DETAILS OF THE STSM:

Reference Code: ECOST-STSM-CM1404-010716-079613

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Title of STSM: Impact of alkali and alkaline earth metals on single particle ignition behaviour of biomass fuels.

Working Group: WG2 Chemistry for control of by-products in Smart Energy Carrier conversion

Type and length of stay: STSM, 1st July – 15th September 2016.

1. PURPOSE OF THE STSM:

The use of biomass in combustion has been increased over the last decades since it is considered as a renewable and CO_2-neutral energy source. Co-firing is an attractive technology that allows the use of biomass fuels in existing power plants. However, the biomass and coal behave differently during combustion [1]. In addition, issues such as preparation of biomass and/or ash-related matters during and after combustion, hinder the clean and efficient utilization of biomass in energy applications [2]. There are a wide range of sources for biomass production, and even for a specific biomass, different planting environments, harvest seasons, and different parts of the biomass can product different ash contents and compositions [2]. Biomass ashes usually include alkali and alkaline earth metals such as Ca and K; and in spite of the fact that these compounds are typically present in low concentrations, in comparison to main biomass components (carbon, hydrogen and oxygen), they may affect or modify the whole combustion process and/or the final emissions of pollutants [3].

In this context, the main purpose of the STSM is to perform a systematic study to evaluate how the pyrolysis, combustion and ignition behavior of biomass is affected by the presence and concentration of alkali and alkaline earth metals. Grape pomace has been used as the reference biomass and Ca and K, respectively, as the reference alkali and alkaline earth metals.

2. WORK CARRIED OUT DURING THE STSM AND THE MAJOR RESULTS

To achieve the main objective of this STSM, a number of activities were carried out including the following ones.

2.1 Demineralization of the raw biomass and its subsequent impregnation with different concentration of K (as alkali metal) and Ca (as alkaline metal).

To prepare the different samples, the raw grape pomace biomass (used as reference biomass in this study) was firstly demineralized by a nitric acid leaching procedure [4]. Subsequently, the demineralized biomass was impregnated with different concentrations of either Ca (using calcium oxalate monohydrate as reactant) or K (using potassium oxalate monohydrate as reactant). The specific Ca and K reactant amounts were selected to cover a wide and realistic range of calcium and potassium concentration in different biomasses (see the work of Tortosa Masiá et al. [5]). Thus, this work includes the analysis of the pyrolysis, combustion and particle ignition behavior of raw grape pomace, demineralized biomass and biomass doped with 0.1% wt., 0.5% wt., 1.08% wt. (equal to Ca concentration in the raw biomass), 3% wt. and 6% wt. Ca and 0.1% wt., 0.5% wt., 0.82% wt. (equal to the K concentration in the raw biomass), 3% wt. and 6% wt. K.

2.2 Single particle ignition experiments, over different temperatures, with air in an optical flat flame McKenna burner.

To evaluate how the ignition behavior of biomass is affected by the presence and concentration of alkali and alkaline earth metals (Ca and K), the tests were carried out in the experimental setup schematic in Figure 1. A detailed description of this experimental setup can be found in [6], but it basically consists of a biomass feeding unit, a McKenna flat flame burner, a gas feeding system and an image acquisition system. The biomass feeding unit consists of a rotameter (to measure the transport air flow rate) and a syringe where the biomass particles are stored. The McKenna flat flame burner consists of a stainless-steel cylinder enveloping a water-cooled bronze porous sintered matrix of 60-mm diameter.

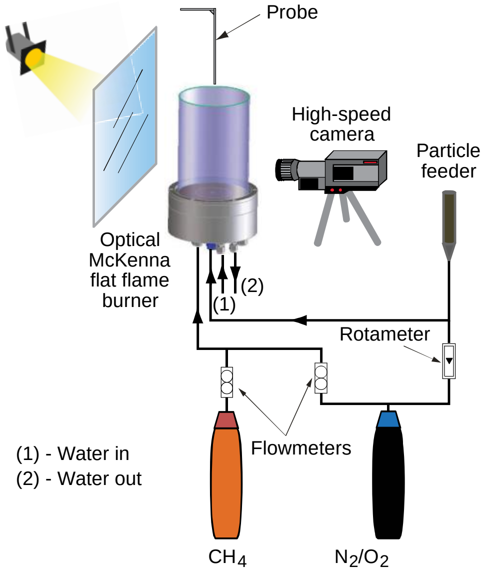

Figure 1. Schematic of the experimental setup.

Two mass flowmeters allowed the control of the methane and primary air flow rates to the burner. The image acquisition system consists of a CMOS high-speed camera Optronis CamRecord CR600x2, and a diffuse led backlight. The camera was equipped with two lenses: a 2x tele-converter and a Nikkor 60 mm f/2.8D. A target with millimeter marks was used for reference calibration before and after each testing period. The specific camera settings used are: 4 aperture, 1/8000 [s] exposure time, 2300 FPS, 200x752 [pix] resolution.

The first part of the study was to determine the specific operating conditions to work with this biomass in the flat flame McKenna burner, i.e.: particle size interval of biomass, gas temperature, air excess ratio …

All samples were sieved into the 200-250 μm size range and dried before the tests. The tests were carried out at λ=1.3 and two conditions: T1 (1575 K gas temperature and 5.4 % dry vol. O_2 at the ignition zone) and T2 (1775 K gas temperature and 5.2 % dry vol. O_2 at the ignition zone).

For each biomass sample and condition, more than 50 particles were analyzed.

2.3 Analysis of the experimental results and interpretation of the data to identify quantitatively how the ignition delay time is affected by the presence and concentration of Ca and K in the biomass.

A Matlab routine was used to calculate the ignition delay time following the luminosity criterion showed in Figure 2.

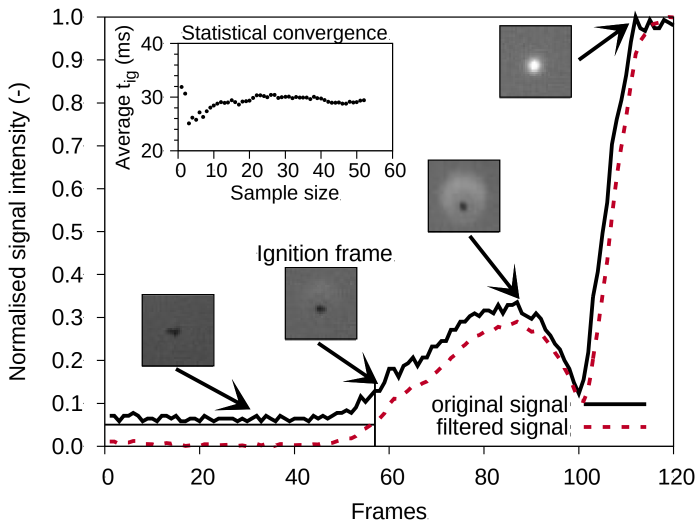

Figure 2. Post-processing test criterion and statistical convergence.

The code reads the data from the frames (original signal), eliminates the background noise (filtered signal), and normalizes the signal intensity to 1. Subsequently the code identifies the frame in which the maximum pixel intensity is closest to the 5 % normalized signal intensity. With the position of the particle and the frame-rate, it is computed the frame-to-frame velocity of the particle. Finally, the ignition delay time is calculated from these velocities and the position of the particle at the ignition frame.

In addition, the signal intensity profiles and images were used to characterize the ignition mode, i.e.: gas-phase ignition and surface ignition. Figure 2 shows the gas-phase ignition of a particle, where the volatile flame occurs in a first place (frames 60 to 100), followed by the char oxidation (from frame 100).

As a summary of the main results, Figure 3 shows the ignition delay time for all the samples and the two conditions considered in this work.

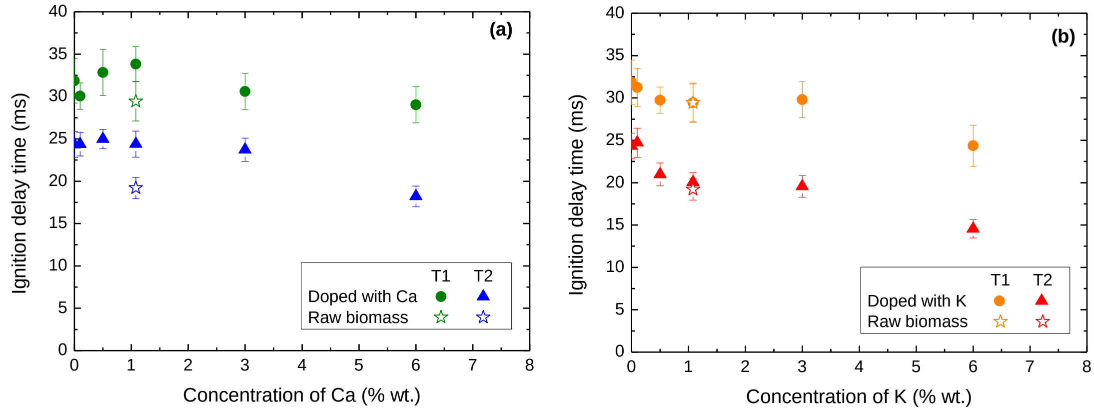

Figure 3. Ignition delay time for operating conditions T1 and T2 for raw grape pomace (Raw biomass), demineralized biomass (0 % wt. minerals) and for the biomass doped with the different concentrations of Ca [a] and K [b].

2.4 Analysis of the pyrolysis and combustion behavior of biomass in the presence of Ca and K.

The evaluation of the pyrolysis and combustion behavior of biomass has been based on the measurement of the change in sample mass as a function of the temperature and time at a constant heating rate of 10 K/min up to 1275 K in either nitrogen or air, using a *Netzsch STA F1 Jupiter* Thermogravimetric analyzer, available at the University of Zaragoza in Spain. The experiments were performed at atmospheric pressure using alumina crucibles and around 5 mg of each biomass sample. Previous to the experiments, for each experimental condition (i.e. combustion (air atmosphere) or pyrolysis (N_2 atmosphere)), a calibration curve was made to avoid any possible fluctuations caused by the apparatus that could influence the experimental measurements.

The peak temperature where the burning rate, dX/dt (min^{-1}), is maximum and the ignition temperature (calculated following the methodology described the literature, i.e. [7]) are used to quantify the reactivity of the different samples.

As a summary of the main results, Figures 4 and 5 show the rate of mass loss for all the samples considered in this work during their pyrolysis in a N_2 atmosphere and combustion with air, respectively.

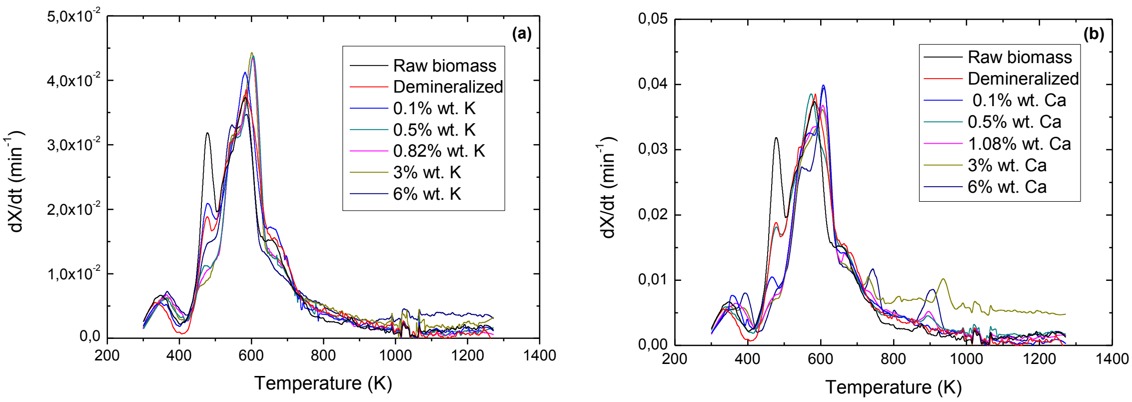

Figure 4. Pyrolysis profiles of raw grape pomace, demineralized biomass and of the biomass doped with the different concentrations of K [a] and Ca [b].

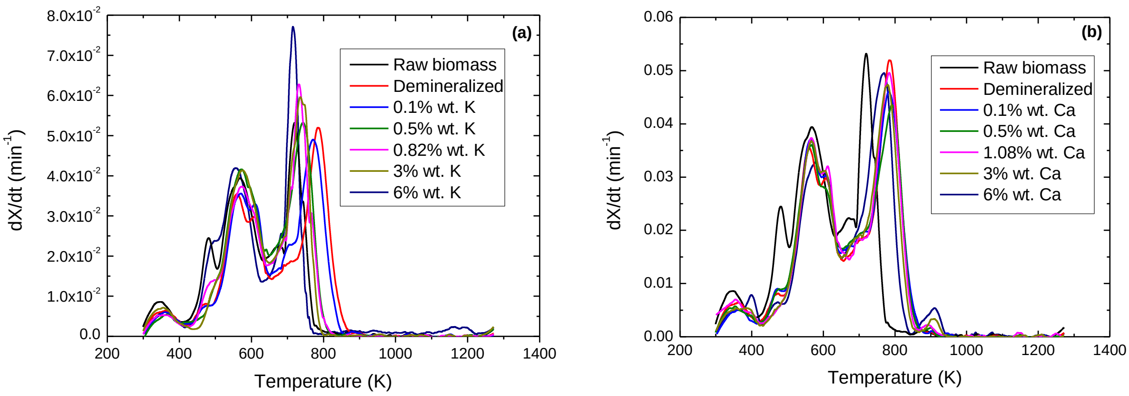

Figure 5. Combustion profiles of raw grape pomace, demineralized biomass and of the biomass doped with the different concentrations of K [a] and Ca [b].

2.5 Kinetics of the pyrolysis and combustion of biomass in the presence of Ca and K.

The TGA results are used to determine the kinetics of the pyrolysis and combustion process of biomass in the presence of Ca and K. This analysis is carried out using the fitting procedure developed by Ferreiro et al. [8]. The method includes a combined genetic algorithm and least squares fitting procedure for the estimation of the activation energy and pre-exponential factor of the pyrolysis and combustion of biomass through the use of the single first order reaction model.

3. HOW THE STSM HAS CONTRIBUTED TO THE ACTION'S AIM

In relation to the SMARTCATs COST Action (CM1404), this STSM is framed within the Working Group 2 activities (WG2: Chemistry for control of by-products in Smart Energy Carriers conversion). In particular, the knowledge of the influence of alkali and alkaline earth metals on the single particle ignition behaviour of biomass, under conditions close to the ones that occur inside industrial boilers, will contribute to define strategies for a clean and efficient utilization of biomass in energy applications.

4. FUTURE COLLABORATION WITH THE HOST INSTITUTION

This research collaboration has been a good opportunity to obtain interesting advances and results concerning the characterization of pyrolysis, combustion and single particle ignition behaviour of biomass fuels, with emphasis in alkali and alkaline earth metals influence. Our intention is to strengthen the cooperation between these research teams and define fruitful future collaborations.

At this point I would like to thanks the host institution (research group of Prof. Mário Costa) for giving me the opportunity to work with them and for all their support during my stay at Instituto Superior Técnico in Lisbon (Portugal).

5. FORESEEN PUBLICATIONS/ARTICLES RESULTING FROM THE STSM

The main results from this research collaboration will be presented at the 2nd General Meeting of the COST Action CM1404, that will take place in Lisbon next November, 2016:

> Impact of calcium and potassium on single particle ignition behaviour of biomass fuels. M. Abián, M.U. Alzueta, A. Carvalho, M. Rabaçal, M. Costa.
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> The impact of calcium and potassium on the pyrolysis and combustion of biomass. M. Abián, M.U. Alzueta, A. Carvalho, M. Rabaçal, M. Costa.

As well as at the forthcoming "Joint meeting of the Portuguese and Scandinavian-Nordic Sections of the Combustion Institute", that will take place 17-18 November 2016 in Lisbon (Portugal):

On the role of calcium and potassium on the combustion characteristics of biomass: from particle ignition to char oxidation. M. Abián, M.U. Alzueta, A. Carvalho, M. Rabaçal, M. Costa.

At present, the authors are preparing the manuscripts to be submitted to an international scientific journal.

6. ACKNOWLEDGEMENTS

The authors acknowledge COST Action CM1404 (EU) for financial support.

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