., refs 4 and 5), potassium (K) is typically the main alkali earth metal and calcium (Ca) is the main alkaline metal present in biomass.4 It is mostly present in biomass as K(g), KOH(g), and KCl(g) provided that Cl is available. Subsequently, these K species can interact with other compounds through different reactions depending upon the given reaction environment. In the absence of chlorine and sulfur, possible reactions include the interaction of K(g) with water vapor to form KOH(g) and the subsequent carbonation of hydroxide at temperatures below 1073 K.4

2KOH + CO2 K2CO3 + H2O

At high enough temperatures (i.e., 1180 K), potassium carbonate can decompose through reaction R2.12

Received: July 24, 2017
Revised: September 27, 2017
Published: September 28, 2017
The presence of K during biomass conversion in the form of either KOH, K2CO3, potassium acetate, or potassium carboxylates promotes the char formation. In addition, K can also act as a catalyst for the devolatilization and char combustion stages of biomass. Ca can be found in biomass in three forms: organically bound, acid soluble, and acid insoluble. Under combustion conditions, acid-insoluble Ca (e.g., Ca silicates) is usually considered inert, whereas organically bound and acid-soluble Ca are readily converted into CaO. Within the combustion chamber, CaO exists as refractory small micrometer-sized particles and will stay as is provided that it is not participating in further reactions. In general, literature works point to a negligible influence of Ca on the main pyrolysis products of biomass. However, the addition of Ca as either CaCO3 or CaO can increase the char combustion rate. Even though K and Ca can catalyze the biomass conversion during both pyrolysis and combustion processes, the relative magnitude of the effect depends upon the given metal. In this way, previous studies highlight the higher catalytic activity of K compared to Ca.

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 a reference point grape pomace biomass. The reference biomass was demineralized and subsequently doped with different concentrations of K (using potassium oxalate monohydrate as a reactant) and Ca (using calcium oxalate monohydrate as a reactant), making a total of 12 different samples. Both pyrolysis and combustion behaviors have been examined in a thermogravimetric analyzer (TGA), and the effects of the presence of the minerals on the sample reactivity was analyzed. To this end, the characteristic temperatures of the initial stage, the peak rate, and the final stage were compared for the different biomass samples for both conversion processes. Additionally, the minimum ignition temperature was estimated using three different graphical methods. Finally, the activation energies of the pyrolysis process and the devolatilization and char oxidation stages in the case of combustion were estimated using an optimization procedure.

### 2. MATERIALS AND METHODS

#### 2.1. Sample Preparation

In this study, grape pomace biomass has been selected as the reference biomass. Grape pomace is a residue generated during the wine production, and it is mainly constituted by skins and seeds. Table 1 lists the main properties of the grape pomace biomass, and Figure 1 provides its particle size distribution.

To prepare the different samples, the raw grape pomace was first demineralized by a nitric-acid-leaching procedure. In particular, 30 g of raw biomass was placed in a flask with 500 mL of ion-exchanged water. pH of the dissolution was adjusted to 2 using HNO3 and stirred for 1 h at 60 °C. Subsequently, the biomass was filtered and washed thoroughly with 200 mL of ion-exchanged water. The washing procedure was repeated 4 times. Finally, the biomass was dried at 105 °C. The complete procedure was repeated twice.

Afterward, the demineralized biomass was impregnated with different concentrations of either K (using potassium oxalate monohydrate as a reactant) or Ca (using calcium oxalate monohydrate as a reactant). The wet impregnation procedure consists of adding different amounts of K or Ca reactant to ion-exchange water to obtain the desired concentrations of K or Ca in the dissolutions. Subsequently, 11 mL of each dissolution was mixed with 5 g of

#### Table 1. Properties of the Raw Grape Pomace Biomass

<table>
<thead>
<tr>
<th>Parameter Value</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proximate Analysis (wt %, As Received)</td>
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</tr>
<tr>
<td>Volatiles</td>
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<tr>
<td>Fixed carbon</td>
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<tr>
<td>Moisture</td>
<td>30.2</td>
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<tr>
<td>Ash</td>
<td>2.8</td>
</tr>
<tr>
<td>Ultimate Analysis (wt %, Dry and Ash-Free Basis)</td>
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<tr>
<td>Carbon</td>
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<tr>
<td>Hydrogen</td>
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<td>Nitrogen</td>
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<tr>
<td>Sulfur</td>
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<tr>
<td>Oxygen</td>
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</tr>
<tr>
<td>Heating Value (MJ/kg)</td>
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<td>High</td>
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</tr>
<tr>
<td>Low</td>
<td>19.8</td>
</tr>
<tr>
<td>Ash Analysis (wt %, Dry Basis)</td>
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<tr>
<td>SiO2</td>
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<tr>
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<tr>
<td>Fe2O3</td>
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<tr>
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<tr>
<td>MgO</td>
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<tr>
<td>P2O5</td>
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</tr>
<tr>
<td>K2O</td>
<td>24.7</td>
</tr>
<tr>
<td>Nb2O</td>
<td>0.4</td>
</tr>
<tr>
<td>Other oxides</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Figure 1. Particle size distribution of the raw grape pomace.

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 concentrations in different biomass residues (see the work of Tortosa-Masia et al.). Thus, the present work includes the analysis of the pyrolysis and oxidation behaviors of raw and demineralized grape pomace and grape pomace doped with 0.1, 0.5, 0.82 (equal to the K concentration in the raw biomass), 3, and 6 wt % K and 0.1, 0.5, 1.08 (equal to the Ca concentration in the raw biomass), 3, and 6 wt % Ca.

#### 2.2. Thermogravimetric Tests

The evaluation of the combustion behavior 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 TGA. 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 behaviors of different biomass residues in TGA experiments. Prior to the experiments, for each experimental condition (i.e., air or N2 atmosphere), a
conversion $X$ and the rate of mass loss $dX/dt$ for the pyrolysis of the demineralized biomass. 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.

### 2.3. Pyrolysis and Combustion Modeling

The TGA results were used to determine the kinetic parameters of the pyrolysis and combustion processes of biomass in the presence of $K$ and $Ca$. This analysis was carried out using the fitting procedure developed by Ferreiro et al. The method includes a combined genetic algorithm from the global optimization toolbox of MATLAB and the least squares (LSQ) fitting procedure of MATLAB for the estimation of the activation energy and pre-exponential factor of both pyrolysis and combustion of biomass through the use of a single first-order reaction model. A detailed description of the procedure can be found elsewhere.

Both pyrolysis and devolatilization are modeled using a single first-order reaction. The reaction rate is defined as a function of the temperature and degree of conversion through eq 3

$$\frac{dm}{dt} = k(T_p)(VM - V_p)$$

where $dm/dt$ is the mass in weight percent at time $t$, $T_p$ is the particle temperature, $VM$ is the maximum volatile matter in weight percent that can be lost, $V_p$ is the total amount of volatile gases in weight percent that have left the particle, and $k(T)$ is the rate constant expressed by the Arrhenius equation (eq 4)

$$k(T_p) = A_v T_p^{n_v} \exp \left( \frac{-E_v}{RT_p} \right)$$

where $R$ is the ideal gas constant (J K$^{-1}$ mol$^{-1}$), $A_v$ is the pre-exponential factor (s$^{-1}$), $E_v$ is the activation energy (J/mol), and $\gamma$ is the temperature power coefficient.

Char combustion is modeled using a single reaction as well. The reaction rate is defined as a function of the temperature, concentration of the oxidizer, and degree of conversion through eq 5

$$\frac{dX}{dt} = k(T_p)P_{O_2}^{n}(1 - X)$$

where $X$ is the biomass conversion, $P_{O_2}$ is the partial pressure of the oxidizer, and $n$ is the reaction order. The rate constant is also expressed by a variation of the Arrhenius equation

$$k_C = A_C \exp \left( \frac{-E_C}{RT_p} \right)$$

In the case of combustion, the total mass loss is defined as the summation of the devolatilization and the char combustion rate.

The kinetic parameters considered for fitting are $A_v$, $\gamma$, $E_v$, $A_C$, $E_C$, $n$, and $n$. The reaction order $n$ was limited to the typical values for the temperatures used in thermogravimetric analysis (i.e., from 0.5 to 1). The temperature power coefficients were limited to the $-10$ to $10$ universe values. The evaluation function to be minimized by the genetic algorithm followed a similar form as that used in the work of Ferreiro et al. Here, the global error is defined as a combination of (i) the error between the predicted and experimental mass loss curve and (ii) the characteristic temperature of the maximum peaks of the DTG curve. In the case of combustion, two peaks are considered: the maximum devolatilization peak and the maximum char combustion peak.

As an example of the qualitative interpretation of the biomass pyrolysis and combustion profiles, Figure 3 shows the experimental and model prediction results for the demineralized biomass. The pyrolysis and combustion models capture, in general, well the overall behavior of the biomass devolatilization and char oxidation processes.
3. RESULTS AND DISCUSSION

3.1. Influence of Potassium and Calcium on the Biomass Pyrolysis and Combustion Processes. To analyze the reactivity of the biomass samples, the peak temperature (PT), where the conversion rate is maximum, is used. Considering a reference PT, it is found that the lower the peak temperature, the higher the reactivity of a fuel.

Figure 4 shows the conversion, X, and the conversion rate, dX/dt, versus the temperature of the raw grape pomace and the demineralized grape pomace up to 1275 K at 10 K/min in the TGA.

The pyrolysis conversion profile of both biomass samples (Figure 4a) is characterized by an initial rapid decomposition, in the 425–650 K temperature interval, followed by a slower process up to a biomass conversion of about 0.8 at 1275 K. This process is related to the release of the volatile matter in biomass. The more rapid initial conversion profile is associated with the subsequent decomposition of hemicellulose and cellulose, and the latter conversion profile is attributed to the slow degradation of lignin. The combustion conversion profile (Figure 4b) shows two rapid conversion stages separated by a gradual transition stage. As in the pyrolysis case, the first stage is related to the volatile matter release, while the second stage is related to a rapid char conversion enhanced by the oxygen in air. For both the raw and demineralized grape pomace, the main volatile matter release stage is finished at around 675 K. However, the char conversion stage is finished at 800 K for the raw biomass and 875 K for the demineralized biomass, pointing to a catalytic effect of metals during the char oxidation process. The demineralized biomass was fully consumed during its interaction with air (0.99 conversion), whereas the maximum conversion for the raw biomass is 0.96.

This difference is attributed to the ash content of the raw grape pomace (cf. Table 1) and supports the effectiveness of the demineralization process.

Figure 4 also shows the pyrolysis and combustion rates. After the first peak at 350 K that corresponds to the water release, for both the pyrolysis and combustion processes, the grape pomace devolatilization shows three distinct peaks. These peaks are generally associated with the release of the three main biomass components: hemicellulose (at 498–598 K), cellulose (at 598–648 K), and lignin (at 523–773 K). The pyrolysis curve corresponding to the demineralized biomass shows three peaks at the same temperature as in the case of the raw biomaceous biomass, pointing to a marginal effect of the ash constituents of grape pomace on the characteristic temperatures of the volatile matter release. However, the magnitude of the peaks is slightly affected by the biomass demineralization treatment. The magnitude of the first peak, associated with hemicellulose, is the most affected. It substantially decreases when the biomass is demineralized. Previous studies indicate that the demineralization processes, such as water or mild acid washing, can separate and sharpen the peaks of the rate curves. In the present work, the hemicellulose peak from the demineralized biomass is significantly decreased, up to almost disappearance, presumably as a result of its chemical degradation during the acid demineralization.

The char oxidation stage exhibits one single peak stronger than the devolatilization general main peak. The mineral content of biomass influences the magnitude and temperature of the char oxidation peak; it is decreased and shifted to higher temperatures when the biomass was demineralized, reinforcing the catalytic effect of metals on char combustion.

To establish how the reactivity of the biomass is affected by the presence and concentration of K and Ca, the pyrolysis and combustion rates from the demineralized biomass are taken as a reference. Therefore, Figures 5 and 6 show the rate of mass loss for the demineralized grape pomace and all of the K- and Ca-doped biomass samples considered in this work during their pyrolysis and combustion, respectively. The conversion profiles used to draw data shown in Figures 5 and 6 are included as Figures 1S and 2S of the Supporting Information, respectively.

The general biomass pyrolysis profile (Figure 5) is neither influenced by the K nor Ca content. Independent of the K and Ca contents, the volatile matter release stage takes place in the 425–650 K temperature interval, with the main devolatilization peak within this range. In the case of the Ca-doped biomass samples, especially for the samples with 3 and 6 wt % Ca, the dX/dt profile shows two distinct peaks, at ~750 and ~925 K, respectively, that can be associated with the Ca transformations at a high temperature. The reactant used in the present work to dope the demineralized biomass with Ca is calcium oxalate monohydrate (CaC₂O₄·H₂O). Its thermal decomposition involves dehydration, decomposition of calcium oxalate to calcium carbonate (CaCO₃), and further decomposition of calcium carbonate to calcium oxide (CaO). Therefore, the characteristic peaks obtained would correspond to the decomposition of CaC₂O₄ to CaCO₃ and the subsequent formation of CaO. It is also interesting to note that the magnitude of the CaC₂O₄ and CaCO₃ decomposition peaks decreases as the amount of Ca used during the impregnation of the biomass decreases. As indicated in the Introduction, during a thermochemical process, Ca is released as small micrometer-sized CaO particles, which would support these observations.
For the K-doped biomass samples, the pyrolysis $\frac{dX}{dt}$ profile does not show any additional peak associated with the presence of K or its concentration. In the case of biomass combustion (Figure 6), the main devolatilization peak is not significantly affected by the K and Ca contents of the biomass. However, K and Ca play a different role on the char oxidation process. In general, the char oxidation is promoted with an increasing K content, 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. For example, the peak temperature is shifted from 786 to 714 K with increasing the K content from 3% to 6 wt % K. These results are in line with the observations of Fuentes et al.\textsuperscript{27} in relation to the catalytic effect of K on the char oxidation stage of biomass conversion and the lower activity of Ca. Moreover, these authors did not observe any effect of Ca on the volatile release stage. For the sample with 6 wt % K, it is interesting to note a small characteristic peak at $\sim$1180 K, which can be related to the decomposition of potassium carbonate (K$_2$CO$_3$) to potassium oxide (K$_2$O);\textsuperscript{12} the thermal conversion of potassium oxalate monohydrate (reactant used to dope the biomass with K) involves dehydration and its decomposition to potassium carbonate (K$_2$CO$_3$).\textsuperscript{38} Table 2 summarized the characteristic temperatures of the volatile matter release and char oxidation regions.

Considering the results of the raw biomass sample and the biomass impregnated with similar amounts of K and Ca (i.e., 0.82 wt % K and 1.08 wt % Ca, respectively), it can be stated that neither K nor Ca is individually responsible for the catalytic effect of the mineral constituents of raw biomass, which points to a synergistic and/or cumulative effect of those minerals that actively catalyze the char oxidation stage of biomass combustion.

3.2. Influence of Potassium and Calcium on the Biomass Ignition Temperature. The minimum ignition temperature from TGA results can be determined by four different graphical methods: (i) the TG−DTG tangent method,\textsuperscript{39} where the ignition temperature is defined by the intersection between the tangent to the TG curve at the main DTG peak and the horizontal line tangent to the TG curve after the water release peak (Figure 7a), (ii) the TG divergence method,\textsuperscript{40} where the ignition temperature is defined by the separation of the pyrolysis and combustion TG curves (Figure 7b), (iii) the DTG decrease method,\textsuperscript{41} where the ignition temperature is defined from the sudden decrease in the DTG curve after the water release stage (Figure 7c), and (iv) the DTG threshold method,\textsuperscript{42,43} where the ignition temperature is determined by the 1%/min weight loss rate decrease after the water release stage (Figure 7d).

The characteristic ignition temperature depends strongly upon the specific graphical method used (see results shown in Figure 7), but results based on a consistent definition of the methodology and considering a reference case can be used to quantitatively compare the combustion behavior of biomass doped with different concentrations of K and Ca.

As discussed in section 3.1, the demineralization process affects the magnitude of the first peak after the water release stage, the hemicellulose peak. In the DTG threshold method, the ignition temperature is determined from the behavior of this first peak (see Figure 7d), and consequently, the results obtained with the biomass samples examined in the present work would not be reliable. Therefore, the DTG threshold method for the determination of the ignition temperature is not considered in this study.

For the K-doped biomass samples, the pyrolysis $\frac{dX}{dt}$ profile does not show any additional peak associated with the presence of K or its concentration.
Figure 7. Graphical depiction of the (a) TG–DTG tangent method, (b) TG divergence method, (c) DTG decrease method, and (d) DTG threshold method used for the determination of the ignition temperature. Reference biomass is demineralized grape pomace.

Table 2. Characteristic Temperatures (K) of the Devolatilization Region of Pyrolysis and the Volatile Matter Release and Char Oxidation Regions of Combustion of the Raw and Demineralized Grape Pomace and Doped with the Different Concentrations of K and Ca

| biomass sample | pyrolysis | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | }
The temperature power coefficient \( \gamma \) laid within the \(-7.5\) to \(-6.5\) interval, independent of the process considered. In this work, \( \gamma \) is considered as an additional parameter for the fitting procedure; consequently, no further information is extracted from these values.

The pyrolysis process shows activation energies between 45 and 54 kJ/mol, and the devolatilization and char oxidation processes show activation energies between 58 and 68 kJ/mol and between 319 and 346 kJ/mol, respectively. The activation energy for the char oxidation is, in general, 5 times higher than that corresponding to the volatile matter release, which is in agreement with the different temperature windows for the occurrence of each of these stages (cf. Table 3). It is also interesting to note that the activation energy of the volatile matter release process during the biomass combustion is quite similar to that corresponding to the biomass pyrolysis, which is in agreement with the similarity of the characteristic temperatures of both processes.

Figure 9 summarizes the individual activation energy of each biomass sample and process. In this figure, the data points with zero concentration correspond to the demineralized biomass sample, and the hollow symbols correspond to the raw biomass sample. The activation energy of the devolatilization process \( (E_V) \) during both the pyrolysis and combustion of biomass is almost insensitive to the variation of the K and Ca.

### Table 3. Kinetic Parameters of Pyrolysis and Combustion of Raw Grape Pomace, Demineralized Grape Pomace, and Doped with Different Concentrations of K and Ca

<table>
<thead>
<tr>
<th>biomass sample</th>
<th>pyrolysis ( E_V ) (kJ/mol)</th>
<th>( A_V ) ( (s^{-1}) )</th>
<th>devolatilization ( E_V ) (kJ/mol)</th>
<th>( A_V ) ( (s^{-1}) )</th>
<th>char oxidation ( E_C ) (kJ/mol)</th>
<th>( A_C ) ( (atm^{-1} s^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw biomass</td>
<td>49.4</td>
<td>( 3.79 \times 10^{21} )</td>
<td>63.0</td>
<td>( 2.18 \times 10^{21} )</td>
<td>319</td>
<td>( 4.84 \times 10^{14} )</td>
</tr>
<tr>
<td>demineralized biomass</td>
<td>50.0</td>
<td>( 7.91 \times 10^{21} )</td>
<td>61.5</td>
<td>( 7.40 \times 10^{21} )</td>
<td>340</td>
<td>( 1.92 \times 10^{14} )</td>
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<tr>
<td>0.1 wt % K</td>
<td>53.0</td>
<td>( 2.10 \times 10^{21} )</td>
<td>63.5</td>
<td>( 4.60 \times 10^{21} )</td>
<td>340</td>
<td>( 4.56 \times 10^{14} )</td>
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<tr>
<td>0.5 wt % K</td>
<td>47.4</td>
<td>( 3.30 \times 10^{21} )</td>
<td>68.0</td>
<td>( 5.38 \times 10^{21} )</td>
<td>327</td>
<td>( 5.39 \times 10^{14} )</td>
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<tr>
<td>0.82 wt % K</td>
<td>53.2</td>
<td>( 3.09 \times 10^{21} )</td>
<td>63.0</td>
<td>( 7.66 \times 10^{21} )</td>
<td>327</td>
<td>( 5.54 \times 10^{14} )</td>
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<tr>
<td>3 wt % K</td>
<td>50.2</td>
<td>( 8.84 \times 10^{21} )</td>
<td>67.8</td>
<td>( 3.93 \times 10^{21} )</td>
<td>333</td>
<td>( 7.85 \times 10^{14} )</td>
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<tr>
<td>6 wt % K</td>
<td>46.2</td>
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<td>58.1</td>
<td>( 6.37 \times 10^{21} )</td>
<td>320</td>
<td>( 4.33 \times 10^{14} )</td>
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<tr>
<td>0.1 wt % Ca</td>
<td>46.0</td>
<td>( 4.55 \times 10^{21} )</td>
<td>56.8</td>
<td>( 8.18 \times 10^{21} )</td>
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<td>( 4.66 \times 10^{14} )</td>
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<td>0.5 wt % Ca</td>
<td>51.7</td>
<td>( 7.71 \times 10^{21} )</td>
<td>58.7</td>
<td>( 3.42 \times 10^{21} )</td>
<td>339</td>
<td>( 1.45 \times 10^{14} )</td>
</tr>
<tr>
<td>1.08 wt % Ca</td>
<td>45.5</td>
<td>( 3.77 \times 10^{21} )</td>
<td>62.3</td>
<td>( 7.21 \times 10^{21} )</td>
<td>346</td>
<td>( 7.12 \times 10^{14} )</td>
</tr>
<tr>
<td>3 wt % Ca</td>
<td>53.8</td>
<td>( 5.84 \times 10^{21} )</td>
<td>59.8</td>
<td>( 4.63 \times 10^{21} )</td>
<td>340</td>
<td>( 2.31 \times 10^{14} )</td>
</tr>
<tr>
<td>6 wt % Ca</td>
<td>46.7</td>
<td>( 3.83 \times 10^{21} )</td>
<td>58.2</td>
<td>( 5.33 \times 10^{21} )</td>
<td>334</td>
<td>( 3.82 \times 10^{14} )</td>
</tr>
</tbody>
</table>
concentrations of biomass, but the activation energy of the char oxidation process ($E_C$) during the combustion of biomass is somewhat sensitive to the mineral content of biomass. In this way, the activation energy of the char oxidation stage from the combustion of the demineralized biomass sample is 6.6% higher than the $E_C$ value of the raw sample of grape pomace.

In the case of K (Figure 9a), the activation energy of the char oxidation process ($E_C$) decreases with the increase of the K concentration until the 0.5 wt % K sample and continues slightly decreasing further up to 6 wt % K, where the $E_C$ value is similar to that corresponding to the raw grape pomace sample. As for the devolatilization process, Ca (Figure 9b) has a marginal effect on the activation energy of the char oxidation process. The $E_C$ value for the biomass samples with different Ca concentrations is very close to the $E_C$ value of the demineralized biomass.

4. CONCLUSION

The individual role of the presence and concentration of K and Ca in the combustion characteristics of grape pomace has been analyzed. The grape pomace was demineralized and, subsequently, doped with K and Ca to obtain doped samples that covered a wide and realistic concentration range of both minerals in different biomass fuels. Specifically, this work includes the analysis of the pyrolysis and oxidation processes in a TGA of raw and demineralized grape pomace and demineralized biomass doped with 0.1, 0.5, 0.82, 3, and 6 wt % K and 0.1, 0.5, 1.08, 3, and 6 wt % Ca.

In general, neither the ignition temperature nor the devolatilization process of biomass is significantly affected by the presence of K and Ca contents lower than 6 wt %. The char oxidation was promoted by the presence of K, with a more noticeable effect as the K concentration in the biomass was increased. In this case, the char oxidation profile of the biomass doped with 6 wt % K was shifted 72 K to lower temperatures compared to the demineralized biomass.

The activation energies for the volatile matter release during the pyrolysis and oxidation of biomass were in the intervals of 45–54 and 58–69 kJ/mol, respectively, while for char oxidation, it was in the interval of 318–346 kJ/mol. The impact of the mineral content of biomass is more significant on the char oxidation process of biomass combustion than on the pyrolysis and devolatilization processes. Neither high concentrations of Ca and K (up to 6 wt % of each individual mineral) nor the minerals present in the raw grape pomace influence the activation energy of the pyrolysis and devolatilization process of biomass combustion. The minerals present in the raw grape pomace and K individually show a catalytic effect on the activation energy of the char oxidation process. This effect is promoted by increased K concentrations. On the contrary, under the conditions of the present work, Ca behaves as an inert.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.7b02161.

Pyrolysis in N₂ of demineralized grape pomace and grape pomace doped with different concentrations of (a) K and (b) Ca (Figure 1S) and combustion with air of demineralized grape pomace and grape pomace doped with different concentrations of (a) K and (b) Ca (Figure 2S) (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work was funded by MINECO and FEDER (Project CTQ2015-65226) and Fundação para a Ciência e a Tecnologia (FCT), through IDMEC, under LAETA Pest-011/EME/E9170/2014. M. Abián acknowledges MINECO and Instituto de Carbóquímica (ICB-CSIC) for the postdoctoral grant awarded (FPDI-2013-16172) and Fundaciones Ibercaja y CAI (Program Ibercaja—CAI for research stays) and COST Action CM1404 (EU) for financial support (reference ECOST-STM-CM1404-017016-079613).

REFERENCES
