Multi-scale modelling of wood degradation using thermally thin wood plates

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ABSTRACT

The mass loss rate is an indicator which defines the mass source term of combustible gases that supply the flames and influences the propagation of wildland fires. In this work, we investigated the thermal degradation of two woods (oak and eucalyptus) using a multi-scale approach. The originality of this work lies in the fact that we used thermally thin plates to carry out the experiments at different scales. At matter scale, experiments were conducted using a thermogravimetric analyser (TGA) under oxidizing atmosphere at several heating rates. We focused on temperatures ranging from 150°C to 650°C in order to study the thermal degradation of dry wood and thus, avoid the dehydration of free water. A kinetic mechanism was determined by using the thermogravimetric results. It consists of four steps, each one based on an Arrhenius law. This mechanism assumes that dry wood is composed of hemicellulose, cellulose and lignin. Each of these components degrades into char, which is then oxidized and releases ashes. The kinetic parameters of the four reactions were calculated by using the gradient descent algorithm method. The kinetic mechanism gives an accurate representation of the mass loss of both woods obtained with TGA. The kinetic mechanism was then tested at material scale using thermally thin wood plates. The experiments were carried out with a cone calorimeter at higher heating rates than used in TGA. Radiant heat fluxes ranging from 20 to 28 kW/m² were imposed at the top of the fuel sample in order to avoid ignition. The mass loss was recorded as well as the temperature at the back surface of the wood, which was supposed to be equal to the temperature of the whole plate. For a radiant heat flux of 20 kW/m², the predicted mass loss and mass loss rate are close to the experimental results for temperatures lower than 400°C. Beyond this value, the prediction underestimated the mass loss. For a radiant heat flux higher than 22 kW/m², the model did not correctly predict the thermal degradation of the plate. This difference is probably due to the assumption of an equilibrium temperature within the plate. Above this level of heat flux, the assumption of a thermally fine plate is no longer valid an it is necessary to take into account the temperature gradient within the plate.

KEYWORDS: kinetic model, multi-scale, thermally thin plate, thermal degradation

NOMENCLATURE LISTING

| Symbol | Description | Greek |
|--------|-------------|-------|
| A | pre-exponential factor (s⁻¹) | | |
| E_a | activation energy (kJ.mol⁻¹) | α | Degree of conversion |
| MLR | mass loss rate (g.s⁻¹) | ω̇ | reaction rate (s⁻¹) |
| m | mass (g) | v | stoichiometric factor |
| m₀ | initial mass (g) | | |
| m_f | final mass (g) | | |
| n | reaction order | 0 | initial |
| p | proportion of constituent | f | final |
| R | gas constant (J.K⁻¹.mol⁻¹) | rad | radiative |
| T | temperature (K) | c | convective |
INTRODUCTION

The mass loss rate of materials is an important indicator that defines the mass source term of combustibles gases that supply the flames and leads the propagation of wildland fires. In detailed models of forest fires, more or less complex kinetic mechanisms are implemented to describe the thermal degradation of vegetative fuels. The kinetic parameters of these mechanisms are often calculated from thermogravimetric experiments at different heating rates [1,2]. During thermogravimetric analysis (TGA), the conditions of degradation are indeed well known and controlled. Unfortunately, the conditions of decomposition in the TGA apparatus are not representative of those encountered in actual fires. The materials are indeed generally in powder form and the heating rates are much lower than those of actual fires. Therefore, before using them in physics-based codes of forest fires, it is necessary to test them at a scale, for which the heating rates are closer to those encountered in fires and for which heat and mass transfers occur. The cone calorimeter is a good way to carry out experiments at the material scale [3–5]. It allows measuring the evolution of mass loss as well as the mass loss rate as a function of time by reaching realistic heating rates because of significant heat fluxes. At this scale, heat and mass transfer phenomena occur in studied sample, especially for thermally thick solid. The knowledge of the thermal properties of the sample is therefore necessary to model correctly the temperature gradient into the sample. This raises a problem since it is difficult to know all these quantities when the material is degrading. Fateh and al. [5], circumvented this difficulty in their multi-scale study on plywood by estimating numerically the thermal properties (conductivity, emissivity, density and specific capacity) using the genetic algorithm of Gpyro. Our work deals with the development of a kinetic mechanism for modeling the thermal degradation of wood under oxidizing atmosphere at different scales, which can be used in physics-based codes of forest fires. Therefore, this kinetic mechanism must be representative of the degradation at all scales but it must remain as simple as possible to avoid a significant increase of the computational time. The originality of our approach consists of using thermally thin wood plates to perform the experiments at matter and material scales. First of all, the kinetic mechanism was determined from TGA experiments done with small samples cut from thermally thin plates. Then, the kinetic parameters were tested at material scale. To focus on the kinetic aspects, instead of using thermally thick material as usually [3–5], we decided to limit as much as possible the temperature gradients in the studied material by using thermally thin wood plates for the experiments with the cone calorimeter. The temperature of the back surface of the plate was recorded and it was considered equal to the temperature of the entire plate. This original approach has two benefits at material scale. First, the use of thermally thin plates reduces the superposition in time of the thermal reactions of degradation within the sample. Secondly, the problem complexity is reduced since it is not necessary to calculate the temperature inside the plate. The temperature being measured experimentally, there is no bias introduced by its calculation and the estimation of the thermal parameters. These experimental conditions, although not representative of actual fire conditions, allow us to focus on the study of the kinetics of wood degradation and to use heating rates that are much higher than those used with thermogravimetric analyzers.

1. MATERIAL AND METHOD

For the experiments, untreated wooden sheets of 0.6 mm thick employed for wood veneer were used as samples. Two kinds of wood were studied: oak (Quercus alba) and eucalyptus (Eucalyptus globulus). TGA experiments were performed using a PerkinElmer TGA Pyris 1. The samples were cut with a hollow punch in the thermal thin plate to obtain samples of \( m_p = 5 \) mg and were placed in a 33 \( \mu l \) open platinum crucible. The furnace was continuously purged with a flowing atmosphere of air at 30 ml/min. The samples were first dried and then heated from 150 to 650°C in order to avoid the devolatilization of free water and to focus on the degradation of dry wood. Experiments were performed with the following heating rates: 2°C/min, 5°C/min, 10°C/min, 20°C/min and 30°C/min. The sample temperature, which is controlled by a thermocouple, did not exhibit any systematic deviation from preset linear temperature programs. All experiments were repeated three times.

The experiments at material scale were carried out with a cone calorimeter apparatus. The sample holder placed horizontally was an open square 10 cm \( \times \) 10 cm basket made of stainless steel. Thermally thin plates of wood 100 \( \times \) 100 \( \times \) 0.6 mm\(^3\) were used as studied material and were placed upon a ceramic wool in the sample holder. Radiant heat fluxes ranging between 20 and 28 kW/m\(^2\) were imposed at the top of the fuel sample. These fluxes were chosen in order to obtain fast heating rates and to avoid flaming combustion. The level of radiant heat flux was check with a heat flux meter prior to each experiment. Before each set of experiments, the load cell was also calibrated and checked using standard weights. Its accuracy was 0.1 g and the sampling frequency was equal to 1 Hz. The smoke extraction was performed with an exhaust fan at a flow rate of 24 l/s. Two K-type thermocouples (sampling frequency of 25 Hz) were placed on the back surface of the plate: one on the center and one in the middle at 1 cm from the edge. As the plates were thermally thin, we considered a unique value...
of the temperature corresponding to the average of the values recorded by both thermocouples. Since the thermocouples induce pressure on the load cell, the measurements of mass loss and temperature were performed separately. At least three repetitions were carried out for each kind of measurement.

2. THERMAL DEGRADATION AT MATTER SCALE

2.1. Description

Figure 1 presents the evolution as function of temperature of the non-dimensional mass loss and mass loss rate (MLR) obtained by TGA for the two woods for a heating rate of 5°C/min, representative of the other conditions. For both woods, the thermal decomposition takes place in four steps. Table 1 presents the rate of change of the non-dimensional mass loss and temperature for these steps at different heating rates. The first step appears between 200 and 300°C and corresponds to the degradation of hemicellulose [6]. The second step takes place between 320 and 400°C. It leads to the most significant peak of mass loss rate and corresponds to the degradation of cellulose [6]. In the third step a shoulder, which corresponds to the degradation of lignin [6] is visible around 350 and 450°C. The last step leads to a peak beyond 450°C and it corresponds to the char oxidation. For both woods, the thermal degradation follows the same trend. However, for oak the thermal degradation of each component appears at lower temperatures than that for eucalyptus, excepted for the first step. With regard to the intensity of the peaks, the main difference occurs for step 1 (hemicellulose). The peak of mass loss of step 1 is indeed 1.7 times higher for oak than eucalyptus. According to literature [7,8], oak contains more hemicellulose than eucalyptus and this can explain the variation observed between the curves.

![Fig.1. Evolution of non-dimensional mass loss and MLR with a heating rate of 5°C/min.](image)

Table 1. Temperatures, MLR/mₜ (in parentheses) and residue obtained with thermogravimetric analysis.

| Species   | Heating rates (°C/min) | Temperature (°C) and MLR/mₜ (ms⁻¹) | Residues (%) |
|-----------|------------------------|------------------------------------|--------------|
|           | Step 1                 | Step 2                             | Step 3       | Step 4       |                |
| Oak       | 2                      | 282 (0.12)                         | 321 (0.34)   | 367 (0.06)   | 465 (0.19)    | 0.62          |
|           | 5                      | 298 (0.32)                         | 339 (0.85)   | 400 (0.13)   | 483 (0.42)    | 0.66          |
|           | 10                     | 310 (0.60)                         | 358 (1.63)   | 406 (0.21)   | 518 (0.64)    | 0.80          |
|           | 20                     | 321 (1.27)                         | 376 (3.51)   | 430 (0.38)   | 549 (0.95)    | 0.57          |
|           | 30                     | 331 (1.97)                         | 383 (5.07)   | 450 (0.55)   | 551 (1.33)    | 0.72          |
| Eucalyptus| 2                      | 282 (0.07)                         | 335 (0.26)   | 386 (0.05)   | 515 (0.14)    | 1.65          |
|           | 5                      | 297 (0.18)                         | 346 (0.76)   | 405 (0.12)   | 547 (0.31)    | 1.60          |
|           | 10                     | 305 (0.37)                         | 360 (1.76)   | 431 (0.22)   | 573 (0.54)    | 1.95          |
|           | 20                     | 314 (0.76)                         | 376 (3.48)   | 438 (0.41)   | 602 (0.89)    | 1.71          |
|           | 30                     | 325 (1.13)                         | 385 (5.43)   | 450 (0.52)   | 660 (1.18)    | 1.72          |

2.2. Kinetic mechanism

Based on the previous results, a kinetic mechanism with four steps and based on an approach by constituents was chosen to model the thermal degradation of the woods. This approach has the advantage of being simple.
Moreover, the identification of the kinetic parameter on the mass loss curves of the wood allows considering the interactions between the constituents during the degradation. Therefore, the dry wood (DW) was assumed to consist of hemicellulose, cellulose and lignin:

\[ DW = p_1 \text{Hemicellulose} + p_2 \text{Cellulose} + p_3 \text{Lignin} \quad (1) \]

Where \( p_1, p_2 \) and \( p_3 \) are the contribution of each constituent of the wood. The degradation of each component was then represented as follows:

- \( \text{Hemicellulose} \rightarrow v_1 \text{Char} + (1 - v_1)\text{Gas} \quad (2a) \)
- \( \text{Cellulose} \rightarrow v_2 \text{Char} + (1 - v_2)\text{Gas} \quad (2b) \)
- \( \text{Lignin} \rightarrow v_3 \text{Char} + (1 - v_3)\text{Gas} \quad (2c) \)
- \( \text{Char} \rightarrow v_4 \text{Ash} + (1 - v_4)\text{Gas} \quad (2d) \)

The degree of conversion \( \alpha \) is defined as follows:

\[ \alpha = \frac{m - m_0}{m_f - m_0} \quad (3) \]

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

Each step of the mechanism corresponds to a global reaction described by the Arrhenius’ law:

\[ \omega_i = (1 - \alpha_i)^{n_i} A_i \exp \left( \frac{-E_a}{RT} \right) \quad \text{for } 1 \leq i \leq 3 \quad (4a) \]

\[ \omega_4 = (p_1 \alpha_1 + p_2 \alpha_2 + p_3 \alpha_3 - \alpha_4)^{n_4} A_4 \exp \left( \frac{-E_{a4}}{RT} \right) \quad (4b) \]

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

\[ \frac{\text{d} \alpha}{\text{d} t} = (1 - v_1) \dot{\omega}_1 + (1 - v_2) \dot{\omega}_2 + (1 - v_3) \dot{\omega}_3 + (p_1 v_1 + p_2 v_2 + p_3 v_3) \dot{\omega}_4 \quad (5) \]

The kinetic parameters \((E_a, A, n \text{ and } v)\) and the constituent proportions were determined by using the gradient descent algorithm method. Table 2 presents the values obtained for both woods. We can see that the kinetic parameters are in the same order of magnitude for these woods. The activation energies are around 160 kJ/mol, 190 kJ/mol and 169 kJ/mol for the degradation of hemicellulose, cellulose and lignin respectively. These values are in agreement with the literature [9, 10]. Regarding the char oxidation, the activation energies are around 120 kJ/mol for both woods. These values are close to the results of Cancellieri and al. [11] but are much lower than those found by Conesa and al. [12] and Agrawal and al. [13], for which the activation energies for char oxidation are between 179 and 219 kJ/mol. Figure 2 presents the comparison of the degree of conversion and the conversion rate for oak and eucalyptus obtained experimentally at 5°C/min and calculated with the kinetic mechanism. The experimental data and the simulations are very close for both woods and it is also the case for the higher heating rates investigated here. Only a few variations appear at the maximum conversion rate and for the char oxidation, for which the kinetic model tends to slightly underestimate the conversion rate. This discrepancy is likely due to the use of a very simple mechanism to model this step. To improve the results at this scale, a more complex mechanism for char oxidation considering the oxygen level will be tested in the future. Despite these slight differences, the degree of conversion is well represented for the different stages of the thermal degradation. The best agreement was obtained for eucalyptus.

| Table 2. Kinetic parameters for oak and eucalyptus using constituent approach. |
|---|---|---|---|---|---|
| Species | Reactions | \( n_i \) | \( \ln(A_i) \text{ (s}^{-1}\text{)} \) | \( E_{a}(\text{kJ/mol}) \) | \( v_i \) | \( p_i \) |
| Oak | 1 | 1.425 | 29.87 | 160.99 | 0.407 | 0.262 |
| | 2 | 1.439 | 31.91 | 189.83 | 0.144 | 0.552 |
| | 3 | 1.461 | 21.82 | 168.39 | 0.157 | 0.186 |
| | 4 | 0.515 | 12.06 | 117.24 | 0.001 | - |
| Eucalyptus | 1 | 1.598 | 29.76 | 159.34 | 0.556 | 0.224 |
| | 2 | 1.466 | 31.93 | 191.06 | 0.179 | 0.546 |
| | 3 | 1.742 | 22.13 | 169.32 | 0.346 | 0.230 |
| | 4 | 0.498 | 11.63 | 121.45 | 0.001 | - |
Fig. 2. a) Degree of conversion and b) Conversion rate – obtained by TGA for oak and eucalyptus at a heating rate of 5°C/min.

3. THERMAL DEGRADATION AT THE MATERIAL SCALE

3.1. Description

Figure 3 presents the time evolution of the temperature and mass loss for the plates of oak and eucalyptus for a radiant heat flux of 20 kW/m². The temperature of the plate increases rapidly to reach a maximum value of 540°C for eucalyptus and 580°C for oak. The heating rate is more significant at the beginning of the experiment with a maximum value of 600°C/min and it decreases after. The mass loss begins around 40 s which corresponds to a temperature of 260°C and it reaches a maximal value around 80 s at 360°C. These results are consistent with the TGA experiments. The mass loss of oak plates is more significant than that of eucalyptus plates. At this heat flux, eucalyptus plate only loses 73% of its initial mass. This behavior can be explained by the fact that the temperature of the plate does not exceed 540°C. According to TGA experiments, the maximal mass loss due to char oxidation occurs after 600°C for heating rates higher than 20°C/min (Table 1). Given the heating rates encountered during the cone calorimeter experiments (Fig. 3b), the char cannot therefore be completely oxidized.

Fig. 3. Time evolution of a) the temperature and heating rate and b) the mass loss and mass loss rate – for a radiant heat flux of 20 kW/m².

3.2. Test of the set of kinetic parameters obtained with TGA experiments

The kinetic mechanism determined from TGA experiments was tested at the material scale. For this, the predicted mass losses were compared to the experimental values for the different heat fluxes and both woods. The same trends were observed for oak and eucalyptus. Figure 4.a and b present the results obtained for the plate of eucalyptus for respectively 20 and 28 kW/m². These heat fluxes were chosen since they are representative of two different behaviors. Until a value of 22 kW/m², the predicted mass loss is close to the experimental one for temperature lower than 400°C. Beyond this threshold, the model overestimates the mass loss. This discrepancy corresponds to the same phenomenon observed at matter scale and can be attributed to the model of char oxidation. For radiant heat fluxes higher than 25 kW/m², the predicted mass loss is delayed in comparison to the experiment. To explain this difference, the global Biot numbers [14] were calculated for each level of heat flux (Fig. 4c). Until 25 s (corresponding to Bi=0.11 and a temperature of 220°C), the evolution of the Biot as function of time is similar whatever the heat flux. After this threshold, two behaviors can be distinguished. For heat fluxes lower than 22kW/m², the Biot number increases quasi-linearly with time until it reaches an asymptotic value. For heat fluxes higher than 25 kW/m², a slope change appears leading to a significant increase of the Biot number. This change of behavior on the curves of Biot number coincides with
the moment at which the predicted and observed mass losses diverge at 28 kW/m². Therefore, for a heat flux higher than 25 kW/m², the plates can no longer be considered as thermally thin and using the back face temperature is no more representative for modeling the plate mass loss. Thus, it is necessary to take into account the temperature gradient within the plate to model the degradation at material scale for such heat fluxes.

![Graph](image)

**Fig.4.** Evolution of a) the mass loss of eucalyptus for a heat flux of 20 kW/m² and b) the mass loss of eucalyptus for a heat flux of 28 kW/m² c) the Biot number for eucalyptus

**CONCLUSION**

The thermal degradation of two kinds of thermally thin wood plates was investigated by using a multi-scale approach. The following results were obtained:

- A kinetic mechanism with four steps was developed to model the thermal degradation of oak and eucalyptus. This model predicts efficiently the thermal decomposition for the levels of heating rates investigated, even if some differences occurred at the maximum conversion rate and for the char oxidation, which are underestimated.
- The use of thermally thin wood plates as samples is original and it has some benefits and drawbacks. It allowed studying the thermal degradation without the knowledge of the thermal properties of the wood and the solving of a thermal balance. However, the test of the set of kinetic parameters obtained from TGA experiments was only possible for levels of radiant heat flux lower than 22 kW/m².

**REFERENCES**

[1] V. Leroy, D. Cancellieri, E. Leoni, Thermal degradation of ligno-cellulosic fuels: DSC and TGA studies, Thermochim. Acta. 451 (2006) 131–138. doi:10.1016/j.tca.2006.09.017.
[2] T. Fateh, F. Richard, J. Zaida, T. Rogaume, P. Joseph, Multi-scale experimental investigations of the thermal degradation of pine needles, Fire Mater. 41 (2017) 654–674. doi:10.1002/fam.2407.
[3] C. Di Blasi, E.G. Hernandez, A. Santoro, Radiative Pyrolysis of Single Moist Wood Particles, Ind. Eng. Chem. Res. 39 (2000) 873–882. doi:10.1021/ie990720i.
[4] M.J. Spearpoint, J.G. Quintiere, Predicting the burning of wood using an integral model, Combust. Flame. 123 (2000) 308–325. doi:10.1016/S0010-2180(00)00162-0.
[5] T. Fateh, T. Rogaume, F. Richard, Multi-scale modeling of the thermal decomposition of fire retardant plywood, Fire Saf. J. 64 (2014) 36–47. doi:10.1016/j.firesaf.2014.01.007.
[6] M.G. Grønli, G. Várhegyi, C.D. Blasi, Thermogravimetric analysis and devolatilization kinetics of wood, Ind. Eng. Chem. Res. 41 (2002) 4201–4208.
[7] M.R. da Silva, G. de O. Machado, J. Deiner, C. Calil Junior, Permeability measurements of brazilian Eucalyptus, Mater. Res. 13 (2010) 281–286. doi:10.1590/S1516-14392010000300002.
[8] R.C. Pettersen, The Chemical Composition of Wood, in: Chem. Solid Wood, American Chemical Society, 1984: pp. 57–126. doi:10.1012/ha-1984-0207.ch002.
[9] Z. Chen, M. Hu, X. Zhu, D. Guo, S. Liu, Z. Hu, B. Xiao, J. Wang, M. Laghari, Characteristics and kinetic study on pyrolysis of five lignocellulosic biomass via thermogravimetric analysis, Bioresour. Technol. 192 (2015) 441–450. doi:10.1016/j.biortech.2015.05.062.
[10] D.F. Arseneau, Competitive Reactions in the Thermal Decomposition of Cellulose, Can. J. Chem. 49 (1971) 632–638. doi:10.1139/v71-101.
[11] D. Cancellieri, E. Innocenti, V. Leroy-Cancellieri, WinGPYRO: A software platform for kinetic study of forest fuels, Fire Saf. J. 58 (2013) 103–111. doi:10.1016/j.firesaf.2013.01.005.
[12] J.A. Conesa, J. Caballero, A. Marcilla, R. Font, Analysis of different kinetic models in the dynamic pyrolysis of cellulose, Thermochim. Acta. 254 (1995) 175–192. doi:10.1016/0040-6031(94)02102-T.
[13] R.K. Agrawal, Kinetics of reactions involved in pyrolysis of cellulose I. The three reaction model, Can. J. Chem. Eng. 68 (1990) 403–412. doi:10.1002/cjce.5450660309.
[14] A. Lamorlette, F. Candellier, Thermal behavior of solid particles at ignition: Theoretical limit between thermally thick and thin solids, Int. J. Heat Mass Transf. 82 (2015) 117–122. doi:10.1016/j.ijheatmasstransfer.2014.11.037.