



New experimental diagnostics in combustion of forest fuels : Microscale appreciation for a Macroscale approach

Cancellieri Dominique¹, Leroy-Cancellieri Valérie^{1*}, Silvani Xavier¹, Morandini Frédéric¹.

¹SPE - UMR CNRS 6134, University of Corsica, Corte, France

5 *Correspondence to:* Valérie Leroy-Cancellieri (vcancellieri@univ-corse.fr)

Abstract. In modelling the wildfire behaviour, a good knowledge of the mechanisms and the kinetic parameters controlling the thermal decomposition of forest fuel is of great importance.

Lab-scale experimental diagnostics as Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Cone Calorimeter (CC) or Fire Propagation Apparatus (FPA) led to valuable results for modelling the thermal degradation of vegetal
10 fuels and allowed several upgrades of pyrolysis models.

But, these works remain beyond large-scale conditions of a wildland or forest fire. In an effort to elaborate the kinetic models under realistic natural fire conditions, a mass-loss device specifically designed for the field scale has been developed. The paper presents primary results gained using this new device, during large-scale experiments of controlled fires. The experimental data collected at the field scale lead to a new insight about thermal degradation processes of natural fuel, when
15 compared to the kinetic laws established in TGA. These new results, provide a global description of the kinetics of degradation of Mediterranean forest fuels.

1 Introduction

In studying the forest fire propagation, kinetic modelling of thermal degradation mechanisms is one of the main prerequisites for the determination of source terms, allowing for the development of realistic models. Numerous Computational Fluid
20 Dynamics (CFD) codes have been developed for predicting the fire spread, the heat release and providing operational tools for the land managers (Linn et al., 2002; Mell et al., 2007). Indeed, physically-based models, initiated by Grishin (Grishin, 1997), account for each mechanism of heat transfer individually and predicts not only the spread rate of the fire but also its complete behavior. The thermal degradation of the solid phase as well as the combustion of the gaseous pyrolysis products are described, requiring the development of specific kinetic models for the vegetation fuels. Appropriate kinetic mechanisms should be
25 coupled with the description of transport mechanisms (heat-, mass-, and momentum-transfer) to provide a more detailed process simulation. The mass-loss rate of the solid is one of the most important parameters in describing the evolution of the solid phase. Indeed, it is directly linked to the mass loss rate due to pyrolysis and represents the initial factor of the combustion process. Such parameters are often determined from small-scale tests such as ThermoGravimetric Analysis (TGA).

T



TGA is a thermoanalytical technique commonly used in solid-phase thermal degradation studies (Ninan, 1989; White et al., 2011). It has gained widespread attention in the thermal analysis of biomass pyrolysis (Di Blasi, 2008; White et al., 2011). TGA measures a decrease in the substrate mass caused by the release of volatiles (devolatilisation) during the thermal decomposition. In practice, the mass of the sample being heated at a specific rate is monitored as a function of temperature or
5 time. TGA requires sufficiently small samples for the diffusion effects to be negligible and for the pyrolysis process to be kinetically controlled (Miller and Bellan, 1997). The experimental data collected under perfectly controlled TGA conditions ensures an accurate determination of the kinetic mechanism. Unfortunately, these experimental conditions are not realistic in term of heating rate with those encountered in forest fire. Sometimes, calorimetric experiments are performed with a Cone Calorimeter (CC) (Schemel et al., 2008) or a Fire Propagation Apparatus (FPA) (Simeoni et al., 2012), but the gap to the real
10 scale is still significant.

Overall, field data collection is demanding and potentially dangerous; however, it is considered the best alternative for improving and validating the fire spread models (Morandini et al., 2006). Consequently, a number of field tools have been proposed; such as thermocouples, heat flux gauges (Silvani et al., 2009), gas sensors (Miranda et al., 2010) audio and video sensors (Stavrakakis et al., 2014). However, according to our knowledge, the accuracy measurement of mass loss have never
15 be done in field experiment conditions.

In view of these limitations, the aim of this study is to propose kinetic models adapted to realistic Mediterranean forest fire conditions. A mass-loss device specifically designed for the field scale has been developed for this purpose. This device can record the mass-loss and temperatures of three vegetation samples submitted to a heat flux from a spreading flame front across a large bed of fuel. One of the main advantage of this system is to submit simultaneously 3 different samples to the same fire
20 front and in identical meteorological conditions, which greatly facilitates the comparison of the thermal behaviours. The choice of this heat flux source allowed to achieve a better correspondence to forest fire conditions. This system can provides characteristic dynamic data such as temperature, mass-loss rate.

In a first time reactional mechanisms are defined from experiments performed in perfectly controlled conditions on thermal thin samples (in TGA). Using these experimental data, kinetic models are proposed for each species. Thanks to these models,
25 the simulation of the mass loss rate is done at higher heating rates, the same as the one measured during field experiment. In the last time, the mass loss rates obtained from the simulation are compared to the experimental data collected at field scale. Very few fire studies are performed directly in the open field focusing on the on-line measurement and monitoring of fuel mass bring about open fires. Moreover, the literature never reported the validation of kinetic models according to comparison with field data



2 Materials

2.1 Samples

The forest fuels used were representative of Mediterranean land, we have selected 3 species with different physiological structures: Rockrose (*Cistus Monspeliensis*), Heather (*Erica Arborea*), Pine (*Pinus Pinaster*). The forest fuels were collected
5 from live shrubs or tree in neighboring forests, close to the University of Corsica. The experiments were performed using branches and twigs with still attached leaves or needles.

In order to focus on oxidative pyrolysis and combustion processes, samples were oven-dried for 24h at 333K (Leroy-Cancellieri et al., 2014). This sample state allow to suppress the dehydration phenomenon and thus the influence of the moisture content on the burning. Dry samples were then kept in the desiccator to protect them from ambient humidity. The moisture
10 content arising from self-rehydration was about 4% for all the samples before testing.

In TGA experiments, the particles with the size of between 38 μm and 100 μm were used.

In field experiments, the samples are intact branches and leaves in order to be close as possible to their natural state. The initial mass of the samples is approximatively $50 \pm 0.001\text{g}$ which is larger by a factor of around 10000 than that of the samples for the experiments performed at the laboratory scale. According to the species it represents a branch about 30cm high.

15

2.2 Laboratory experiments

Mass loss is one of the main parameters used for the kinetic characterisation of thermal degradation mechanisms. It is known as the major driving parameter for the characterisation of source terms. Moreover, the mass loss provides qualitative and quantitative data on different reactions which take place in the heated solid (Kissinger H.E., 1957). In order to investigate the
20 mass loss behavior, thermogravimetric experiments were carried out in a thermogravimetric analyzer (PerkinElmer, Pyris 1 TGA). For each sample, 5mg of dried above-ground biomass was heated from 350K to 900K under dynamic conditions at a heating rate of $30\text{K}\cdot\text{min}^{-1}$. The TGA furnace was flushed with air at a rate of $20\text{mL}\cdot\text{min}^{-1}$ to maintain the oxidative atmosphere for thermal degradation of particles in the course of experiments. Each experiment was repeated at least thrice. The precision of temperature measurements was $\pm 2\text{K}$.

25

2.3 Field experiments

To investigate the scale effect and to highlight the similarities and differences between laboratory and field experiments, a device especially designed for field has been created. It allows the simultaneously records of the mass-loss and the temperature when samples are exposed to a heat source. In order to achieve the real fire conditions, the heat source is a fire front. The
30 description of this mass-loss prototype and its usage is detailed in the following sections.



2.3.1 Differential mass loss prototype setup

The prototype consists of two parts: the one responsible for measurements and the one responsible for data acquisition. The characteristics of each part are given below.

5 Analog measurement devices

The device was sized to be one-fifth the width of the plot to burn. This ensures that the fire completely encompasses the system during its propagation.

The device includes three load cells integrated in a welded ceramic box (1260mm × 170mm × 100mm), covered with a 50mm
10 thick refractory lining (Thermal Ceramics Kaowool 1600).

Taking into account the fact that the meteorological and fire conditions are difficult to reproduce perfectly, we decided to install the three load cells on the apparatus to follow the behaviour of three species subjected to the same fire propagation. With such three species available in the prototype, the differential analysis between the samples can be performed independent of the external conditions.

15 The three load cells (LSB 200, Futek®) have a maximum capacity of $450\text{g} \pm 0.1\%$ and having a width of 6.8mm, a height of 19mm, and a length of 17.5mm. Samples are introduced in the load cells through the stainless tube mounted on top of each cell. The height and the diameter of this tube (190mm × 20mm) were reckoned up to avoid any lift effect. Moreover, the position and the height of the sample in the tube can be adjusted to optimize the interaction between the flame and the sample. The distance between each supporting tube (500mm) was chosen such that the decomposition of a particular branch could not
20 affect the neighbouring branch. Thus, the plant will only be affected by the fire front in front of the device.

To measure the temperature acting on the sample and the heating rate of the fire, thermocouples were placed in a vertical position at the end of each tube. The position of the branch is adjusted in height so as the thermocouple is placed at mid-height of the fuel branch. This configuration ensures the determination of the real temperature to which the sample is subjected.

The K-type thermocouples were selected according to their temperature range, with an upper limit of $1300 \pm 0.5^\circ\text{C}$ (Omega®
25 HKMTSS-010G-8, diameter: 25µm).

Data acquisition and process

The acquisition system is integrated into a thermal box with a Multi-Layer Aluminization (Z-Flex®) shield. A remote wireless
30 acquisition system is actually impossible to use because of the disturbances introduced by the thermal shield. The temperature inside the thermal box is controlled using a thermocouple. If necessary, it is adjusted by a fan, when the temperature of the thermal box is rising. A laptop located inside the box is used to transmit the data simultaneously through a USB interface using custom software.



The mass-loss data are recorded using the Sensit software of Futek with a frequency of 2.5Hz.

The temperature data are synchronised with the mass-loss data recorded with the same frequency, by the acquisition unit Omega® TC-08. This system can accommodate up to eight thermocouples with an acquisition frequency of 10Hz. Figure 1 depicts the entire mass-loss prototype.

5

Figure 1

One of the main advantages of this prototype is that three different species can be subjected to the same external heating conditions in line and be analysed simultaneously under the same field conditions.

10 **2.3.2 Experimental and meteorological conditions**

The field tests took place in an open field terrain with no slope, situated in the Unit Instruction and Civil Security Intervention No. 5 of Corte in Corsica. The three species are subjected to the same heat source: the fire spreading over a wood-wool bed. This fuel was selected for the reasons of good repeatability of the heating conditions.

15 About 120 kg of weight wood-wool was used, forming a bed of 10 m at length and almost 6 m at width. The average height of the bed has been selected appropriately to comply with a fuel load of 2 kg.m⁻². The orientation of the fuel bed was based on the meteorological forecast of the day of the experiment, following the wind direction. A linear ignition was performed at the bottom of the wood wool bed.

20 The wind velocity and direction were recorded using a two-dimensional ultrasonic anemometer at 2.5m above the ground surface to reflect the average wind acting on the fire front. The anemometer was located in the direction of the propagation (at the end of the plot). The wind data were recorded using another (synchronised) data logger at a sampling rate of 1Hz. The average velocity of the wind measured during the experiment was 1.2 m.s⁻¹ and its direction was close to South Est (143°). During the campaign the wind was relatively constant with a standard deviation of 0.44 m.s⁻¹.

25 The devices deployed on the site are depicted in the figure 2 which presents the overall experimental setup.

Figure 2

30 The prototype was placed near the end of the bed to ensure the steady state of the fire propagation. The experiments were performed in the area with no slope and were replicated three times on the same day to ensure identical surrounding conditions.

Figure 3



3 Results

3.1 Laboratory experiments

Using TGA, the thermal degradation in air is characterised by a continuous weight loss until the point when the weight becomes almost constant. The first derivative of such thermogravimetric curves (i.e. $-dm/dt$) yields the maximum reaction rate. Such a procedure is known as Derivative Thermogravimetry (DTG). The character of the TGA curve, in combination with the

corresponding DTG peaks, gives a clear indication of the number of stages in thermal degradation. Figure 4 presents the experimental results on the thermal degradation of fuels heated at $30\text{K}\cdot\text{min}^{-1}$ from 350 to 900K under air sweeping.

Figure 4

10

A clear similarity in the decomposition process can be observed for the three species. Such similarities implies that there could be a general kinetic scheme to describe biomass thermochemical degradation under air atmosphere. TGA curves exhibit two stages of weight loss, which are confirmed in DTG by two peaks (*cf.* Figure 4). Despite the complex chemical process, experimental data suggest that a two-step model of global reactions can describe the most important features of the thermal and oxidative degradation of plants. The first mass loss due to decomposition begins slowly and accelerates rapidly in the temperature range of 290-340°C. The second mass loss follows the first one and reaches an overall mass loss of more than 90%. Moreover, the oxidative process is claimed to have two stages. The first stage is the volatilisation of main biomass compounds and the production of char residue at low temperatures. The second stage includes the decomposition of lignin and the combustion of the charcoal produced at the preceding stage (Fang et al., 2006). The same phenomena were observed and recorded by other authors as well (Branca and Di Blasi, 2004; Safi et al., 2004; Shen et al., 2009).

15

In order to compare biomass thermal behavior, DTG is frequently used to determine several temperature indexes: ignition temperature (T_i), final temperature of the first process (T_{f1}), final temperature of the second process (T_{f2}). T_i is defined as the inflection point of DTG at start of the degradation, while $T_{f1,2}$ are defined as the inflection points at the end of each stage.

25

Table 1

For the heating rate considered in this study, the onset temperature is the lowest for Heather, higher for Pine, and yet higher for Rockrose. This observation can be used as the ignition criterion, since the onset temperature marks out the beginning of oxidation reactions. The fuels with low onset temperatures are most ignitable, and they burn easily. These results will be compared to the field-scale experiments.

30

Using the TGA data, a kinetic model for each specie will be done in the section 4.



3.2 Field experiments

Figure 5 presents the temperature as a function of time, according to the data recorded while the plot was burning.

Figure 5

5

The temperature profiles were nearly the same for the three species with a maximum at 926K. The behaviour of the temperature indicates that the effect of the fire front on the prototype can be considered as a straight line. It is noteworthy that the temperature behaviour was similar in two other repetitions performed during the campaign. Using the evolution of temperature during the course of the experiment, the heating rate was estimated for each plant. The average of the heating rates during the heating phase were obtained: 13.2K.s⁻¹ for Pine, 12.9K.s⁻¹ for Heather, and 12.1K.s⁻¹ for Rockrose. Figure 6 demonstrates the mass loss synchronised to the temperature vs time data shown above.

10

Figure 6

15 The heating rate can be approximate at a median value of 12.7±0.6 K.s⁻¹ for all species. This result accredit the fact that the temperature measurement in 3 points with 500 mm difference is homogenous along the whole test field. Heather starts to lose its mass more quickly than Rockrose and Pine. This observation is in agreement with the laboratory experiments. Indeed, Heather exhibits a low onset temperature implying that this species will ignite prior to the two other species. The behaviour exhibited in TGA is similar as the one observed at the field scale. The order of the rate of degradation among species determined at the laboratory scale is kept at the field scale (the degradation is fast for Heather and Rockrose, and it is slower for Pine).

20

4 Kinetic analysis

Thermogravimetric data were used to find the best set of kinetic parameters for our three species. Using TGA measurements, the conversion degree α is defined as:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \quad (1)$$

25 With m the mass, m_0 the initial mass and m_f the final mass of the sample.

When the TGA experiments are conducted under non-isothermal conditions, the rate of heterogeneous solid-state reactions can be described as:

$$\frac{d\alpha}{dt} = \frac{1}{\beta} A e^{-\frac{E_a}{RT}} f(\alpha) \quad (2)$$



where $f(\alpha)$ is the conversion function (reaction model), A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, and β is the heating rate.

The kinetic parameters A , E_a , and $f(\alpha)$ can be estimated from the TGA experimental data by a variety of techniques (Vyazovkin et al., 2011; Vyazovkin and Wight, 1998). To obtain a reliable kinetic description of the processes under investigation, we used an approach that combines accurate isoconversional methods with model-fitting methods (Chrissafis, 2009; Pratap et al., 2007). This two-step approach is the so-called Hybrid Kinetic Method (HKM), which was developed earlier by Cancellieri *et al.* (Cancellieri et al., 2005). At the first step, isoconversional methods provide $E_a(\alpha)$ and the reaction model. At the second step, these initial data are used in a model-fitting technique to obtain the pre-exponential factor and the n^{th} -order model. Such a multi-step procedure allows the selection of the models that might otherwise be indistinguishable because of the poor quality of the regression fit when performed independently. In other words, such an approach gives the highest probability of selecting the most accurate kinetic triplet (A , E_a , and the model).

The laboratory experiments for our three species support the following two-step kinetic mechanism. The first process is modelled as



The second reaction deals with the oxidation of the chars produced during the first process:



Both reactions (I) and (II) can be described by the following differential equations (we consider an n^{th} -order model):

$$\frac{d\alpha_1}{dt} = \frac{1}{\beta} A_1 e^{-\frac{E_{a1}}{RT}} (1 - \alpha_1)^{n_1} \quad (3)$$

$$\frac{d\alpha_2}{dt} = \frac{1}{\beta} A_2 e^{-\frac{E_{a2}}{RT}} (\alpha_1 - \alpha_2)^{n_2} \quad (4)$$

The use of HKM allowed us to obtain the kinetic parameters listed in Table 2.

25

Table 2

4.1 Comparisons

Considering the two-stage mechanism and the kinetic parameters listed in Table 2, the mass-loss of each species can be simulated at the average heating rate measured during field experiment, which is $12.7 \pm 0.6 \text{ K}\cdot\text{s}^{-1}$ for all species. These numerical

30



simulations were then compared to the experimental mass-loss recorded at field-scale. Figure 7 compares the mass loss obtained experimentally for each species and the data of modelling according to Eqs. (3) and (4).

Figure 7

5

Generally, simulations are in good agreement with the experimental mass-loss rate even if there are some differences (as an attempt). For Rockrose, the model does not accurately fit the data in the range $0.85 > m/m_0 > 0.60$, probably because the initiation and preheating mechanisms are more complex than in the model described by the simple Arrhenius equation of order n . For Heather, experiments exhibit an accelerated degradation process which can be explained by the very fine structure of this species with branches as short as 2mm. On the contrary, Pine consists of single branches of 6mm diameter. Such thickness of the sample is responsible for the incomplete degradation.

10

The species are characterized in order to provide suitable input parameters. With accurate input parameters, models implemented CFD codes could predict the propagation of fire. To obtain a reliable description of the processes and a good agreement of simulation modellers need to know the mass-loss rate on the whole degradation. This parameter \dot{m} is defined as:

15

$$\dot{m} = \frac{(m_0 - m_f)}{(t_0 - t_f)} \quad (5)$$

With m the mass, t_0 the initial time and t_f the final time of the experiment.

To validate the kinetic mechanism and its parameters, the mass-loss rate obtained from field scale experiments is compared to the one determined for the simulation performed with the kinetic model. These data are summarized in the table 3.

20

Table 3

The main scope of this large scale test campaign is to reveal the thermal behaviour of different species in the same experimental conditions. The data obtained in the table 3 highlight the importance to take into account the physiological and chemical nature of species. Indeed, the mass-loss rate of pine is 50% lower than the heather and 40% lower than the rockrose. The significant differences must be integrate in CFD models to ensure a reliable characterization of source terms.

25

5 Conclusion

The stochastic conditions of fire imply great difficulties for the reproducibility of measurements. For these conditions, a differential mass-loss prototype has been designed with the aim to validate kinetic models adapted to the field scale. Comparatives mass losses data on three different plant species have never been recorded simultaneously. Moreover, it is the first time that the kinetics of decomposition of biomass have been validated under real wildland fire conditions, thus ensuring reliable characterization of source terms.

30



The technology presented in this paper is based on a completely new approach where the development of a new field mass loss device, combined with recent progress in the understanding of the behavior achieves never before recorded data. An experimental device, perfectly adapted to the biomass specificity based on a completely new differential approach has been developed. The prototype has been tested with three Mediterranean species. The results collected from field experiments
5 emphasise the influence of various parameters such as: the ignition temperature, biomass type and anatomical structure. However, the two-stage kinetic model based on the TGA data, seems to fit well the experimental data obtained at the field scale. Using the field scale measurements, the kinetic validity of the scheme is then extended outside TGA. This study allowed to validate the kinetics of decomposition of various biomasses under real wildland fire conditions, thus ensuring reliable characterization of source terms.
10 However, there were flawed predictions caused by the natural physiology of the samples (thickness and size of the leaves and branches). In fact, the initiation stage of preheating is strongly related to the physiology. Further studies will be focussed on the integration of sample thickness in the model as an inhibiting parameter.

Acknowledgement

15 The authors thanks the Unit Instruction and Civil Security Intervention No. 5 of Corte in Corsica for the provision of their field.

References

- 20 Branca, C. and Di Blasi, C.: Global interinsic kinetics of wood oxidation, *Fuel*, 83(1), 81–87, doi:10.1016/S0016-2361(03)00220-5, 2004.
- Cancellieri, D., Leoni, E. and Rossi, J. L.: Kinetics of the thermal degradation of Erica arborea by DSC: Hybrid kinetic method, *Thermochim. Acta*, 438(1–2), 41–50, doi:10.1016/j.tca.2005.07.013, 2005.
- Chrissafis, K.: Kinetics of thermal degradation of polymers, *J. Therm. Anal. Calorim.*, 95(1), 273–283, doi:10.1007/s10973-008-9041-z, 2009.
- 25 Di Blasi, C.: Modeling chemical and physical processes of wood and biomass pyrolysis, *Prog. Energy Combust. Sci.*, 34(1), 47–90, doi:10.1016/j.pecs.2006.12.001, 2008.
- Fang, M. X., Shen, D. K., Li, Y. X., Yu, C. J., Luo, Z. Y. and Cen, K. F.: Kinetic study on pyrolysis and combustion of wood under different oxygen concentrations by using TG-FTIR analysis, *J. Anal. Appl. Pyrolysis*, 77(1), 22–27, doi:10.1016/j.jaap.2005.12.010, 2006.
- 30 Grishin A.M.: *Mathematical modeling forest fire and new methods fighting them*, Publishing House of the Tomsk University., F. Albini, Tomsk, Russia., 1997.



- Kissinger H.E.: Reaction kinetics in differential thermal analysis, *Anal. Chem.*, 29, 1702–1706, 1957.
- Leroy-Cancellieri, V., Cancellieri, D., Leoni, E., Simeoni, A. and Filkov, A. I.: Energetic potential and kinetic behavior of peats, *J. Therm. Anal. Calorim.*, 117(3), 1497–1508, doi:10.1007/s10973-014-3912-2, 2014.
- Linn, R., Reisner, J., Colman, J. J. and Winterkamp, J.: Studying wildfire behavior using FIRETEC, *Int. J. Wildland Fire*, 11(4), 233–246, doi:10.1071/wf02007, 2002.
- Mell, W., Jenkins, M. A., Gould, J. and Cheney, P.: A physics-based approach to modelling grassland fires, *Int. J. Wildland Fire*, 16(1), 1–22, doi:10.1071/WF06002, 2007.
- Miller, R. S. and Bellan, J.: A Generalized Biomass Pyrolysis Model Based on Superimposed Cellulose, Hemicellulose and Lignin Kinetics, *Combust. Sci. Technol.*, 126(1–6), 97–137, doi:10.1080/00102209708935670, 1997.
- 10 Miranda, A. I., Martins, V., Cascão, P., Amorim, J. H., Valente, J., Tavares, R., Borrego, C., Tchepel, O., Ferreira, A. J., Cordeiro, C. R., Viegas, D. X., Ribeiro, L. M. and Pita, L. P.: Monitoring of firefighters exposure to smoke during fire experiments in Portugal, *Environ. Int.*, 36(7), 736–745, doi:10.1016/j.envint.2010.05.009, 2010.
- Morandini, F., Silvani, X., Rossi, L., Santoni, P.-A., Simeoni, A., Balbi, J.-H., Louis Rossi, J. and Marcelli, T.: Fire spread experiment across Mediterranean shrub: Influence of wind on flame front properties, *Fire Saf. J.*, 41(3), 229–235, doi:10.1016/j.firesaf.2006.01.006, 2006.
- 15 Ninan, K. N.: Kinetics of solid state thermal decomposition reactions, *J. Therm. Anal.*, 35(4), 1267–1278, doi:10.1007/BF01913047, 1989.
- Pratap, A., Lilly Shanker Rao, T., Lad, K. and Dhurandhar, H.: Isoconversional vs. Model fitting methods, *J. Therm. Anal. Calorim.*, 89(2), 399–405, doi:10.1007/s10973-006-8160-7, 2007.
- 20 Safi, M. J., Mishra, I. M. and Prasad, B.: Global degradation kinetics of pine needles in air, *Thermochim. Acta*, 412(1–2), 155–162, doi:10.1016/j.tca.2003.09.017, 2004.
- Schemel, C. F., Simeoni, A., Biteau, H., Rivera, J. D. and Torero, J. L.: A calorimetric study of wildland fuels, *Exp. Therm. Fluid Sci.*, 32(7), 1381–1389, doi:10.1016/j.expthermflusci.2007.11.011, 2008.
- Shen, D. K., Gu, S., Luo, K. H., Bridgwater, A. V. and Fang, M. X.: Kinetic study on thermal decomposition of woods in oxidative environment, *Fuel*, 88(6), 1024–1030, doi:10.1016/j.fuel.2008.10.034, 2009.
- 25 Silvani, X., Morandini, F. and Muzy, J.-F.: Wildfire spread experiments: Fluctuations in thermal measurements, *Int. Commun. Heat Mass Transf.*, 36(9), 887–892, doi:10.1016/j.icheatmasstransfer.2009.06.008, 2009.
- Simeoni, A., Thomas, J. C., Bartoli, P., Borowieck, P., Reszka, P., Colella, F., Santoni, P. A. and Torero, J. L.: Flammability studies for wildland and wildland–urban interface fires applied to pine needles and solid polymers, *Fire Saf. J.*, 54, 203–217, doi:10.1016/j.firesaf.2012.08.005, 2012.
- 30 Stavrakakis, P., Agapiou, A., Mikedi, K., Karma, S., Statheropoulos, M., Pallis, G. C. and Pappa, A.: A scale-up field experiment for the monitoring of a burning process using chemical, audio, and video sensors, *Environ. Sci. Pollut. Res.*, 21(2), 891–900, doi:10.1007/s11356-013-1945-x, 2014.
- Vyazovkin, S. and Wight, C. A.: Isothermal and non-isothermal kinetics of thermally stimulated reactions of solids, *Int. Rev. Phys. Chem.*, 17(3), 407–433, doi:10.1080/014423598230108, 1998.
- 35



Vyazovkin, S., Burnham, A. K., Criado, J. M., Pérez-Maqueda, L. A., Popescu, C. and Sbirrazzuoli, N.: ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data, *Thermochim. Acta*, 520(1–2), 1–19, doi:10.1016/j.tca.2011.03.034, 2011.

5 White, J. E., Catallo, W. J. and Legendre, B. L.: Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies, *J. Anal. Appl. Pyrolysis*, 91(1), 1–33, doi:10.1016/j.jaap.2011.01.004, 2011.



Table 1 : Characteristic temperatures of thermal degradation of species at $\beta = 30\text{K}\cdot\text{min}^{-1}$

Parameters \ Specie	Ti (K)	Tf ₁ (K)	Tf ₂ (K)
Rockrose	572	684	812
Heather	538	631	827
Pine	549	643	818



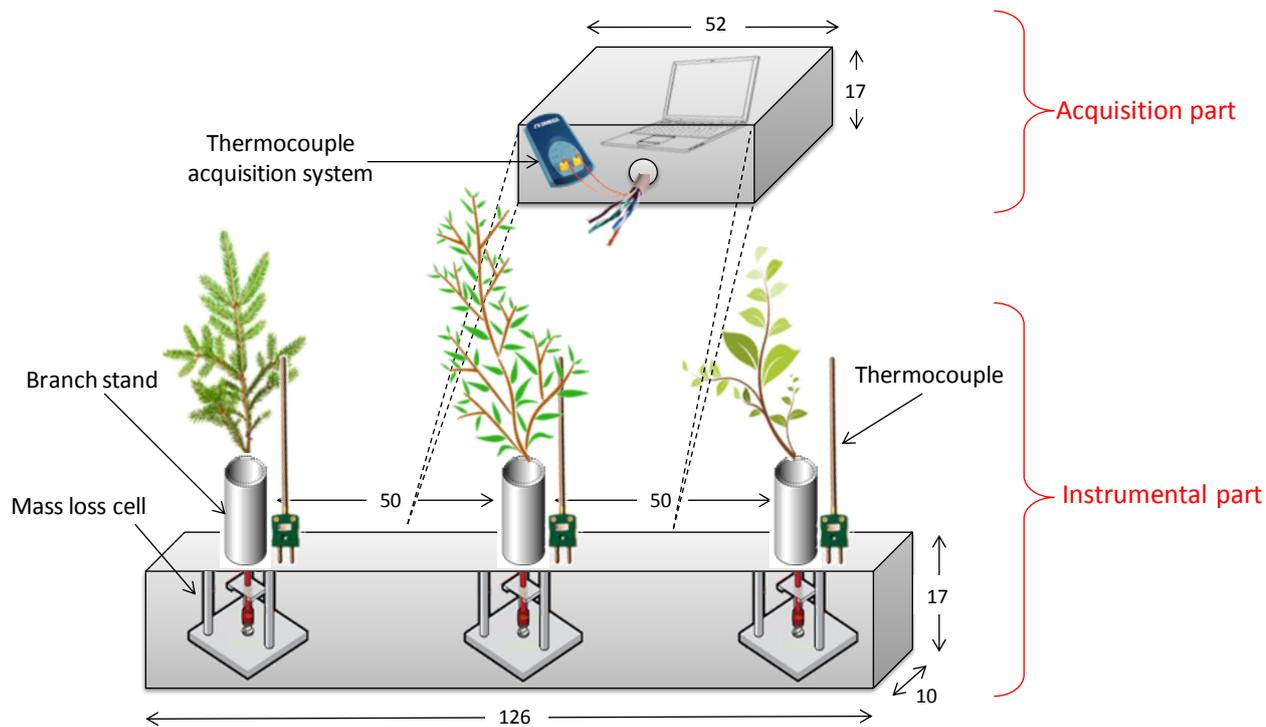
Table 2: Summary of kinetics parameters [22].

	$Virgin_{(s)} \rightarrow Char_{(s)} + Gas_{(g)}$			$Char_{(s)} \rightarrow Residue_{(s)} + Gas_{(g)}$		
	n_1	E_{a1} (kJ.mol ⁻¹)	A_1	n_2	E_{a2} (kJ.mol ⁻¹)	A_2
Rockrose	3.74	120	22.10	0.52	128	14.50
Heather	2.63	80	12.90	0.52	114	12.50
Pine	3.97	118	23.20	0.43	128	14.20



Table 3: Mass-loss rate of each species

	$\dot{m}_{\text{exp}} \text{ (g.s}^{-1}\text{)}$	$\dot{m}_{\text{sim}} \text{ (g.s}^{-1}\text{)}$
Rockrose	0.01508	0.00941
Heather	0.01842	0.01084
Pine	0.00907	0.00851



5

Figure 1: The differential mass-loss prototype

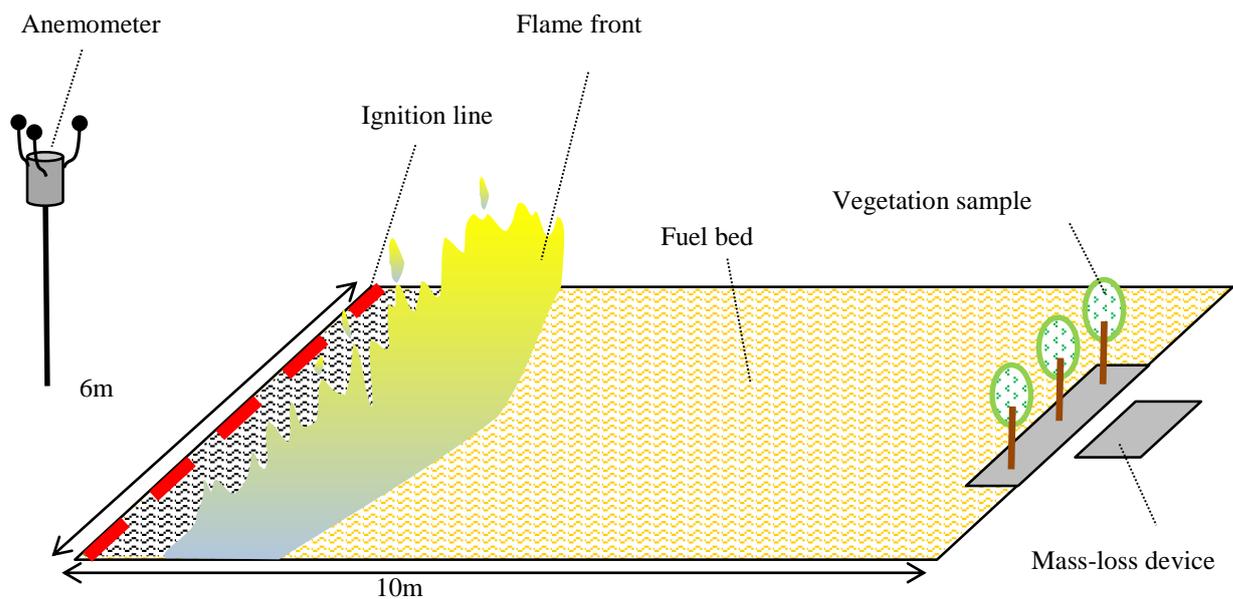
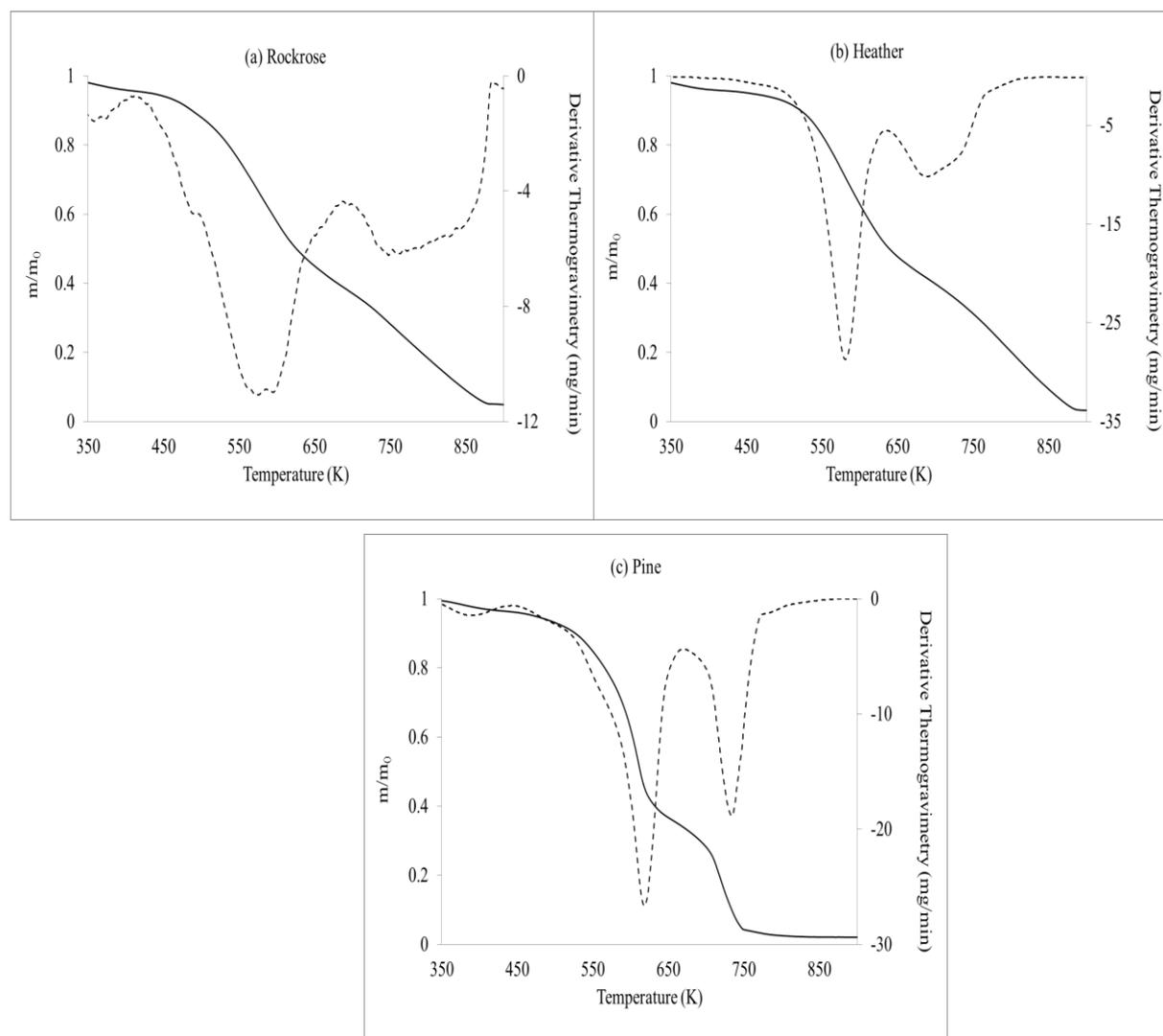


Figure 2: Experimental configuration



5

Figure 3: Differential mass loss prototype in real fire conditions



5

Figure 4: TGA (lines) and DTG (dotted) of oven dried of Rockrose (a), Heather (b), Pine (c) samples obtained with a linear heating rate of 30 K/min under air atmosphere.

10

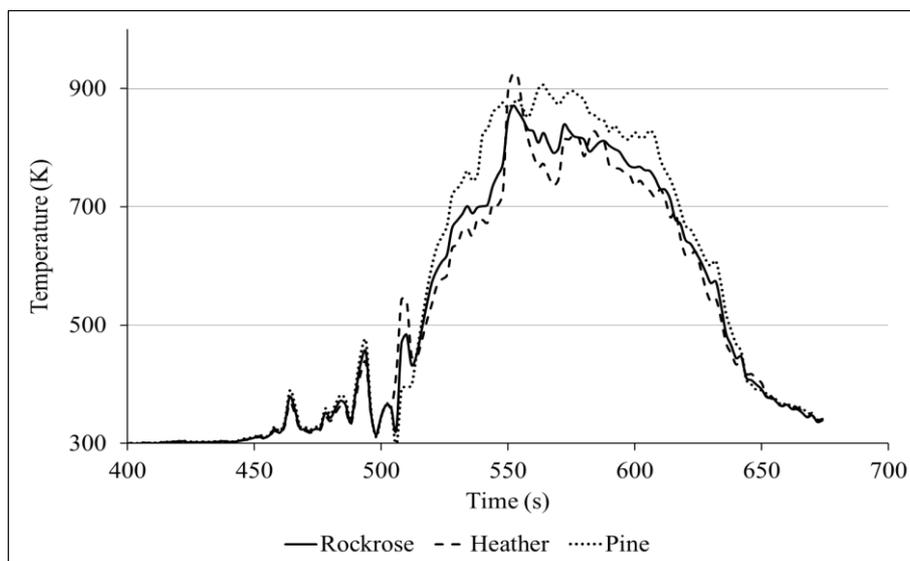


Figure 5: Temperature vs. Time obtained during a field experiment.

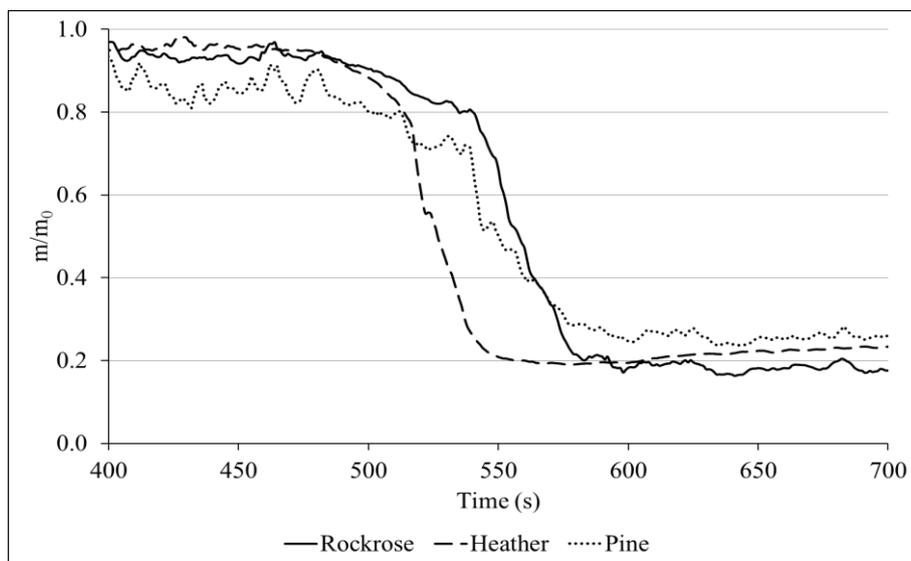
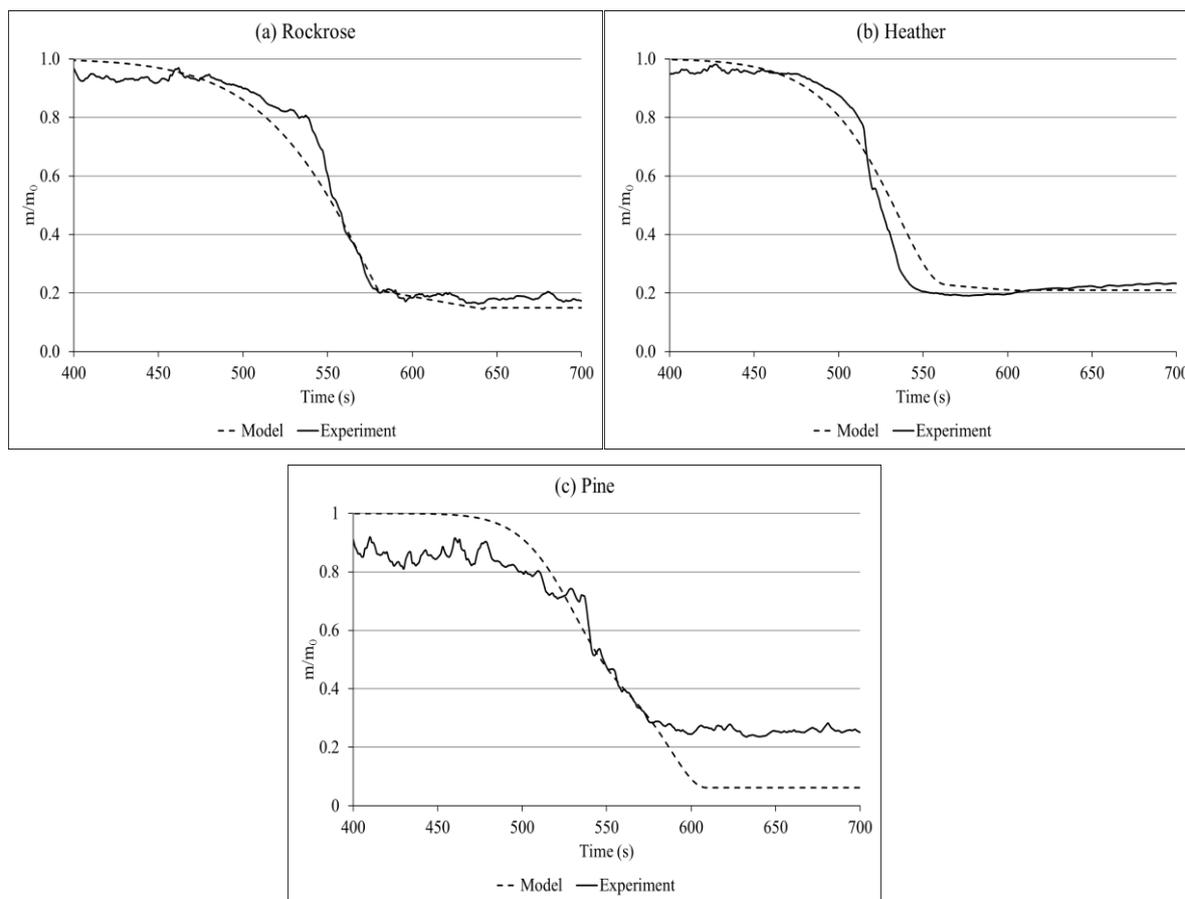


Figure 6: Experimental mass losses obtained at field scale.

5



5

Figure 7: Experimental (solid line) and modeled (dashed line) mass loss for (a) Rockrose, (b) Heather and (c) Pine.

10