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DOMINGOS XAVIER VIEGAS

ADAI/CEIF, UNIVERSITY OF COIMBRA, PORTUGAL

Multi-scale modeling of the thermal degradation of woods

Guillaume Gerandi*, Virginie Tihay-Felicelli, Paul-Antoine Santoni, Valérie Leroy-Cancellieri, Dominique Cancellieri

Université de Corse, CNRS UMR 6134 SPE, Campus Grimaldi,BP 52, 20250 Corte, France, {gerandi_g@univ-corse.fr}*

Abstract

The modeling of the mass loss rate of vegetation is a key feature in models of forest fire as it allows quantifying the source term of combustible gases that supply the flames. In this work, we investigated the thermal degradation of two woods (oak and eucalyptus) using a multi-scale approach. At matter scale, experiments were carried out with a thermogravimetric analyser (TGA) under oxidizing atmosphere at several heating rates. We focussed on temperatures ranging from 150°C to 650°C in order to avoid the effect of the desication of free water and to consider only the thermal degradation of dry wood. Three kinetic mechanisms of degradation, each one consisting of four steps were developed by using the thermogravimetric results. The first one is based on an approach by constituents, the second one follows a lumped approach and the third one takes into account the formation of "active wood" which corresponds to a reduction in degree of polymerization. The kinetic parameters were calculated for each mechanism by using a genetic algorithms method. The lumped approach proved to be the mechanism that best represents the thermal decomposition of both woods. It was then tested at the material scale in the case of thermally thin wood plates heated with two radiant heat fluxes of 20 and 25 kW/m². These experiments were carried out with a cone calorimeter. The radiant heat flux was imposed at the top of the fuel sample. The mass loss rate was recorded as well as the temperature at the back surface of the wood, which was assumed equal to the temperature of the whole plate. For a radiant heat flux of 20 kW/m², the lumped approach predicted a mass loss close to the experimental results for temperatures lower than 400°C. Above this threshold, the prediction underestimated the mass loss. Then, for a radiant heat flux of 25 kW/m², the lumped approach did not allow predicting correctly the thermal degradation of the plate. For such radiant heat fluxes, the temperature gradient within the plate has to be taken into account to test the kinetic mechanisms of degradation at material scale.

Keywords: Fuel degradation, multi-scale, fire model input

1. Introduction

A reliable modeling of the mass loss rate of vegetation is a key feature in detailed models of forest fires (Mell *et al*. 2009). The gas quantity released by the vegetal fuel corresponds to this mass loss and it supplies the flame spread during the fire. An accurate modeling of the mass loss is thus a crucial point to obtain accurate propagation models of forest fires. In detailed models of forest fire, more or less complex kinetic mechanisms are implemented to describe the thermal degradation of plant fuels. The kinetic parameters associated with these mechanisms are generally calculated from thermogravimetric experiments at different heating rates (Leroy *et al*. 2006, Di Blasi 2008, Poletto *et al*. 2012), which are much lower than those encountered in actual fires. At this scale, the experimental conditions are well-controlled but they are not representative of those encountered in actual fires. The test of these mechanisms at a larger scale with higher heating rates and where heat and mass transfers occur is essential before using them in physics-based codes of forest fires. Cone calorimeter experiments are interesting tests to assess the ability of these thermal mechanisms to model the mass loss of materials. The cone calorimeter allows reaching realistic heating rates thanks to important radiant heat fluxes and tests are performed at material scale. With this device, the thermal transfers within the material influence the degradation for thermally thick samples. For such case, the problem

is complex since the degree of conversion varies within the material and its thermal parameters must be known or estimated.

There are many different approaches to modeling the thermal degradation of wood. The first approach considers that the wood decomposes in tars, chars and gases. The tars decompose then into gas and char according to two parallel reactions (referred to as secondary reactions) (Thurner and Mann 1981, Di Blasi 1993, Shafizadeh and Chin 1977). Another type of kinetic approach considers that wood consists of three biopolymers, which are hemicellulose, cellulose and lignin. Each of these polymers then decompose independently (Di Blasi 2008, Di Blasi 1993) and can be studied separately. Other approaches for the thermal degradation of wood have considered successive stages of degradation of virtual compounds. For example, Fateh et al. (Fateh *et al*. 2013) used a six steps successive kinetic mechanism to describe the thermal degradation of plywood whereas Benkorichi et al. (Benkorichi *et al*. 2017) tested a model with seven steps to represent the thermal degradation of pine needles. Finally, the last approach considers the reduction of the degree of polymerization during the degradation by introducing an "active" material. This approach was used by Shafizadeh and Bradbury (Shafizadeh and Bradbury 1979) to represent the cellulose decomposition.

In this context, we proposed to evaluate three kinetic mechanisms describing the thermal decomposition of two woods: oak and eucalyptus under oxidizing atmosphere. For this, the study was conducted at matter and material scales by using thermally thin wood plates. This kind of plates has two advantages. First of all, small pieces of this plate can be used in TGA experiments. Unlike the use of powder, the structure of the sample is not altered while avoiding temperature gradients in the material. For experiments at the material scale, using thermally thin plate avoids the temperature gradients inside the plate and the necessity of determining the thermal parameters of the material. Therefore, these experimental conditions allow to focus only on the kinetics of wood decomposition. The work presented hereafter is divided into three parts. The first section describes the experimental devices used for the experiments at both scales and the tested kinetic mechanisms. The second section presents the evaluation of the kinetic mechanisms on TGA experiments. In the last section, we present the results of the tests at material scale with regards to the kinetic mechanism, that showed the performance at matter scale.

2. Materials and Methods

2.1. Experimental devices

The multi-scale experiments were performed with two species of woods: oak (*Quercus alba*) and eucalyptus (*Eucalyptus globulus*) by using wooden sheets of 0.6 mm depth thick. For all experiments, the wood plates were oven-dried at 60°C during 24 hours to remove the moisture.

Experiments at matter scale were conducted with a PerkinElmer Pyris 1 thermogravimetric analyzer under oxidizing atmosphere. The samples were cut from the thermal thin plate in discs of 5 mm diameter corresponding to an initial dry mass of 4.4 mg ($\pm$ 0.6 mg) and 6.2 mg ($\pm$ 0.5 mg) for oak and eucalyptus, respectively. The discs were placed in a 33 µl open platinum crucible. The samples were heated up to 650°C with five heating rates varying between 2 and 30 °C/min. To focus on the thermal degradation, we only considered the mass loss recorded between 150 and 650°C in order to avoid the effects of the dehydration of free water. The sample temperature was controlled by a thermocouple and did not exhibit any systematic deviation from preset linear temperature programs. Three repetitions were done for each kind of wood and each heating rate.

The experiments at material scale were carried out with a cone calorimeter (Babrauskas *et al*. 1992). Pieces of $100 \times 100 \times 0.6$ mm^3 were cut in the wooden sheets for samples. Then, they were placed on ceramic wool in a sample holder mesh basket of 10×10 cm^2 made of stainless steel (Tihay-Felicelli *et al*. 2016). They were oven dried at 60°C during 24 hours before each experiment. The sample holder

was then positioned on a load cell over an insulating ceramic. Before each set of experiments, the load cell was calibrated using standard weighs. Its precision was 0.1 g and the sampling frequency was equal to 1 Hz. Two radiant heat fluxes (20 and 25 kW/m²) were imposed at the top of the plates. They were chosen in order to obtain fast heating rates while avoiding the flaming. The level of radiant heat flux was checked by using a flux meter before each experiment. The smoke extraction was set up with an exhaust fan at a flow rate of 24 l/s. The plate temperature was recorded by two K-type thermocouples with a sampling frequency of 25 Hz. They were placed on the back surface of the plate in order to avoid the radiation sent by the cone calorimeter. The first thermocouple was located at the center of the plate. The other one was placed at 1 cm from the edge of the plate. As the plates were assumed thermally thin, we considered that the temperature of the plate could be represented by the average of the values recorded with both thermocouples. The mass loss and temperature measurements were performed separately because thermocouples induce pressure on the load cell, which alter the initial mass and the mass loss recorded. At least three replicates were done for each experimental setup.

2.2. Kinetic mechanisms

Based on the literature (Di Blasi 1993, Shafizadeh and Chin 1977, Shafizadeh and Bradbury 1979), three kinetic mechanisms with four stages were developed for the thermal decomposition of dry wood. For all kinetic mechanisms, the degree of conversion α is defined as follows:

$$\alpha = \frac{m-m_0}{m_f-m_0} \tag{1}$$

Where m is the mass. The subscripts 0 and f correspond to the initial time and the final time respectively.

The first mechanism is based on an approach by constituents (Di Blasi 2008, Di Blasi 1993, Grønli et al. 2002) (called constituent approach). The dry wood (DW) is assumed to consist of hemicellulose, cellulose and lignin:

$$DW = p_1 \text{ Hemicellulose} + p_2 \text{ Cellulose} + p_3 \text{ Lignin} \tag{2a}$$

$$\text{Hemicellulose} \rightarrow v_1 Char + (1-v_1)Gas \tag{2b}$$

$$\text{Cellulose} \rightarrow v_2 Char + (1-v_2)Gas \tag{2c}$$

$$\text{Lignin} \rightarrow v_3 Char + (1-v_3)Gas \tag{2d}$$

$$\text{Char} \rightarrow v_4 Ash + (1-v_4)Gas \tag{2e}$$

Where p_1, p_2 and p_3 represent the mass proportion of each component in the wood composition.

The reaction rates of these steps are defined as follows:

$$\dot{\omega}_i = (1-\alpha_i)^{n_i}.A_i.exp\left(-\frac{E_{a_i}}{R.T}\right) \qquad \text{for } 1 \leq i \leq 3 \tag{3a}$$

$$\dot{\omega}_4 = (p_1\alpha_1 + p_2\alpha_2 + p_3\alpha_3 - \alpha_4)^{n_4}.A_4.exp\left(-\frac{Ea_4}{R.T}\right) \tag{3b}$$

The total conversion rate was then obtained with the following equation:

$$\frac{d\alpha}{dt} = (1-v_1)\dot{\omega}_1 + (1-v_2)\dot{\omega}_2 + (1-v_3)\dot{\omega}_3 + (1-v_4)(p_1v_1 + p_2v_2 + p_3v_3)\dot{\omega}_4 \tag{4}$$

The second mechanism (called lumped approach) (Shafizadeh and Chin 1977, Fateh *et al.* 2013, Benkorichi *et al.* 2017) considers the following steps where the dry wood is degrading in other forms of wood before leading to char and ashes:

$$DW \rightarrow v_1 DW_1 + (1 - v_1)Gas \tag{5a}$$

$$DW_1 \rightarrow v_2 DW_2 + (1 - v_2)Gas \tag{5b}$$

$$DW_2 \rightarrow v_3 Char + (1 - v_3)Gas \tag{5c}$$

$$Char \rightarrow v_4 Ash + (1 - v_4)Gas \tag{5d}$$
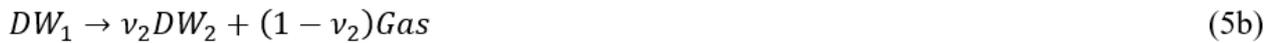
For this mechanism, the reaction rates of these steps are defined as follows:

$$\dot{\omega}_1 = \frac{d\alpha_1}{dt} = (1 - \alpha_1)^{n_1} A_1 \exp\left(-\frac{E_{a_1}}{RT}\right) \tag{6a}$$

$$\dot{\omega}_i = \frac{d\alpha_i}{dt} = (\alpha_{i-1} - \alpha_i)^{n_i} A_i \exp\left(-\frac{E_{a_i}}{RT}\right) \qquad \text{for } 2 \leq i \leq 4 \tag{6b}$$

The total conversion rate was then obtained as follows:

$$\frac{d\alpha}{dt} = (1 - v_1)\dot{\omega}_1 + (1 - v_2)v_1\dot{\omega}_2 + (1 - v_3)v_1 v_2\dot{\omega}_3 + (1 - v_4)v_1 v_2 v_3\dot{\omega}_4 \tag{7}$$

In the third mechanism (called active mechanism) (Shafizadeh and Bradbury 1979, Bradbury *et al.* 2003), the degradation of dry wood includes a first step that accounts for the formation of "active wood", which corresponds to a reduction in degree of polymerization. Then the degradation of active wood leads to gas, tar and char. Then tars and chars undergo respectively devolatilization and oxidation:

$$DW \rightarrow v_1 Active\ wood + (1 - v_1)Gas \tag{8a}$$

$$Active\ wood \rightarrow v_2 Char + v_3 Tar + (1 - v_2)Gas \tag{8b}$$

$$Tar \rightarrow Gas \tag{8c}$$

$$Char \rightarrow v_4 Ash + (1 - v_4)Gas \tag{8d}$$

The reaction rates of this mechanism are calculated with the following relationships:

$$\dot{\omega}_1 = \frac{d\alpha_1}{dt} = (1 - \alpha_1)^{n_1} A_1 \exp\left(-\frac{E_{a_1}}{RT}\right) \tag{9a}$$

$$\dot{\omega}_2 = \frac{d\alpha_2}{dt} = (\alpha_1 - \alpha_2)^{n_2} A_2 \exp\left(-\frac{E_{a_2}}{RT}\right) \tag{9b}$$

$$\dot{\omega}_3 = \frac{d\alpha_3}{dt} = (\alpha_2 - \alpha_3)^{n_3} A_3 \exp\left(-\frac{E_{a_3}}{RT}\right) \tag{9c}$$

$$\dot{\omega}_4 = \frac{d\alpha_4}{dt} = (\alpha_2 - \alpha_4)^{n_4} A_4 \exp\left(-\frac{E_{a_4}}{RT}\right) \tag{9d}$$

The total conversion rate was then obtained thanks to the following equation:

$$\frac{d\alpha}{dt} = (1 - v_1)\dot{\omega}_1 + (1 - v_2 - v_3)v_1\dot{\omega}_2 + v_1 v_3\dot{\omega}_3 + (1 - v_4)v_1 v_2\dot{\omega}_4 \tag{10}$$

The kinetic parameters (E_a, A, n and v) of each reaction as well as the constituent proportions were determined by using the genetic algorithms method. To determine the best set of kinetic parameter, the following objective function was minimized:

$$\mathcal{F} = \sum_{i=1}^{N}\left(\alpha_i^{exp} - \alpha_i^{cal}\right)^2 + \left(\left[\frac{d\alpha}{dt}\right]_i^{exp} - \left[\frac{d\alpha}{dt}\right]_i^{cal}\right)^2 \tag{11}$$

Where the exponents *exp* and *cal* represent the experimental and calculated values and N the number of points of the experiments.

The performance of each set of parameters was calculated for each evaluated curve as:

$$Fit = \sqrt{\frac{\mathcal{F}}{N}} \tag{12}$$

3. Thermal degradation at matter scale

3.1. Experimental results

Figure 1 presents the evolution of the non-dimensional mass loss and the rate of change of mass (which corresponds to the mass loss rate divided by the initial mass) obtained by TGA for oak and eucalyptus with a heating rate of 10 °C/min representative of the other conditions. For both woods, the thermal degradation takes place in four steps, which is consistent with the kinetic mechanisms tested. The mass loss rate exhibits a first peak around 300°C followed by the most significant mass loss rate peak at about 350°C. A shoulder is then visible around 400°C. Finally, the last peak takes place after 500°C that corresponds to the char oxidation. For both woods, the non-dimensional mass loss and the rate of change of mass follow the same trends even if some differences can be observed. The different steps appear at the same temperature for both woods excepted for the char oxidation, which appears between 450°C and 500°C for oak and beyond 550°C for eucalyptus. This phenomenon comes from a longer duration of the shoulder observed for eucalyptus. By comparing the intensity of the rates of change of mass, we observe that the main difference occurs for the first step. The peak is nearly two times higher for oak than eucalyptus. According to literature (Grønli *et al*. 2002), this first reaction corresponds mainly to hemicellulose degradation, the second one to cellulose degradation whereas the shoulder is characteristic of lignin degradation. According to literature (da Silva *et al*. 2010, Pettersen 1984), the percentages of hemicellulose, cellulose and lignin correspond to 28%, 40% and 25% respectively for oak and to 17%, 46% and 33% for eucalyptus. Therefore, oak has more hemicellulose and less lignin than eucalyptus. This is in agreement with a higher rate of change of the first reaction for oak and with a longer duration of the shoulder for eucalyptus.
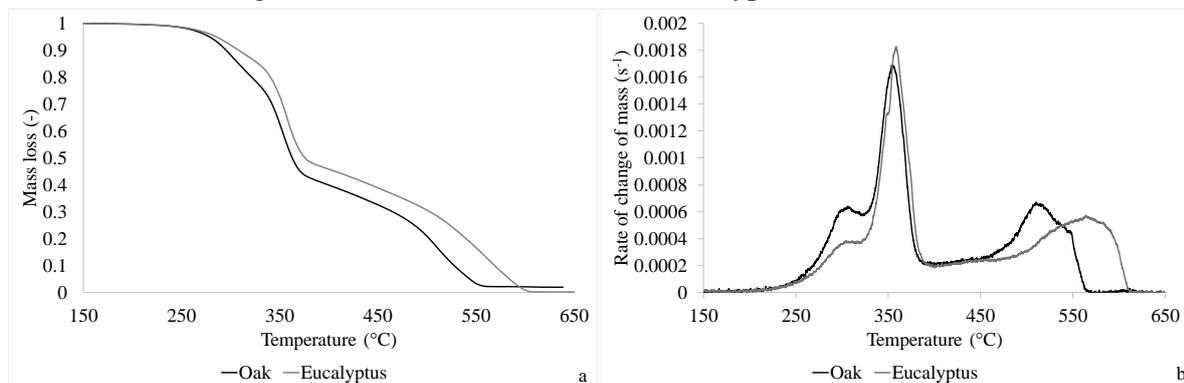
Figure 1- Evolution of a) the mass loss and b) the rate of change of mass at a heating rate of 10 °C/min for oak and eucalyptus.

3.2. Mass loss simulation

The experimental curves obtained by TGA with the five heating rates were used to calculate the set of parameters used in the three kinetic mechanisms. Table 1, 2 and 3 present the values obtained for both woods. Considering the constituent approach, the activation energies for the degradation of hemicellulose, cellulose and lignin are around 160 kJ/mol, 190 kJ/mol and 169 kJ/mol for both woods. These values are in agreement with literature (Chen *et al*. 2015, Arseneau 1971). Regarding the lumped approach, the activation energies of the three first reactions are between 161.1 and 188.9 kJ/mol for

oak and between 143.4 and 300.0 kJ/mol for eucalyptus. These values are higher than those obtained for pine needles in the literature (Benkorichi *et al*. 2017, Fateh *et al*. 2017). For the active approach, the activation energies of the three first reactions are between 109 and 197 kJ/mol and vary little for both woods. These values are higher than those found in the literature for cellulose (around 58 kJ/mol) (Bradbury *et al*. 2003). Concerning the char oxidation, there is little difference between the mechanisms. For the constituent and the lumped approaches, the activation energies are around 120 kJ/mol whereas for the active mechanism the value is around 130 kJ/mol for both woods. These values are close of the results of Cancellieri et al. (Cancellieri *et al*. 2013) but are much lower than those found by Conesa et al. (Conesa *et al*. 1995), for which the activation energies for char oxidation are between 179 and 219 kJ/mol. To compare the accuracy of the three mechanisms on the prediction of TGA curves, the mean value of the performance parameter calculated for the five heating rates (equation 12) was indicated in tables 1 to 3. In addition, figure 2 shows the experimental and predicted mass losses for a heating rate of 10 °C/min for both woods. All kinetic mechanisms provide good predictions of the mass loss. The mass evolutions calculated with the three mechanisms by using the optimized model parameters are indeed very close to the experiments. The performance factor varies indeed between 0.96×10^{-2} and 1.84×10^{-2}. The best agreement was obtained with the lumped approach for both woods.

Table 1 - Kinetic parameters for oak and eucalyptus with constituent approach.

Species	Reactions	n_i	$\ln(A_i)$ (s^{-1})	E_{ai} (kJ/mol)	v_i	p_i	Mean Fit (-)
Oak	1	1.43	29.87	160.99	0.41	0.26	1.37×10^{-2}
	2	1.44	31.91	189.83	0.14	0.55	
	3	1.46	21.82	168.39	0.16	0.19	
	4	0.52	12.06	117.24	0.00	-	
Eucalyptus	1	1.59	29.76	159.34	0.56	0.22	1.84×10^{-2}
	2	1.47	31.93	191.06	0.18	0.55	
	3	1.74	22.13	169.32	0.35	0.23	
	4	0.50	11.63	121.45	0.00	-	

Table 2 - Kinetic parameters for oak and eucalyptus with the lumped approach.

Species	Reactions	n_i	$\ln(A_i)$ (s^{-1})	E_{ai} (kJ/mol)	v_i	Mean Fit (-)
Oak	1	1.17	29.72	161.06	0.84	1.27×10^{-2}
	2	1.32	31.67	188.92	0.45	
	3	1.89	22.29	164.89	0.66	
	4	0.59	12.41	118.05	0.00	
Eucalyptus	1	1.40	25.97	143.42	0.88	0.96×10^{-2}
	2	1.64	39.22	227.15	0.52	
	3	3.00	46.22	300.00	0.72	
	4	0.71	11.57	119.12	0.00	

Table 4 - Kinetic parameters for oak and eucalyptus with the active approach.

Species	Reactions	n_i	$\ln(A_i)$ (s^{-1})	E_{ai} (kJ/mol)	v_i	Mean Fit (-)
Oak	1	0.63	18.19	109.14	0.86	1.78×10^{-2}
	2	0.82	24.73	188.81	0.31	
	3	2.62	33.41	195.54	0.64	
	4	0.50	14.58	128.63	0.04	
Eucalyptus	1	0.65	19.06	111.51	0.92	1.20×10^{-2}
	2	1.02	25.66	187.64	0.37	
	3	1.82	33.48	197.68	0.52	
	4	0.85	13.95	134.45	0.00	
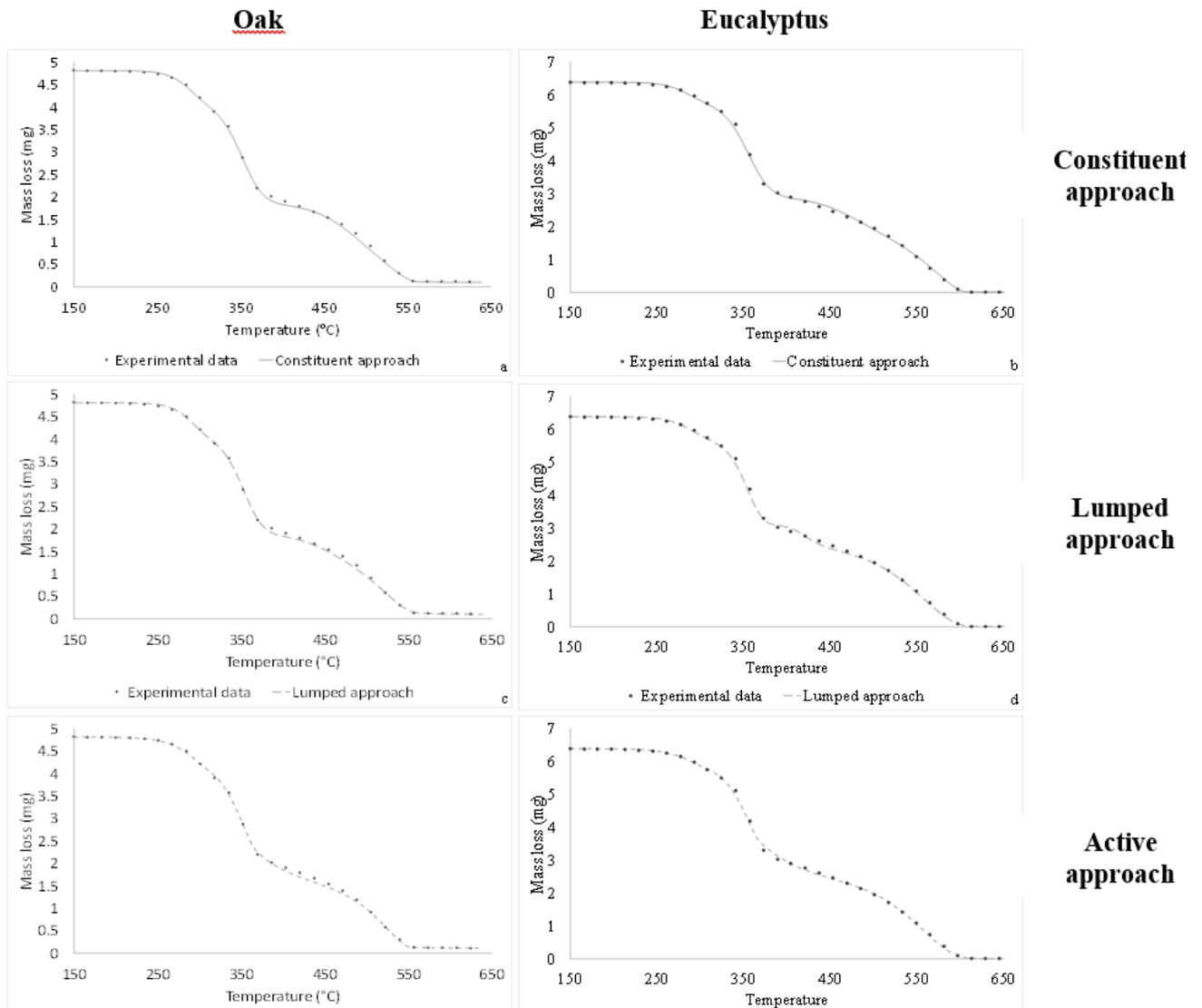
Figure 2 - Comparison of the experimental and predicted mass losses for a heating rate of 10 °C/min for oak and eucalyptus: a and b) with constituent approach c and d) with lumped approach e and f) with active approach.

4. Thermal degradation at material scale

4.1. Experimental results

Figure 3 presents the time evolution of the temperature and the mass loss for the plates of oak and eucalyptus exposed to a radiant heat flux of 25 kW/m². For both woods, the mean temperature recorded at the back surface of the plate follows the same trend. After the shutter opening, the plate temperature increases quasi-linearly until reaching a temperature of 615°C. For oak, the temperature increases slightly faster than that for eucalyptus. The plates begin to degrade around 20 s (Fig. 3.b) which corresponds to a temperature of 230°C for oak and 180°C for eucalyptus. The mass loss is maximal near 60 s corresponding to a temperature around 400°C. These results are consistent with the TGA experiments where the maximum mass loss rate occurs around 350°C (Fig. 1). Although no flaming occurred during the experiments, both plates lost their entire initial mass at the end of the tests. These observations are consistent with TGA experiments (Fig. 1.a).
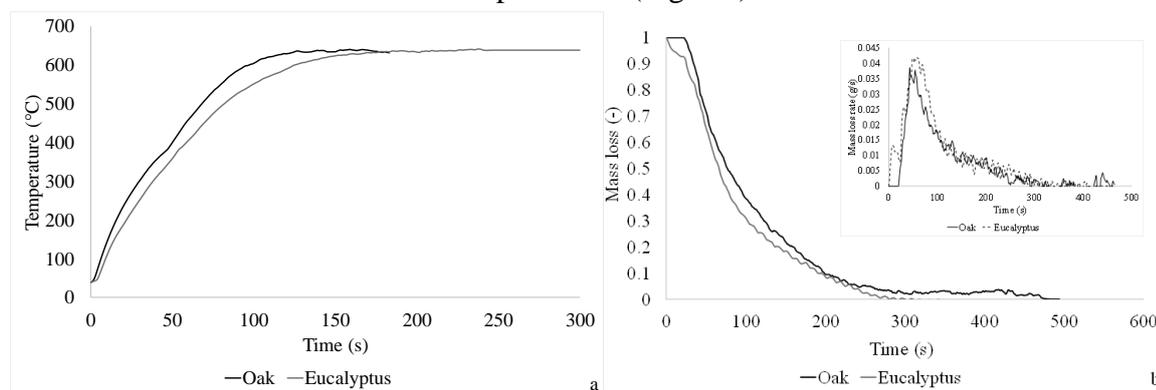
Figure 3 - Time evolution of a) the mean temperature at the back surface and b) the mass loss and mass loss rate – for a radiant heat flux of 25 kW/m².

4.2. Test of the lumped approach

The experiments performed with the cone calorimeter were used to test the lumped approach, corresponding to the kinetic mechanism with the best performance at matter scale. Figure 4 shows the experimental and predicted mass loss obtained with the lumped approach for oak and eucalyptus for two levels of radiant heat flux (20 and 25 kW/m²). Two behaviors can be observed. For oak and eucalyptus with a radiant heat flux of 20 kW/m², until 180 s (400°C), the mass loss calculated with the lumped approach shows a good agreement with the experimental data. Above this threshold the model prediction overestimates the mass loss. It suggests that the model for char oxidation needs to be modified at this scale. For a radiant heat flux of 25 kW/m², a delay occurs for both woods between the simulated and experimental mass after 30 s (corresponding to a temperature of 200°C) leading to a bad mass loss prediction. To understand why the kinetic mechanism provides a good prediction at 20 kW/m² but a bad one at 25 kW/m², the temperatures of the lower and upper faces were measured (Fig. 5). Although the wood plates are very thin (0.6 mm), at 25 kW/m², there is a temperature gradient inside the plate. The upper surface of the wood has indeed a higher temperature. The assumption of a thermally thin material is no more valid for this radiant heat flux. This temperature difference has strong consequences. The upper surface will indeed begin to degrade before the lower face. Taking the back face temperature to perform the mass loss prediction introduces therefore a delay. Consequently, the temperature gradient within the plate has to be taken into account to model the degradation at material scale for such radiant heat fluxes.
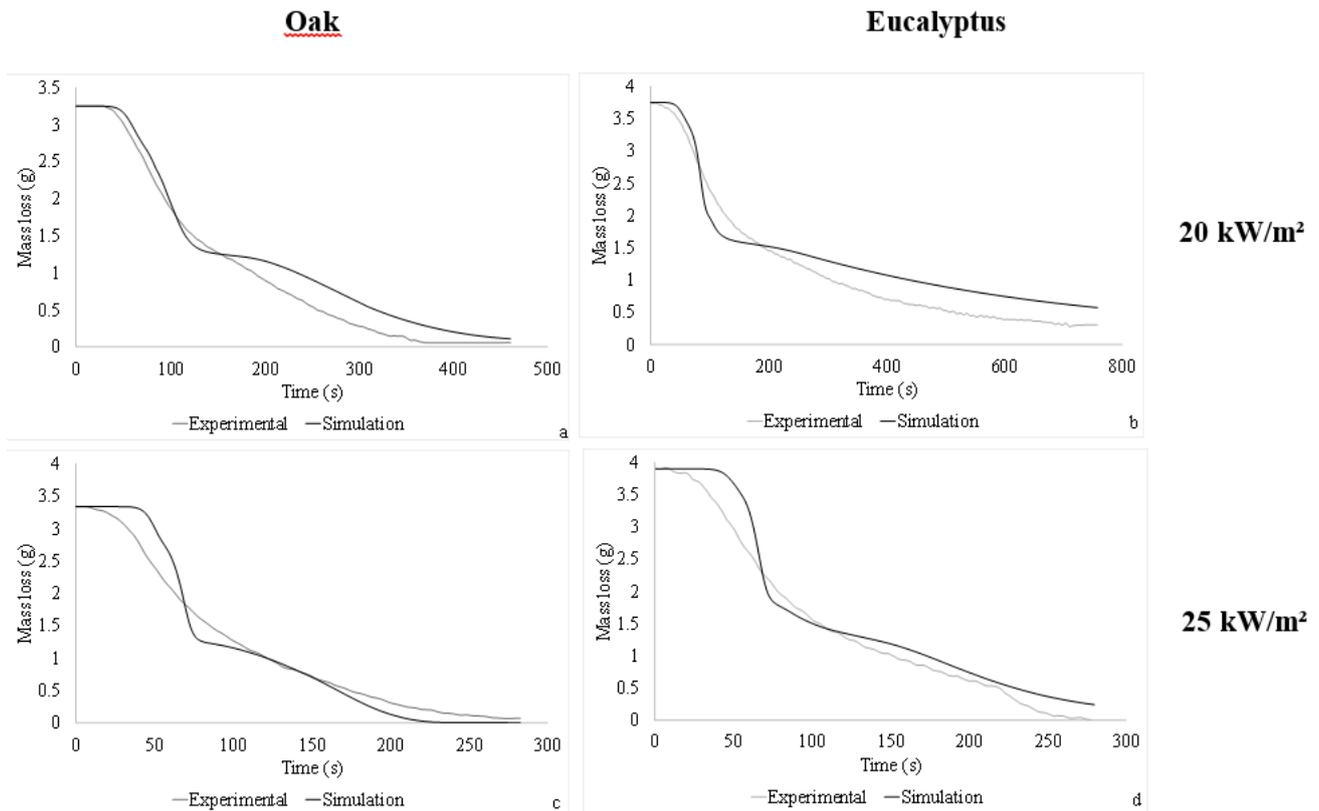
Figure 4 - Comparison between experimental and predicted mass loss for: a) oak at 20 kW/m² b) eucalyptus at 20 kW/m² c) oak at 25 kW/m² and d) eucalyptus at 25 kW/m²
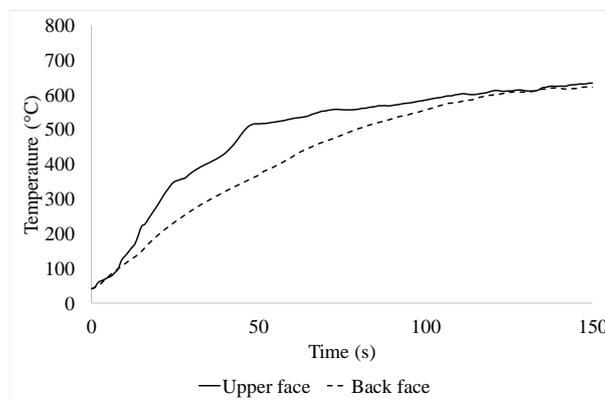
Figure 5 - Temperature recorded on the back and upper faces of the oak plate exposed to a radiant heat flux of 25 kW/m²

5. Conclusion

In this article, three kinetic mechanisms were tested in order to model the thermal degradation of wood plates at matter and material scales. To focus only{Bibliography} on kinetics, thermally thin wood plates were used for the experiments at the different scales. The main results can be summarized as follows:

- The three models predict efficiently the thermal decomposition at matter scale for the different heating rates investigated.

- The use of thermally thin wood plates allows testing kinetic mechanisms at 20 kW/m² without the knowledge of the thermal properties of the wood. A good concordance was observed between the experimental and predicted results except for char oxidation. For a radiant heat flux of 25 kW/m², the use of plates with 0.6 mm depth did not allow a thermal equilibrium within the depth of the sample. For such radiant heat flux, the temperature gradient within the plate has to be taken into account to test the kinetic mechanisms of degradation at material scale.

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