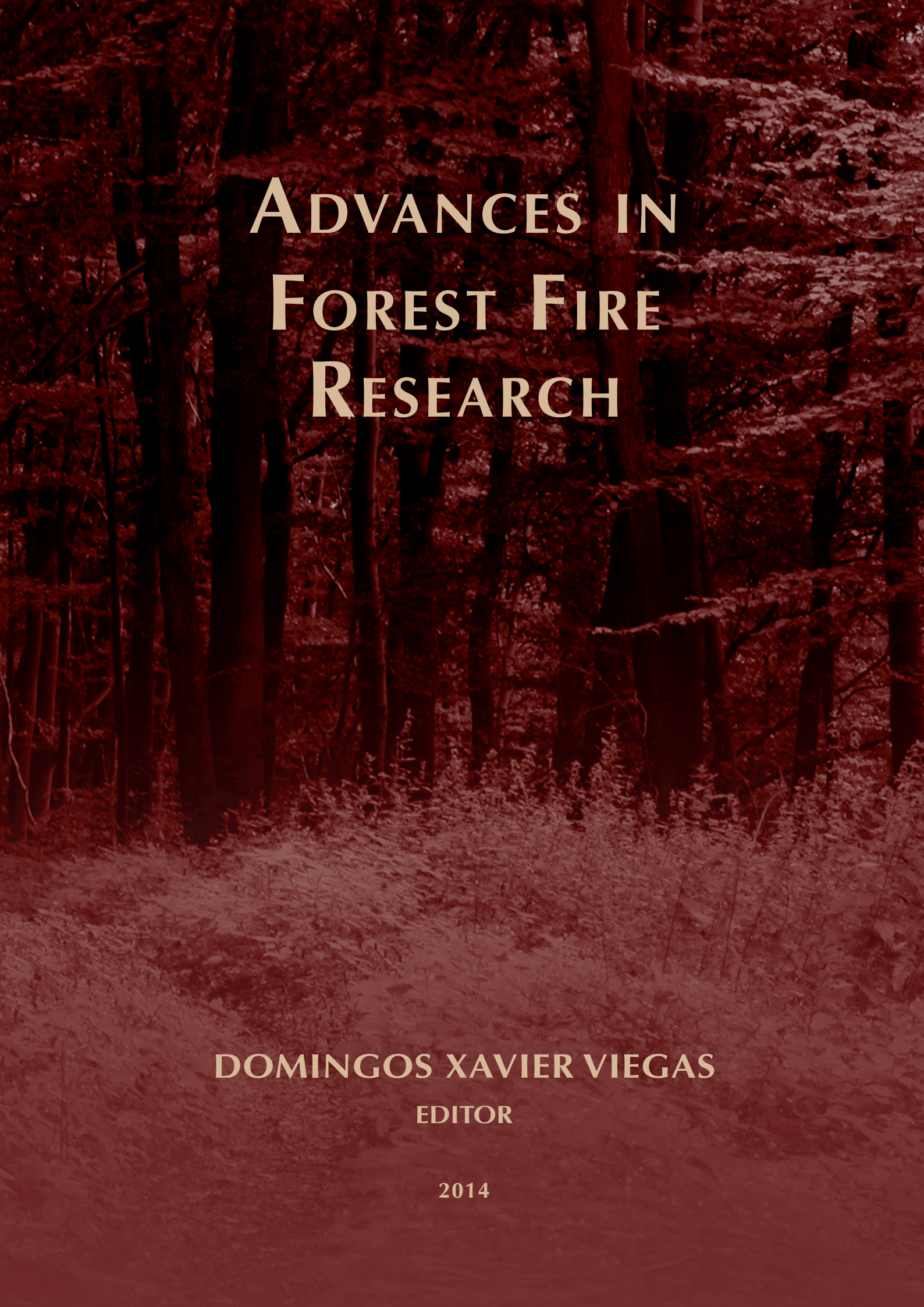

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Multi-scale kinetic model for forest fuel degradation

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Abstract
In modelling wildfire behaviour, a good knowledge of mechanisms and kinetic parameters controlling the thermal decomposition of forest fuel is of great importance. Generally, the pyrolysis models are determined from experiments carried out in thermal device (i.e. TGA and DSC). This kind of tools ensures an accurate determination of kinetic parameters in perfectly controlled conditions. But the gap of a larger scale, for their uses in forest fire conditions, is still far. To corroborate the kinetic models in realistic forest fire conditions, a mass loss device specially designed for field scale has been developed. The system includes three load cells with a max load at 400 g and 2.7 Hertz for the frequency acquisition. Each load cell is sit on top of a stainless tube in which the sample is hold. The position and height of the sample in the tube could be adjusted to optimize the interaction with the height of the flame and the sample. To obtain the temperature impacting the sample, a thermocouple K is placed at the end of each tube set to the same frequency acquisition as load cells. The device is integrated in a welded ceramic box that was lined with a 15 mm thick refractory lining. The acquisition system is included into an armored thermal box. For this first campaign of measures, we have selected species which have been previously studied for the kinetic modeling and presenting different typologies: Rockrose, Heather and Pine. One of the main advantages of this prototype is that 3 different species can be submitted, in line, to the same external heating conditions and are simultaneous analyzed. The heating source is a fire spread of wood wool bed. This fuel have been selected for a good repeatability of heating conditions Before each test, a fuel bed with various loads (0.5, 1 and 2 kg/m2) has been uniformly distributed and the prototype has been placed around the end of the bed to ensure the steady state. In these experimental conditions the samples, of intact branches and leaves, are closest to their natural state. Experimental field-scale results have been compared to numerical simulations based on Arrhenius law.
The simulations have been performed considering a two-steps mechanism previously obtained by the authors using TGA data. In a general point of view, the simulations have a good agreement with the experimental mass loss rate even if some differences appear (as attempt). For the rockrose, the model do not match accurately in the range of $0.7 < m/m0 < 0.9$ probably because the mechanisms of initiation and preheating are more complex than a simple Arrhenius equation of order n. Concerning the heather, experiments exhibit an accelerate degradation process which can be explain by the very fine structure of this specie. Conversely, Pine has a different structure which is constituted by a single branch with a diameter of 6 mm. This thickness of sample involves an incomplete degradation. Considering the very important gap between laboratory and field scale, the kinetic scheme gives satisfactory modeling.

***Keywords**: field-scale, mass loss prototype, kinetic analysis*

1. Introduction

In studying forest fire propagation, kinetic modeling of thermal degradation mechanisms is one of the main prerequisites for the determination of source terms, allowing the development of realistic models. Numerous Computational Fluid Dynamics (CFD) codes have been developed for predicting fire spread and providing operational tools for land managers. Those codes include various sub-models describing the different phenomenon involved in case of fire such as the pyrolysis model (Morvan and Dupuy 2004) which describes the thermal decomposition of the solid.
In order to describe the evolution of the solid phase, the mass loss rate of the solid is one of the most important parameters. Indeed it is directly linked with the pyrolysis gas flow rate and represents the initial factor of the combustion process.

In modelling fire behaviour the knowledge of the mechanisms and kinetic parameters controlling the thermal decomposition of forest fuel it is of great important. Indeed, adequate kinetic mechanisms should be coupled with the description of transport phenomena (heat, mass and momentum transfer) in order to provide detailed process simulation.
The thermoanalytical technique commonly used in solid-phase thermal degradation studies is the ThermoGravimetric Analysis (TGA) (Ninan 1989; White *et al.* 2011) which has gained widespread currency in thermal studies of biomass pyrolysis (Di Blasi 2008). TGA measures the decrease in substrate mass caused by the release of volatiles, or devolatilization, during thermal decomposition. In TGA, the mass of a sample being heated at a specific rate is monitored as a function of temperature or time. The TGA requires sample sizes sufficiently small such that the diffusion effects become negligible and the pyrolysis is kinetically controlled (Miller and Bellan 1997). The experimental data gathered in the perfectly controlled conditions of the TGA ensures an accurate determination of kinetic mechanism. Unfortunately, these experimental conditions are not realistic with those encountered in real forest fire. Sometimes, experiments were performed in calorimetry (with cone or FPA)(Schemel *et al*. 2008), but the gap of a larger scale is still far.
Based on these observations, the aim of this study is to propose a kinetic model for Mediterranean fuels adapted to realistic forest fire conditions. In this purpose, a mass loss device specially designed for field scale has been developed. This device can record in real time and simultaneously the mass loss and the temperature of 3 samples when they are submitted to a heat flux. Always with the aim of bringing it closer to a forest fire, the heat flux is a flame front created by the spread of a bed of straw. The experimental values conducted at field-scale have been compared to kinetic laws established in TGA.

2. Materials and Methods

2.1. Biomass fuels

Plant materials have been collected in Corsica from a natural Mediterranean ecosystem situated far away from urban areas in order to prevent any pollution on the samples. Heather, Rockrose and Pine are the representative species of different strata of vegetation concerned by wildland fires. The properties of the species are shown in Table 1. All the fuels are expressed in their chemical equivalent formula, which is a function of their major elements (C, H and O) obtained from the ultimate analysis on a dry basis. The heating values (high and low) were measured using a bomb calorimeter and the calorific capacities were determined using a Differential Scanning Calorimeter (DSC). The surface-to-volume ratio and density were measured following the methodology proposed by Moro (Moro 2006).

Table 1. Physico-chemical parameters of fuels

Properties	Parameters	Rockrose	Heather	Pine
Chemical	Formula	C4,24 H6,49 O 2,66	C4,58 H7,32 O 2,35	C4,26 H6,83 O 2,62
Thermal	High Heating Value (kJ kg-1)	20905	20988	21566
	Low Heating Value (kJ kg-1)	19745	19703	20239
	Calorific capacity (kJ kg-1 °C-1)	1912	1939	2050
Physiologic	Surface to volume ratio (m-1)	2217	3801	3057
	Fuel density (kg m-3)	912	614	511

2.2. Laboratory experiments

For kinetic characterization of thermal degradation mechanisms the mass loss is one of the main prerequisites. This parameter has been chosen as the major driving parameter for the characterization of source terms. Moreover, the mass loss provides qualitative and quantitative information regarding the different reactions taking place in the heated solid (Kissinger H.E. 1957). Thermogravimetric experiments were carried out in a thermogravimetric analyzer (PerkinElmer Pyris 1 TGA). The precision of the temperature measurement was ±2 K. For each sample, 5 mg of dried and ground biomass was heated from 350 K up to 900 K under dynamic conditions at heating rates of 20 K min^{-1}. During the experiments the furnace of the TGA is flushed with 20 mL min^{-1} air to maintain an oxidative atmosphere for thermal degradation of particles. Each experiment was repeated at least three times.

2.3. Field experiments

To cross the gap of real fire, we transpose the principle of the TGA at the field scale. In this purpose, we have created a device in which samples are exposed to a heating source (a fire front) and the weight loss and temperature are simultaneously recorded. The next sections are dedicated to the description of this mass loss prototype and its use.

2.3.1. *Differential mass loss prototype set up*

The prototype consists of two parts: one dedicated to measurement and the other dedicated to data acquisition. The characteristics of each are detailed below.

The instrumental part:

The size of the device has been calculated to be 1/5 of the width of the plot to burn. In this way, the system will completely encompass during the propagation.
The device includes 3 load cells which are integrated in a welded ceramic box (1260 mm × 170 mm × 100 mm) that was lined with a 50 mm thick refractory lining (Thermal Ceramics Kaowool 1600).
Given that the meteorological and fire conditions are difficult to perfectly reproduce, we make the choice of install 3 load cells on apparatus to follow the behaviour for 3 species submitted to the same fire propagation. With three species on the prototype, a differential analysis between samples becomes possible free from the external conditions.
The 3 load cells (Futek®) have a maximum lift of 450 g for 6.8 mm width, 19 mm height and 17.5 mm length. A stainless tube is sit on top of each load cell in order to insert the sample inside. The height and the diameter of this tube (190 mm x 20 mm) have been reckoned to avoid any lift effect. Moreover, the position and height of the sample in the tube could be adjusted to optimize the interaction with the height of the flame and the sample.
The distance between each supporting tube (500 mm) has been chosen so that the decomposition of a branch does not affect the neighbouring branch. Thus, the plant will only be affected by the fire front of the beforehand device.
To obtain the temperature impacting the sample and the punctual heating rate of the fire propagation, thermocouples are placed at the end of each tube. Thermocouples K have been selected according to their temperature ranging to 1300 ± 0.5 °C (Omega® HKMTSS-010G-8) diameter: 25 µm.

The acquisition part:

The acquisition system is integrated into a thermal Multi-Layer Aluminization (Z-Flex®) shield box. A deported wireless acquisition system is actually impossible to use because of disturbances caused by the thermal shield. The temperature inside the thermal box is controlled using a thermocouple and adjusted if necessary by a fan if the temperature of the thermal box is rising. Inside the box, a laptop

is included in which the data are simultaneously transmitted through a USB interface and using custom software.

The mass loss data are recorded using Sensit the Futek's software with a frequency of 2.5 Hz.
The temperature data are synchronized with mass losses data acquisition recorded with the same frequency thanks to acquisition unit Omega® TC-08. This system can accommodate up to 8 thermocouples with an acquisition frequency of 10 Hz. The figure 1 presents the whole mass loss prototype.

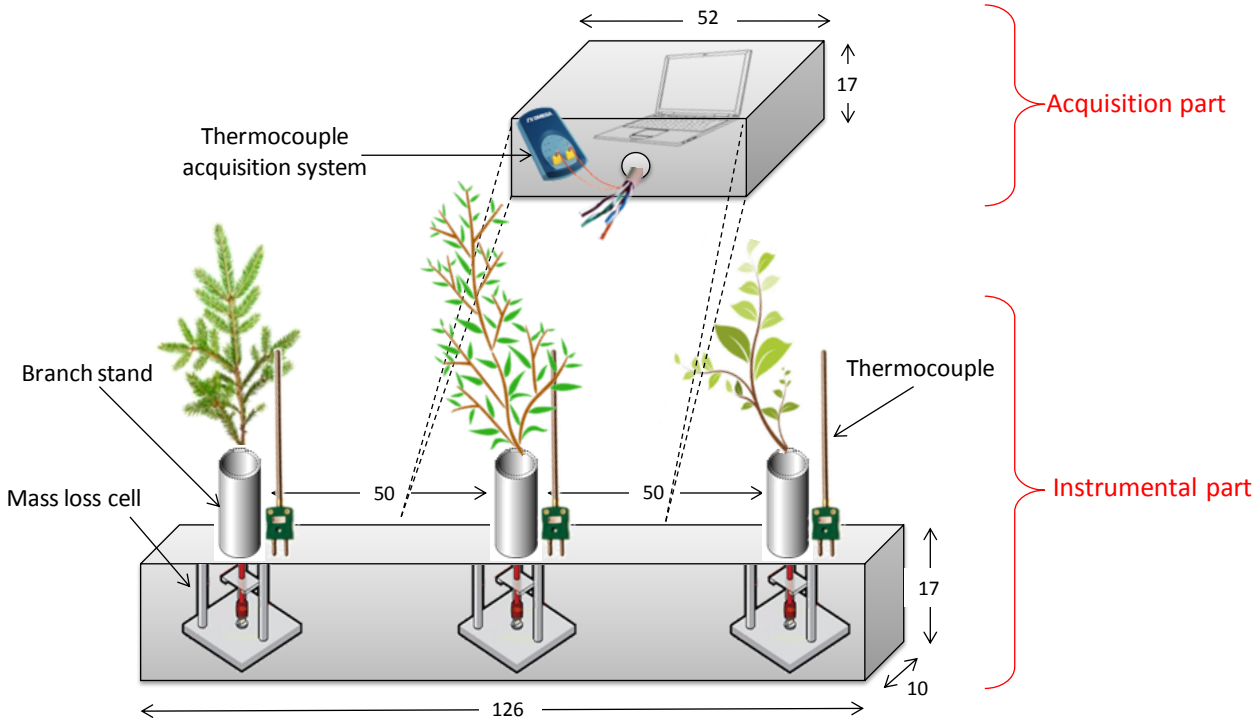


Figure 1. The differential mass loss prototype

One of the main advantages of this prototype is that 3 different species can be submitted, in line, to the same external heating conditions and are simultaneous analyzed in the same field conditions.

2.3.2. *Experimental conditions*

All experiments have been carried out on 3 species presenting different typologies: Rockrose, Heather and Pine. In these experimental conditions the samples of intact branches and leaves, are closest to their natural state. This initial mass of the sample (around 50g) represent a factor 10000 compared to experiments performed at laboratory scale with crushed samples.
The 3 species are submitted to the same heating source which is a fire spread of wood wool bed. This fuel has been selected for a good repeatability of heating conditions.
Before each test, a fuel bed of 6 m wide and 10 m long has been uniformly distributed with a fuel load of 2 kg m^{-2}. The prototype is placed around the end of the bed to ensure the steady state of propagation. The experiments have been performed in an area with no wind and no slope and were replicated three times.

Figure 2. Differential mass loss prototype in field conditions

2.4. Kinetic Analysis

The thermogravimetric data have been used to find the best set of kinetic parameters for three species. Using TGA experiments, in case of non-isothermal conditions, the rate of heterogeneous solid-state reactions can be described by:

$$\frac{d\alpha}{dt} = \frac{1}{\beta} A\, e^{-\frac{E_a}{RT}} f(\alpha) \qquad \text{(Eq. 1)}$$

where f(α) is the conversion function (reaction model) with $\alpha = m_0 - m/m_0 - m_\infty$, A is the pre-exponential factor, Ea is the activation energy, R is the gas constant and β is the heating rate.

The estimation of the kinetic parameters (*A*, E_a, *f(α)*) from TGA experimental data can be done with a variety of techniques (Vyazovkin and Wight 1998; Vyazovkin *et al.* 2011). In order to obtain a reliable kinetic description of the investigated processes, we used an approach that combines the accuracy of isoconversional methods with model-fitting methods (Pratap *et al.* 2007; Chrissafis 2009). This approach, called Hybrid Kinetic Method (HKM), has been developed in a earlier work (Cancellieri *et al.* 2005). It is based on two steps; the first uses isoconversional methods to provide $E_a(\alpha)$ and the reaction model. The second step requires these initiation data to be injected in a model fitting method to obtain the pre-exponential factor and n^{th}-order. This allows selection of models that might otherwise be indistinguishable based on the quality of the regression fit alone. From your point of view, such an approach gives the highest probability of selecting the most accurate kinetic triplet (*A*, E_a, and the model).

3. Results

3.1. TGA experiments

During thermal degradation in air, weight loss occurs continuously until the weight becomes almost constant. Figure 3 presents the experimental results of fuels thermal degradation from 350 to 900 K, under air sweeping.

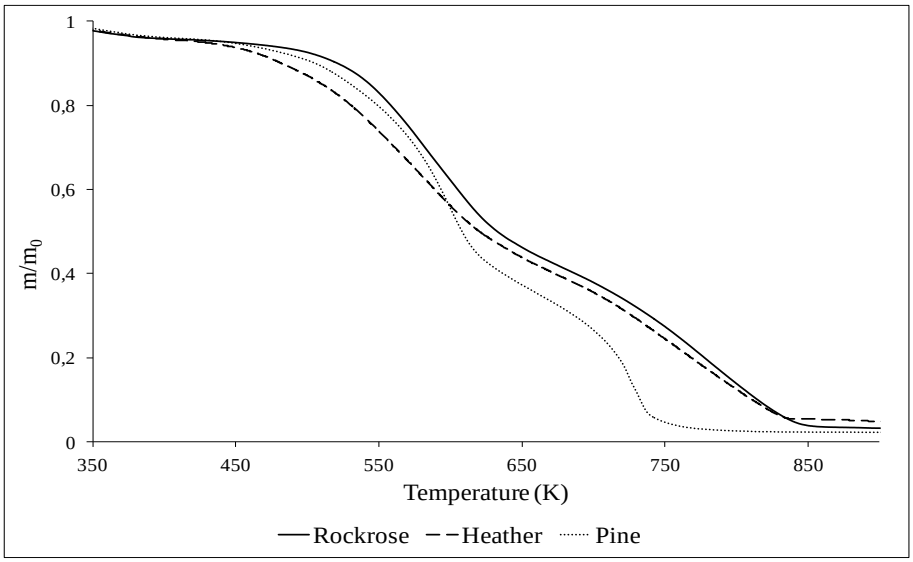
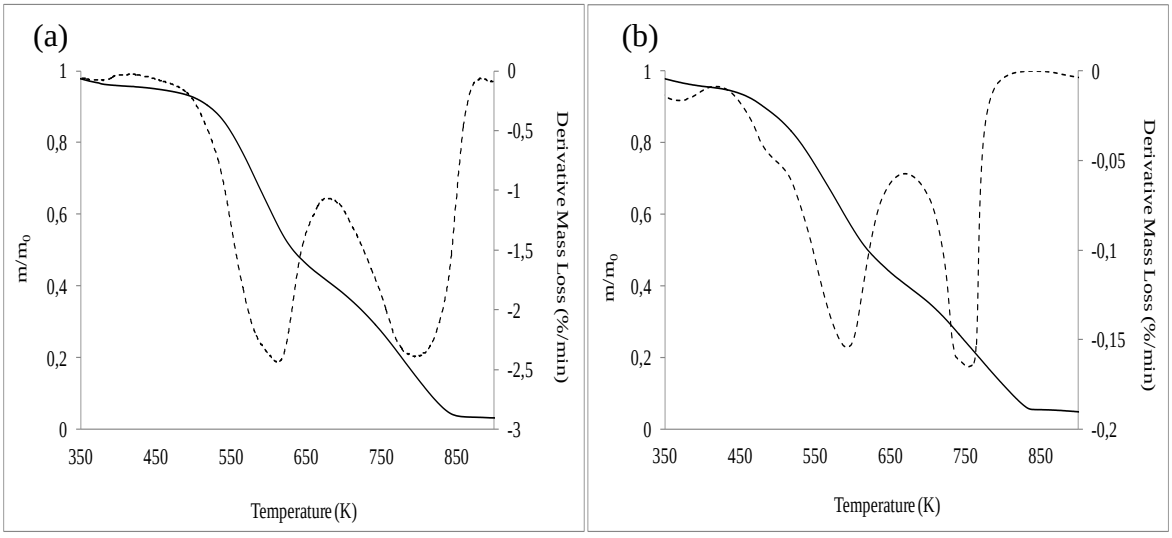


Figure 3: TGA curves of samples obtained with a linear heating rate of 20 K min^{-1} under air atmosphere.

Despite of the complex composition and chemical process, experimental observations suggest that a 2-steps of global reactions can capture the most important behaviour of the thermal and oxidative degradation of plants. Figure 3 highlights that for the heating rate considered in this work, Heather has the lower onset temperature, followed by Pine and in fine, Rockrose. This criterion is very helpful as it can be used as an ignition criterion since onset temperature measures the starting of oxidation reactions. The fuels with low onset temperature are the most ignitable and they burn easily. These results will be confronted to field scale experiments.

Taking the first derivative of such thermogravimetric curves (i.e., −dm/dt) curves, known as derivative thermogravimetry (DTG), provides the maximum reaction rate. The nature of a TGA curve in combination with the corresponding DTG peaks gives a clear indication of the number of stages of the thermal degradation.



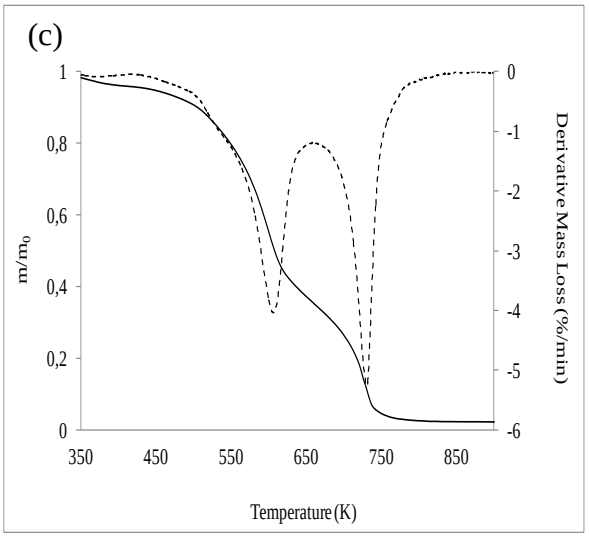


Figure 4: TGA (lines) and DTG (dotted) of oven dried of Rockrose (a), Heather (b), Pine (c) samples obtained with a linear heating rate of 20 K.min^{-1} under air atmosphere (Cancellieri et al. 2013)

TGA curves show two steps of weight loss confirmed in DTG by 2 peaks. The oxidative process is claimed to have two steps: the first step is volatilization of the main biomass constituents and production of char residue at low temperature; the second step includes the decomposition of lignin and the combustion of the charcoal generated in the early stage (Fang *et al.* 2006). The same phenomena are observed and recorded by other authors (Branca and Di Blasi 2004; Safi *et al.* 2004; Shen *et al.* 2009).

3.2. Kinetic parameters

According to laboratory experiments, it would seem wise to consider a 2-steps mechanism. This scheme seems to be suitable for the 3 species. The first process is modeled as:

$Virgin_{(s)} \rightarrow Char_{(s)} + Gas_{(g)}$ (1)

The second reaction concerns the oxidation of chars formed during the first process: $Char_{(s)} \rightarrow Residue_{(s)} + Gas'_{(g)}$ (2)

The two reactions (1) and (2) can be traduced in the two following differential equations (Eq. 2) and (Eq. 3), considering a n-th order model.

$$\frac{d\alpha_1}{dt} = \frac{1}{\beta} k_{01}\, e^{-\frac{E_{a1}}{RT}}\, (1-\alpha_1)^{n_1} \quad \text{(Eq. 2)}$$

$$\frac{d\alpha_2}{dt} = \frac{1}{\beta} k_{02}\, e^{-\frac{E_{a2}}{RT}}\, (\alpha_1-\alpha_2)^{n_2} \quad \text{(Eq. 3)}$$

Applying the HKM has allowed to obtain the kinetics parameters presented in the table 2.

Table 2 : Summary of kinetics parameters (Cancellieri et al. 2013).

	$Virgin_{(s)} \rightarrow Char_{(s)} + Gas_{(g)}$			$Char_{(s)} \rightarrow residue_{(s)} + Gas_{(g)}$		
	n_1	Ea_1 (kJ.mol^{-1})	ln k_{01}	n_2	Ea_2 (kJ.mol^{-1})	ln k_{02}
Heather	2.63	80	12.90	0.52	114	12.50
Pine	3.97	118	23.20	0.43	128	14.20
Rockrose	3.74	120	22.10	0.52	128	14.50

3.3. Field Experiements

The experimental campaign took place on 21 June 2012 in Corsica, in the South of France. The plot is located in an area with no slope. The figure 5 presents the temperature versus time data recorded during the burn of a plot.

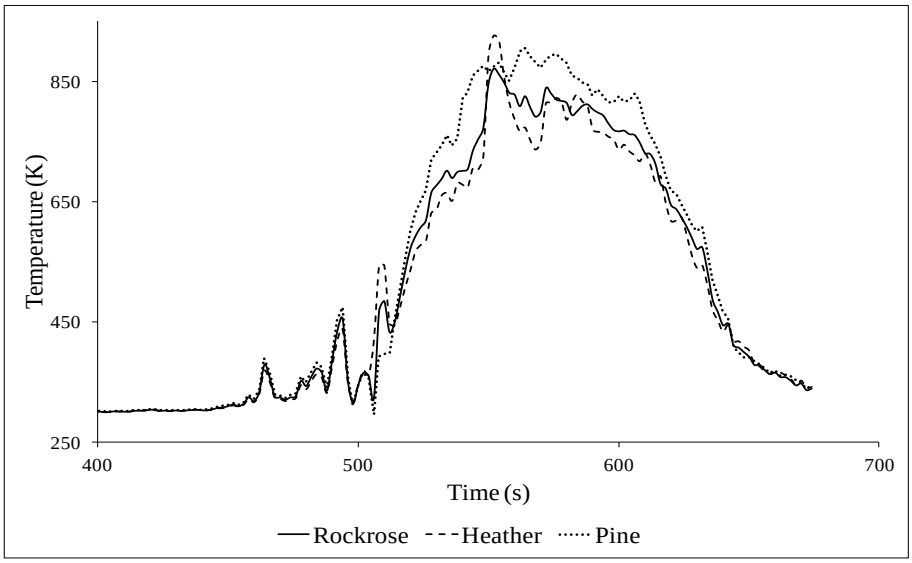


Figure 5: Temperature vs. Time obtained during a field experiment.

The temperature profiles were sensibly the same for the 3 species with a maximum at 926 K. The behavior of the temperature indicates that the fire front can be considered as a straight line impacting the prototype. It is important to note that the temperature behavior is the similar for the 2 other repetitions made during the campaign. Using the evolution of the temperature during the experiment, the heating rate is deduced for each plant. The maximum heating rates obtained are 13.2 for Pine, 12.1 for Heather and 11.1 K s^{-1} for Rockrose. The figure 6 exhibits the mass loss synchronized to the temperature and time data displayed above.

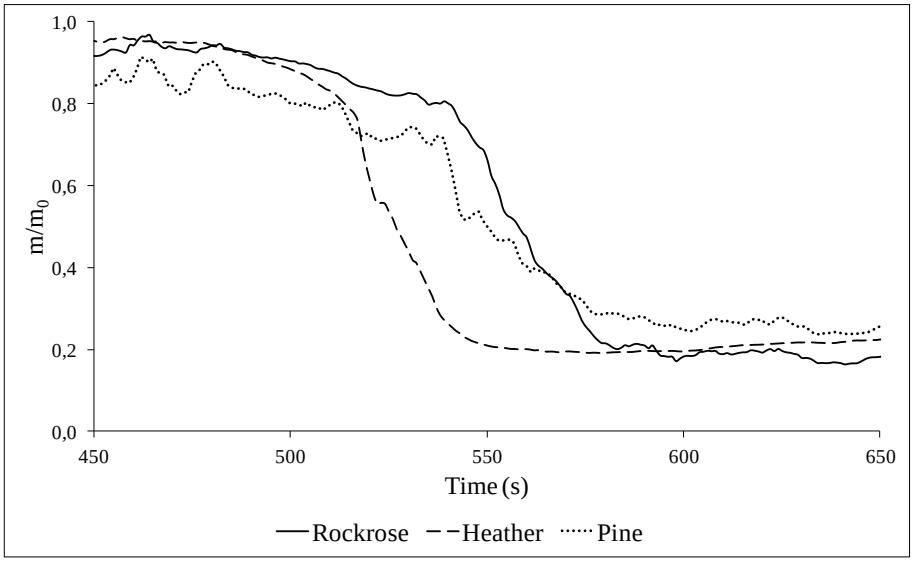


Figure 6. Experimental mass losses obtained at field scale.

The mass loss of Heather starts quickly compared to Rockrose and Pine. This observation is in agreed with the laboratory experiments. Indeed, the Heather presents a low onset which indicates that it is the specie which will ignite firstly compared to the 2 others. The behavior exhibit in TGA is corroborated at field scale. For Heather and Rockrose the degradation is fast while for Pine is slower.

3.4. Comparisons

Experimental field-scale results have been compared to numerical simulations based on Arrhenius law with kinetic parameters obtained for laboratory scale. According to the figure 5 the heating rates deducted are used for the simulations. The simulations have been performed considering the 2-steps mechanism and the kinetic parameters presented in the table 2. The figure 5 compares for each species the mass loss obtained experimentally and the data modelled according to the Eq. 2 and Eq. 3.

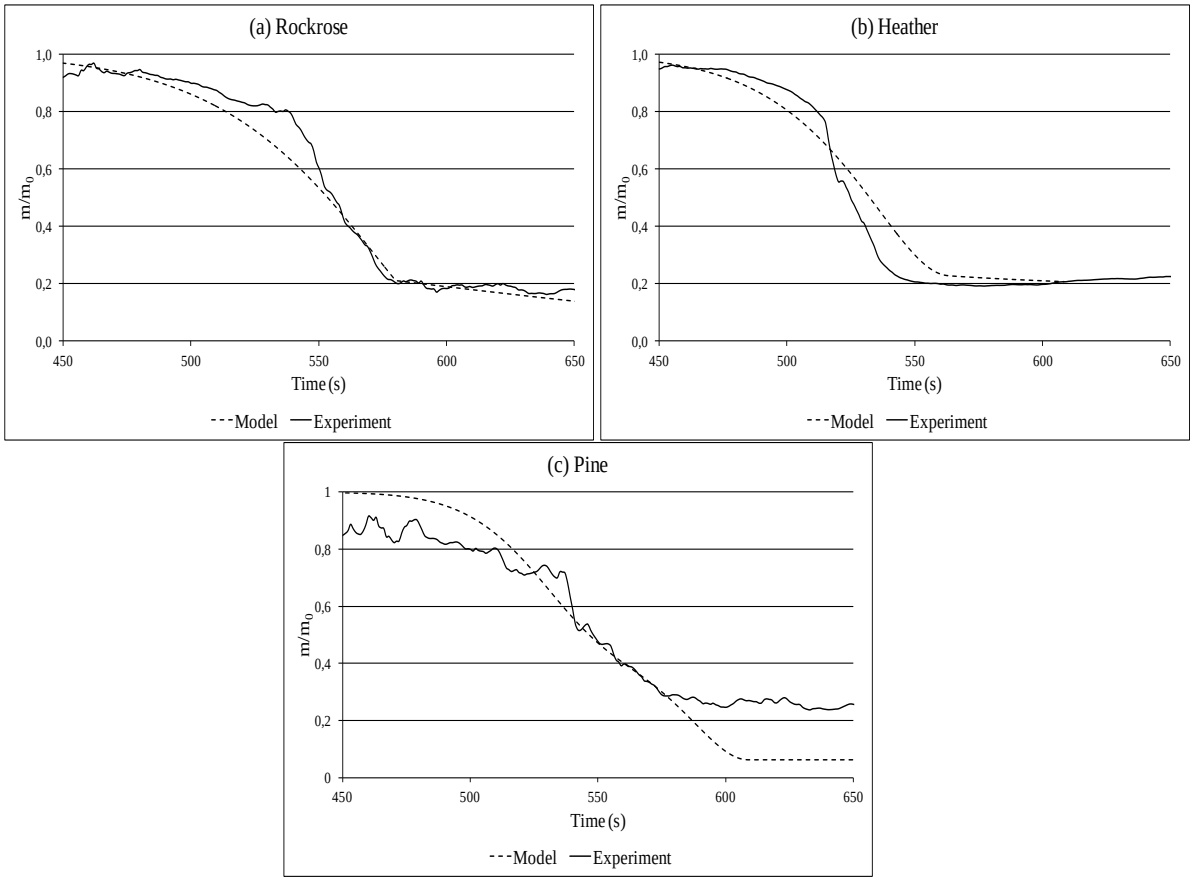


Figure 7. Experimental (solid line) and modeled (dashed line) mass loss for (a) Rockrose, (b) Heather and (c) Pine.

In a general point of view, the simulations have a good agreement with the experimental mass loss rate even if some differences appear (as attempt). For the Rockrose, the model do not match accurately in the range of $0.85 > m/m_0 > 0.60$ probably because the mechanisms of initiation and preheating are more complex than a simple Arrhenius equation of order n. Concerning the Heather, experiments exhibit an accelerate degradation process which can be explain by the very fine structure of this specie with branches of 2 mm. Conversely, Pine has a structure which is constituted by a single branch with a diameter of 6 mm. This thickness of sample involves an incomplete degradation.

4. Conclusion

A differential mass loss prototype has been designed with the aim to validate kinetic models adapted to field scale. This is the first time that the kinetics of decomposition of solid fuels is validated in real wildland fire condition, thus helping to a reliable characterization of a source term.
The prototype has been tested with 3 species in different conditions of fuel bed loads. Kinetic model previously tested on TGA data seems to well fit the experimental results obtained at field-scale.
The kinetic validity of the schemes is then exported outside the TGA. It is also found that the kinetic scheme with 2-steps gives a good agreement but flawed predictions are occasioned by the natural physiology of the samples (thickness, size of leaves and branches). In fact the initiation step of preheating is strongly related to the physiology. Future works will focus on the integration of the thickness in the model as an inhibitor parameter.

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