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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 N_2 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 CO_2-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.[6] Usually, K is regarded as an undesirable biomass component as a result of its critical role in important ash-related problems (e.g., alkali-induced slagging, silicate melt-induced slagging, ash fusion, and bed agglomeration).[1,7] In contrast and despite the calcium sulfate deposits found on the cold reactor surfaces, Ca can inhibit the occurrence of silicate melt-induced slagging and bed agglomeration as a result of the formation of melting calcium potassium phosphates and silicates at high temperatures.[1,8,9]

K is mostly present in biomass in a soluble form (e.g., in an ionic form in salts or as organically bound K ions).[1] Two characteristic temperature intervals have been identified for the release of K, as alkali metal, during biomass pyrolysis.[10] K associated with the organic phase is expected to be released coinciding with the onset of the pyrolysis process (453−773 K), whereas inorganic K, from the ash component of the resulting char, would be released at higher temperatures (>773 K).

During combustion, soluble K is mainly released to the gas phase 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.[11]

$$2KOH + CO_2 \leftrightarrow K_2CO_3 + H_2O \quad \text{(R1)}$$

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

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$$K_2CO_3 \leftrightarrow K_2O + CO_2 \quad (R2)$$

The presence of K during biomass conversion in the form of either KOH,[13] K_2CO_3,[14] potassium acetate,[15] or potassium carboxylates[16] promotes the char formation.

In addition, K can also act as a catalyst for the devolatilization and char combustion stages of biomass.[10,17−20]

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.[1] 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.[21] In general, literature works point to a negligible influence of Ca on the main pyrolysis products of biomass.[22,23] However, the addition of Ca as either $CaCO_3$[24,25] or CaO[25,26] can increase the char combustion rate.

Even though K and Ca can catalyze the biomass conversion during both pyrolysis and combustion processes,[18] 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.[27]

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.

Table 1. Properties of the Raw Grape Pomace Biomass

parameter	value
Proximate Analysis (wt %, As Received)	
volatiles	48.4
fixed carbon	18.6
moisture	30.2
ash	2.8
Ultimate Analysis (wt %, Dry and Ash-Free Basis)	
carbon	51.1
hydrogen	6.7
nitrogen	1.9
sulfur	0.2
oxygen	40.1
Heating Value (MJ/kg)	
high	21.2
low	19.8
Ash Analysis (wt %, Dry Basis)	
SiO_2	5.5
Al_2O_3	1.0
Fe_2O_3	1.2
CaO	37.8
SO_3	1.7
MgO	7.2
P_2O_5	19.7
K_2O	24.7
Na_2O	0.4
other oxides	0.8

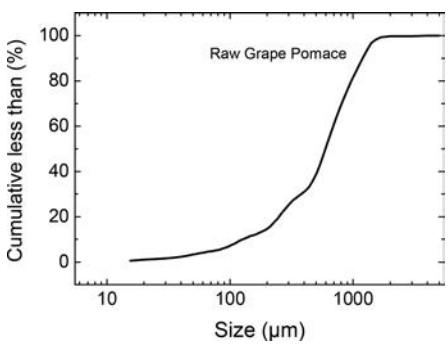

Figure 1. Particle size distribution of the raw grape pomace.

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.[28] 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 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.

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 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-Masiá et al.[4]). 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.[29,30] Prior to the experiments, for each experimental condition (i.e., air or N_2 atmosphere), a

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calibration curve was made to avoid possible fluctuations caused by the apparatus that could influence the measurements.

The figures show the biomass pyrolysis and combustion reactivities as the mass loss rate, dX/dt (min^{-1}), defined through eq 1, versus the reaction temperature, T (K).

$$\frac{dX}{dt} = \frac{1}{m_0}\frac{dm}{dt} \tag{1}$$

Here, m_0 and m are the initial mass of biomass and the mass of biomass at time t in the TGA tests, respectively. Thus, the biomass conversion, X, is defined by

$$X = \frac{m_0 - m}{m_0} \tag{2}$$

To determine the uncertainty in the experimental procedure, the experiments were repeated at least 3 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. As an example of the comparison results obtained, Figure 2 shows the

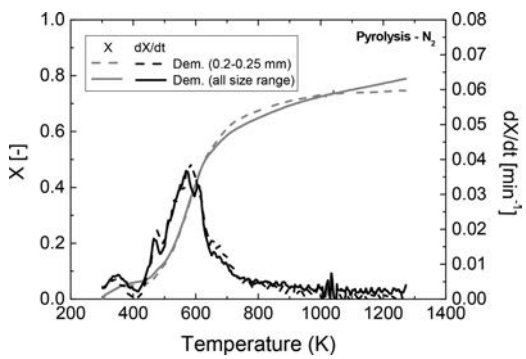

Figure 2. Typical pyrolysis profiles of the demineralized grape pomace.

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.[30] 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.[30]

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

$$\frac{dm}{dt} = k(T_p)(VM - V_g) \tag{3}$$

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_g 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)

$$k_V = A_V T_p^{\gamma} \exp\left(\frac{-E_V}{RT_p}\right) \tag{4}$$

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 γ is the temperature power coefficient.

Char combustion is modeled using a single reaction as well.[31] The reaction rate is defined as a function of the temperature, concentration of the oxidizer, and degree of conversion though eq 5

$$\frac{dX}{dt} = k(T_p)P_{O_2}{}^{n}(1 - X) \tag{5}$$

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

$$k_C = A_C \exp\left(\frac{-E_C}{RT_p}\right) \tag{6}$$

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, γ, E_C, A_C, E_V, 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),[32] and the temperature power coefficients were limited to the −10 to 10 universe values.[30] The evaluation function to be minimized by the genetic algorithm followed a similar form as that used in the work of Ferreiro et al.[30] Here, the global error is defined as a combination of (i) the error between the predicted and experimental mass loss curve (TG) and (ii) the characteristic temperature of the maximum peaks of the rate curve (DTG). 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.

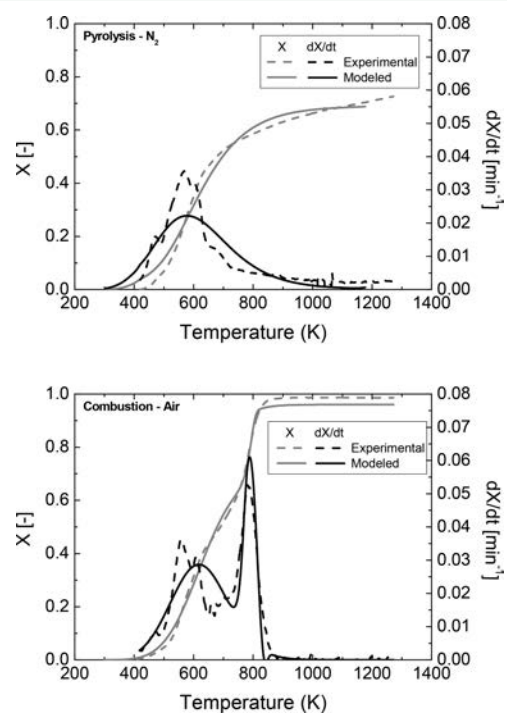

Figure 3. Typical pyrolysis and combustion profiles of the demineralized grape pomace. Experimental data, dashed lines; model data, continuous lines.

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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,[33] 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, d*X*/d*t*, versus the temperature of the raw grape pomace and the demineralized grape pomace during the pyrolysis and combustion processes.

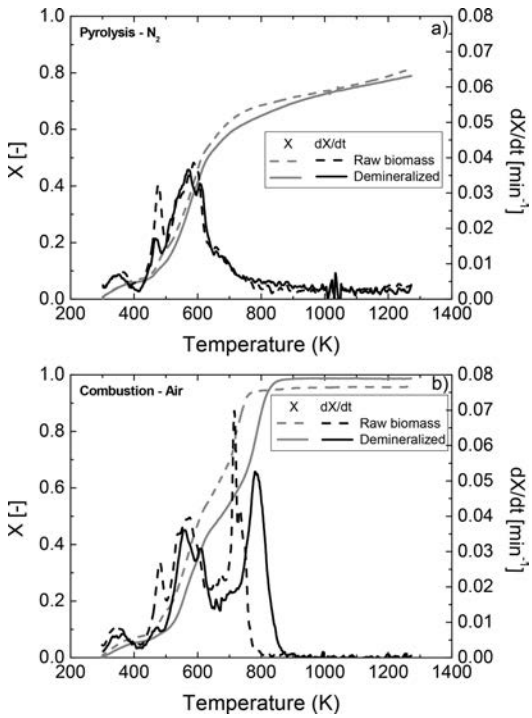

Figure 4. (a) Pyrolysis in N_2 and (b) combustion with air of raw and demineralized grape pomace up to 1275 K at 10 K/min in the TGA.

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.[34] 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).[5] The pyrolysis curve corresponding to the demineralized biomass shows the three peaks at the same temperature as in the case of the raw 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[35,36] 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.[37]

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 d*X*/d*t* 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 ($CaC_2O_4{\cdot}H_2O$). Its thermal decomposition involves dehydration, decomposition of calcium oxalate to calcium carbonate ($CaCO_3$), and further decomposition of calcium carbonate to calcium oxide (CaO).[38] Therefore, the characteristic peaks obtained would correspond to the decomposition of CaC_2O_4 to $CaCO_3$ and the subsequent formation of CaO. It is also interesting to note that the magnitude of the CaC_2O_4 and $CaCO_3$ 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.

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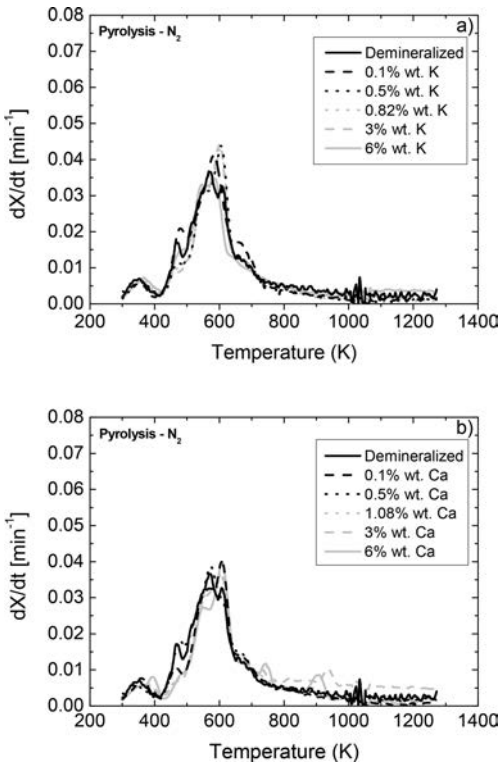

Figure 5. Pyrolysis profiles of demineralized grape pomace and grape pomace doped with the different concentrations of (a) K and (b) Ca.

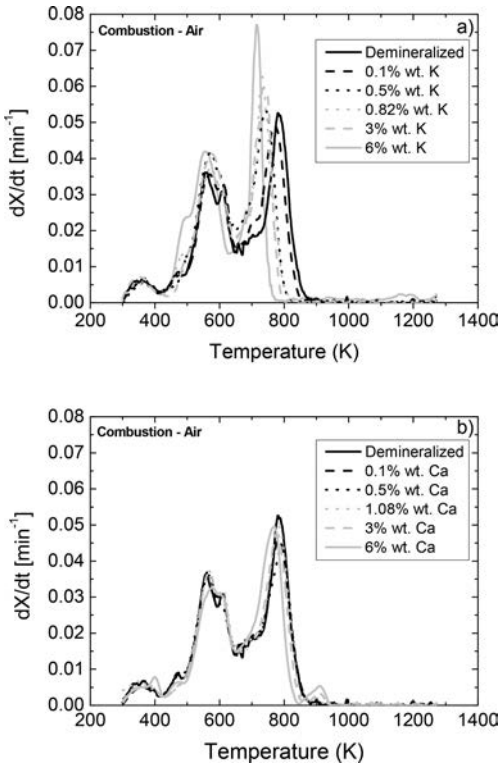

Figure 6. Combustion profiles of demineralized grape pomace and grape pomace doped with different concentrations of (a) K and (b) Ca.

For the K-doped biomass samples, the pyrolysis 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 demineralized biomass to 6 wt % K. These results are in line with the observations of Fuentes et al.[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 observed 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 ∼1180 K, which can be related to the decomposition of potassium carbonate (K_2CO_3) to potassium oxide (K_2O);[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_2CO_3).[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,[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,[40] where the ignition temperature is defined by the separation of the pyrolysis and combustion TG curves (Figure 7b), (iii) the DTG decrease method,[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,[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.

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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[a]

				combustion					
	pyrolysis			devolatilization			char oxidation		
biomass sample	T_i	PT_{dev}	T_f	T_i	PT_{vol}	T_f	T_i	PT_{char}	T_f
raw biomass	412	586	626	420	569	633	634	722	775
demineralized biomass	420	576	646	418	565	656	657	786	875
0.1 wt % K	400	583	637	420	572	652	653	772	853
0.5 wt % K	420	607	640	418	572	647	648	743	821
0.82 wt % K	420	607	637	420	572	641	642	736	825
3 wt % K	422	600	635	432	575	647	648	736	800
6 wt % K	420	586	626	418	558	631	632	714	775
0.1 wt % Ca	420	607	643	430	565	645	646	786	878
0.5 wt % Ca	415	572	641	424	569	652	653	793	878
1.08 wt % Ca	420	604	644	424	568	670	671	786	868
3 wt % Ca	424	607	640	428	569	649	650	779	860
6 wt % Ca	426	608	646	430	579	654	655	768	843

[a] T_i, initial temperature of the stage; PT, peak temperature; and T_f, final temperature of the stage.

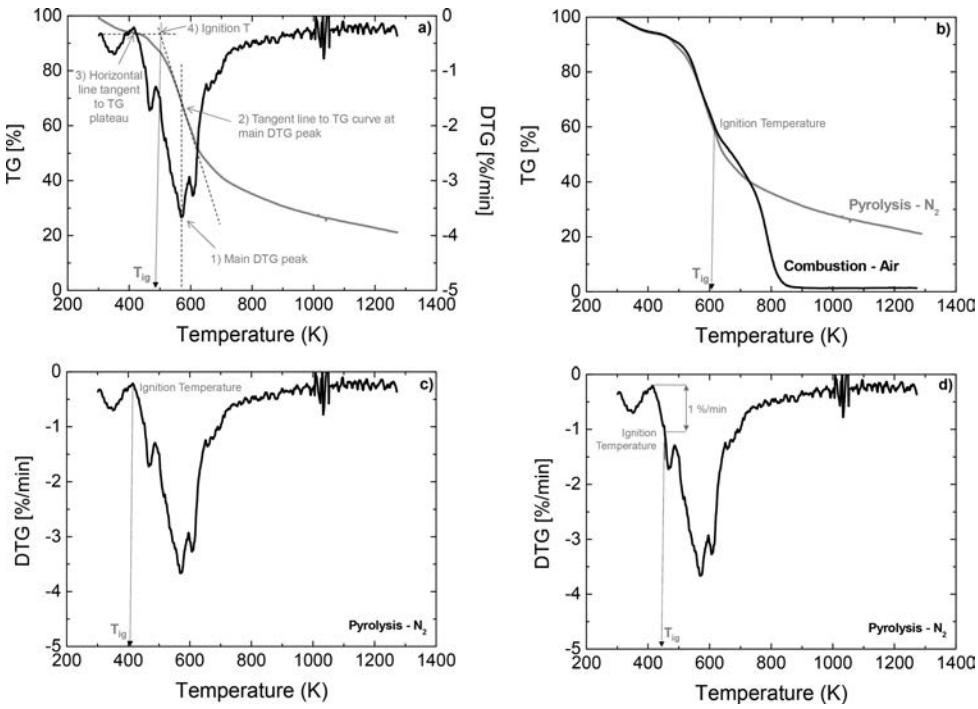

Figure 7. Graphical depiction of the (a) TG−DTG tangent method, (b) TG divergence method, (c) DTG decrease method, and (d) DTG threshold method used for the determination of the ignition temperature. Reference biomass is demineralized grape pomace.

Figure 8 shows the ignition temperature of the raw and demineralized grape pomace and doped with K and Ca. Independent of the method used for the determination of the T_{ig}, data, the figure indicates that neither the demineralization process nor the presence of K and Ca (from low to high concentrations) significantly modifies the minimum ignition temperature of the biomass. For all biomass samples analyzed, the characteristic ignition temperatures (T_{ig}) obtained with the DTG decrease method are in the order of 425 K, with the TG−DTG tangent method in the order of 515 K, and with the TG divergence method, the ignition temperatures increase further to values around 645 K.

3.3. Influence of Potassium and Calcium on the Activation Energies. Table 3 shows a summary of the kinetic parameters (activation energy and pre-exponential factor) obtained for the devolatilization process during the biomass pyrolysis and the volatile matter release and char oxidation processes during the biomass combustion. The values reported in Table 3 are the averaged values from three runs for each biomass and condition. The variation of the coefficients reported for the activation energy values were in all cases lower than 10% for the pyrolysis process and lower than 2 and 2.2% for the devolatilization and char oxidation processes, respectively, during combustion.

For all of the samples analyzed, the pre-exponential factor values for the pyrolysis and devolatilization processes (A_V) were in the order of 10^{21} and the pre-exponential factor values for the char oxidation process during combustion (A_C) were in the

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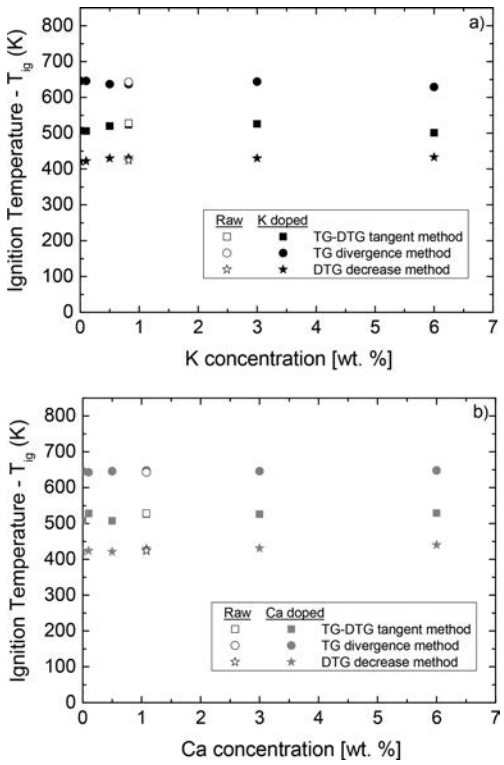

Figure 8. Characteristic ignition temperatures of raw and demineralized grape pomace and doped with different concentrations of (a) K and (b) Ca.

order of 10^{18}. The temperature power coefficient (γ) laid within the −7.5 to −6.5 interval, independent of the process considered. In this work, γ 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

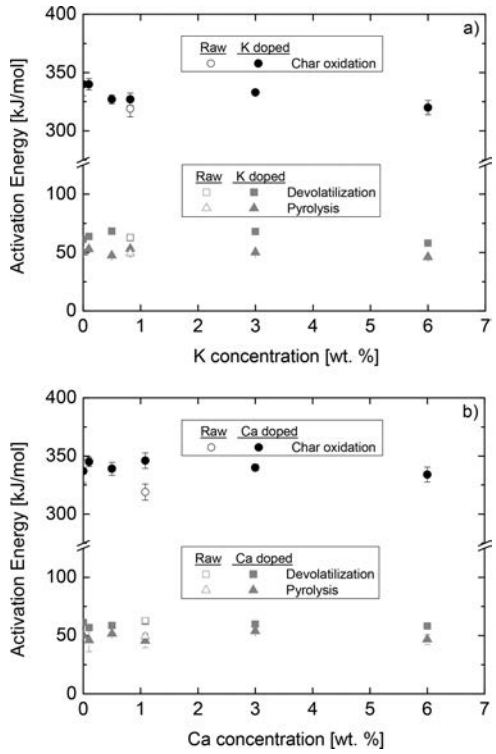

Figure 9. Activation energies of the pyrolysis and oxidation of raw and demineralized grape pomace and doped with different concentrations of (a) K and (b) Ca.

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

			combustion			
	pyrolysis		devolatilization		char oxidation	
biomass sample	E_V (kJ/mol)	A_V (s^{-1})	E_V (kJ/mol)	A_V (s^{-1})	E_C (kJ/mol)	A_C (atm^{-1} s^{-1})
raw biomass	49.4	3.79×10^{21}	63.0	2.18×10^{21}	319	4.84×10^{18}
demineralized biomass	50.0	7.91×10^{21}	61.5	7.40×10^{21}	340	1.92×10^{18}
0.1 wt % K	53.0	2.10×10^{21}	63.5	4.60×10^{21}	340	4.56×10^{18}
0.5 wt % K	47.4	3.30×10^{21}	68.0	5.38×10^{21}	327	5.39×10^{18}
0.82 wt % K	53.2	3.09×10^{21}	63.0	7.66×10^{21}	327	5.54×10^{18}
3 wt % K	50.2	8.84×10^{21}	67.8	3.93×10^{21}	333	7.85×10^{18}
6 wt % K	46.2	5.50×10^{21}	58.1	6.37×10^{21}	320	4.33×10^{18}
0.1 wt % Ca	46.0	4.55×10^{21}	56.8	8.18×10^{21}	345	4.66×10^{18}
0.5 wt % Ca	51.7	7.71×10^{21}	58.7	3.42×10^{21}	339	1.45×10^{18}
1.08 wt % Ca	45.5	3.77×10^{21}	62.3	7.21×10^{21}	346	7.12×10^{18}
3 wt % Ca	53.8	5.84×10^{21}	59.8	4.63×10^{21}	340	2.31×10^{18}
6 wt % Ca	46.7	3.83×10^{21}	58.2	5.33×10^{21}	334	3.82×10^{18}

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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 N_2 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.

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