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# An alternative wood pyrolysis model based on TGA and cone calorimeter tests

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## Abstract

Understanding the process of pyrolysis is crucial to achieve continuous progress in the efficient use of wood as a fuel source in various applications. In the literature, a wide range of kinetic models for wood pyrolysis has been introduced, varying from simpler to more complex and predictive. Some of these models are mathematical, with the sole objective of fitting the experimental results. The others are physical models that describe the underlying chemical processes involved in wood thermal degradation, but they tend to be more complex and time-consuming. In our study, a compromise between these two categories of models was established. A new physical and simple kinetic model of wood thermal degradation was proposed. This model was validated using a multi-scale approach. At micro scale, the thermal degradation of wood was studied using thermogravimetric analysis (TGA). TGA experiments were conducted with two wood species, beech and spruce, in an inert atmosphere at five different heating rates. Based on the latter analysis, our kinetic model of wood thermal degradation was established. Its associated kinetic parameters were determined by fitting the experimental mass loss and mass loss rate data. Good agreement was achieved between the experimental and numerical results. At bench scale, tests were performed in a controlled atmosphere chamber placed in front of a cone calorimeter. The thermal degradation of wood was studied at two heat fluxes in an inert atmosphere obtained by a constant argon injection. The kinetic model developed at the micro scale was implemented into a one-dimensional pyrolysis model, taking into account both thermal and mass transfer phenomena within the wood. The validity of the 1D pyrolysis model was established by comparing the numerical results with the mass loss, mass loss rate, and temperature profile measured during cone calorimeter tests.

*Keywords:* Wood, Pyrolysis, Thermogravimetric analysis, Kinetic, Cone calorimeter, Modelling

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## 1. Introduction

Biomass is currently the world's largest renewable energy source, providing a scalable, flexible and, in many instances, the only reliable source of energy [1]. The term "biomass" commonly refers to all organic materials derived from plants, with wood being the primary type. For many years, wood has been employed

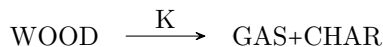


Figure 1: One step global reaction mechanism.

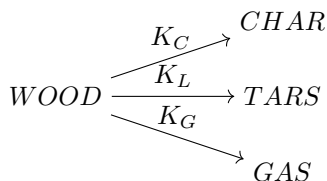


Figure 2: Independent competitive reactions scheme proposed by Shafizadeh and Chin [11].

5 mainly to cook food, heat space and satisfy the construction needs of buildings, works of art and furniture [2].  
 6 Today, the sustainable production of heat and energy from wood is at the centre of scientific and industrial  
 7 interest. Actually, the proper use of wood energy as a substitute for fossil fuels can have a particular impact  
 8 on climate change by reducing the net release of carbon into the atmosphere [1] through sequestration in  
 9 biomass and long-lived products. On the other hand, wood energy can also have an economic advantage  
 10 by satisfying the growing demand for energy. The question is, how can wood energy be used sustainably to  
 11 achieve these benefits?

12 For this purpose, research has aimed to characterise the pyrolysis, gasification and combustion of wood  
 13 in order to design efficient and environmentally sustainable units. However, an accurate study of these  
 14 techniques requires a global understanding of their fundamental processes, especially the primary pyrolysis  
 15 phase. Pyrolysis, the thermal degradation of wood, is a potentially useful thermochemical conversion process.  
 16 It is considered not only as an independent process for the production of bio-oil and biochar, but also as  
 17 a first step of the gasification and combustion processes [3]. Therefore, knowledge of the wood pyrolysis  
 18 behaviour, especially as a function of wood sample size, provides the quantitative basis for a general rigorous  
 19 modelling approach applicable to any wood application in any scale [4, 5].

20 Many researchers have studied the thermal degradation behaviour of wood using thermogravimetric anal-  
 21 ysis (TGA). At this scale, small particles are used to ensure the absence of internal heat and mass transfer.  
 22 The results obtained from TGA tests are used to determine reaction mechanisms and kinetic data of wood  
 23 pyrolysis. In the literature, numerous kinetic schemes for wood pyrolysis have been carried out. Many authors  
 24 [6, 7, 8] have considered a one-step global reaction that converts wood to volatile products and char without  
 25 a detailed description, as shown in Fig. 1. Other authors such as Caballero *et al.* [9] and Thunman *et al.*  
 26 [10] have used kinetic schemes with independent competitive reactions. These schemes follow the proposal  
 27 of Shafizadeh-Chin [11] shown in Fig. 2.

28 Multi-stage mechanisms were also used in the literature [12, 13, 14, 15], suggesting the presence of interme-  
 29 diate components as shown in Fig. 3. Furthermore, there are many authors who consider that the description

## Nomenclature

$\alpha_{abs}$	Average absorptivity [-]	$K_0$	Pre-exponential factor [ $s^{-1}$ ]
$\Delta h$	Reaction heat [ $J \cdot kg^{-1}$ ]	$m_0$	Initial mass [ $kg$ ]
$\lambda$	Thermal conductivity [ $W \cdot m^{-1} \cdot K^{-1}$ ]	$C_p$	Thermal capacity [ $J \cdot kg^{-1} \cdot K^{-1}$ ]
$q_e''$	External heat flux per unit area [ $kW \cdot m^{-2}$ ]	$E$	Activation energy [ $kJ \cdot mol^{-1}$ ]
$q_{loss}''$	Heat losses per unit area [ $kW \cdot m^{-2}$ ]	$h$	Thermal convective coefficient [ $W \cdot m^{-2}$ ]
$Q_r''$	sum of reaction heat [ $kW \cdot m^{-2} \cdot K^{-1}$ ]	$L$	Thickness of the sample [ $m$ ]
$\rho$	Density [ $kg \cdot m^{-3}$ ]	$R$	Universal gas constant [ $J \cdot mol^{-1} \cdot K^{-1}$ ]
$\sigma$	Stefan-Boltzman constant [ $W \cdot m^{-2} \cdot K^{-4}$ ]	$T$	Temperature [ $K$ ]
$\varepsilon$	Emissivity [-]	$t$	Time [ $s$ ]
$K$	reaction rate [ $s^{-1}$ ]	$x$	Distance from the exposed surface [ $m$ ]

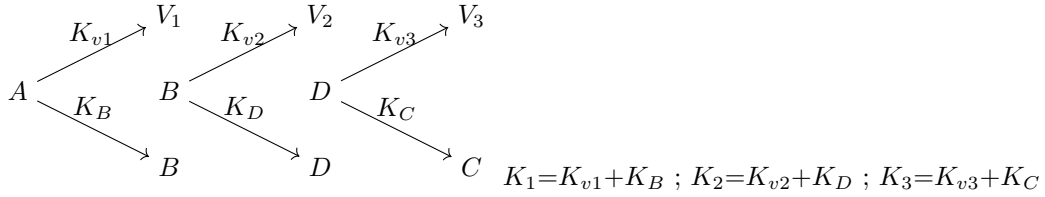


Figure 3: Multi-stage pyrolysis mechanisms proposed by Di Blasi and Branca [14] (A is the wood, B and D are intermediate components).

of wood pyrolysis with only one component is not accurate enough. For instance [16, 17, 18, 19, 20, 21] assumed that the wood pyrolysis is the sum of its main components: cellulose, hemicellulose and lignin. This reaction scheme, shown in Fig. 4, can be applied to a variety of wood species, as the content of cellulose, hemicellulose and lignin varies from one type of wood to another. A major disadvantage of this reaction scheme is that it neglects the interactions between the different components and ignores the influence of minerals. Table 1 summarises the main mechanisms of wood/biomass pyrolysis in the literature. A wide variation in the kinetic parameters can be observed in the literature. At a first glance, it appears that the degradation reactions of lignocellulosic material are more commonly assumed to be first-order reactions. The activation energy of the one-component reaction presents widely variable values, roughly comprised between

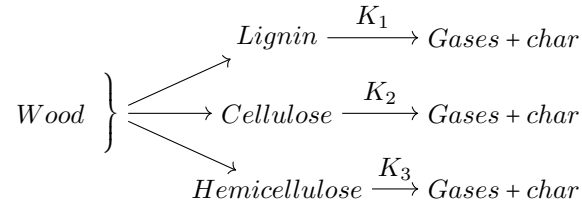


Figure 4: Independent parallel reactions model.

44 and 243  $\text{kJ} \cdot \text{mol}^{-1}$ . Likewise, the activation energies vary between 86 and 147  $\text{kJ} \cdot \text{mol}^{-1}$  for hemicellulose, 193 and 236  $\text{kJ} \cdot \text{mol}^{-1}$  for cellulose, and 46-181  $\text{kJ} \cdot \text{mol}^{-1}$  for lignin. This variation may be due to the large variability of the biomass resource, the operating conditions and the mathematical treatment of the experimental data. The variation observed in this context may also be ascribed to the compensation effect of Arrhenius parameters. Changes in the activation energy ( $E_a$ ) could be partly or entirely offset by adjustments in the pre-exponential factor or reaction order, and conversely [22, 23].

Table 1: Summary of one-component and multi-component mechanisms of lignocellulosic material pyrolysis.

Reaction mechanism	Author (Ref.)	Biomass	Experimental system	Size/mass	Reaction order	Kinetic constants: E ( $\text{kJ} \cdot \text{mol}^{-1}$ ), A ( $\text{s}^{-1}$ )
Fig.1	Tang <i>et al.</i> [6]	Ponderosa Pine	Dynamic TGA 325-350 °C	20-100 mg	1	$K = 6.5 \times 10^9 \exp(226/\text{RT})$
Fig.1	Thurner and Mann [7]	Oak	Isothermal tube furnace 300-400 °C	650 $\mu\text{g}$	1	$K = 2.47 \times 10^6 \exp(106.5/\text{RT})$
Fig.1	Wagenaar <i>et al.</i> [8]	Pine	Isothermal TGA 380 °C	100-125 $\mu\text{g}$	1	$K = 1.4 \times 10^{10} \exp(150/\text{RT})$
Fig.2	Font <i>et al.</i> [9]	Olive stones	Dynamic TGA 2, 10 and 25 $\text{K} \cdot \text{min}^{-1}$	3-4 mg	1.58 0.667 7.21	$k_C = 1.27 \times 10^{13} \exp(163.4/\text{RT})$ $k_L = 4.3 \times 10^{13} \exp(194.6/\text{RT})$ $k_G = 6.59 \times 10^{16} \exp(188.1/\text{RT})$
Fig.2	Thunman <i>et al.</i> [10]	Pine	Pyrex reactor	-	1 1 1	$k_C = 1.3 \times 10^8 \exp(140/\text{RT})$ $k_L = 2.0 \times 10^8 \exp(133/\text{RT})$ $k_G = 1.08 \times 10^7 \exp(121/\text{RT})$
Fig.3	Ward and Braslaw [12]	Lignin	Isothermal TGA 300 °C	0.25mm	1 1 1	$k_1 = 9.6 \times 10^8 \exp(186.73/\text{RT})$ $k_2 = 1.57 \times 10^{16} \exp(205.9/\text{RT})$ $k_3 = 1.13 \times 10^{17} \exp(240/\text{RT})$
Fig.3	Miller and Bellan [13]	Cellulose	Isothermal tube furnace 300-450 °C	$\leq 80 \mu\text{g}$	1 1 1	$k_1 = 2.8 \times 10^{19} \exp(242.4/\text{RT})$ $k_2 = 3.28 \times 10^{14} \exp(196.5/\text{RT})$ $k_3 = 1.3 \times 10^{10} \exp(150.5/\text{RT})$
Fig.3	Di blasi and Branca [14]	Beech	Isothermal tube furnace 300-450 °C	$\leq 80 \mu\text{g}$	1 1 1	$k_1 = 2.7 \times 10^4 \exp(76.2/\text{RT})$ $k_2 = 5.9 \times 10^9 \exp(142.8/\text{RT})$ $k_3 = 9.97 \exp(43.8/\text{RT})$
Fig.3	Di blasi and Branca [15]	Beech	Dynamic TGA 5, 10, 20, 40 $\text{K} \cdot \text{min}^{-1}$ from the initial temperature to 500 °C	5 mg	1 1 1 1.54	$k_1 = 6.29 \times 10^7 \exp(106/\text{RT})$ $k_2 = 8.6 \times 10^{17} \exp(226/\text{RT})$ $k_3 = 7.83 \times 10^6 \exp(114/\text{RT})$ $k_4 = 1.10 \times 10^{12} \exp(183/\text{RT})$
Fig.4	Gronli <i>et al.</i> [18]	Birch	Dynamic TGA 5 $\text{K} \cdot \text{min}^{-1}$ from the initial temperature to 500 °C	5 mg	1 1 1	$k_{\text{Hemicellulose}} = 7.96 \times 10^2 \exp(100/\text{RT})$ $k_{\text{Cellulose}} = 4.06 \times 10^7 \exp(236/\text{RT})$ $k_{\text{Lignin}} = 1.8 \exp(46/\text{RT})$
Fig.4	Branca <i>et al.</i> [19]	Beech	Dynamic TGA 5, 20, 80 $\text{K} \cdot \text{min}^{-1}$ from the initial temperature to 500 °C	20 mg	1 1 1	$k_{\text{Hemicellulose}} = 2.527 \times 10^{11} \exp(147/\text{RT})$ $k_{\text{Cellulose}} = 1.379 \times 10^{14} \exp(193/\text{RT})$ $k_{\text{Lignin}} = 2.202 \times 10^{12} \exp(181/\text{RT})$
Fig.4	Barneto <i>et al.</i> [21]	Rice straw pulp	Dynamic TGA 5, 10, 20 $\text{K} \cdot \text{min}^{-1}$ from the initial temperature to 500 °C	10-100 mg	1 1 1	$k_{\text{Hemicellulose}} = 2.19 \times 10^9 \exp(86/\text{RT})$ $k_{\text{Cellulose}} = 1.17 \times 10^{15} \exp(206/\text{RT})$ $k_{\text{Lignin}} = 8.97 \times 10^2 \exp(62/\text{RT})$

45 For coarse or "thermally thick" wood samples, the internal gradients cannot be neglected. In this case, the  
46 chemistry of thermal decomposition is influenced by heat and mass transfer effects. It is therefore necessary  
47 to take into account in the modelling process the complex nature of wood, the coupling between chemical  
48 kinetics, heat transfer and mass transfer that takes place during the pyrolysis process of solid samples. Many  
49 efforts, both experimental and theoretical [24, 25, 26, 27], have been carried out to better understand the  
50 complex mechanisms interacting in the thermal degradation of thermally thick wood samples. Among all these  
51 researchers, many authors have studied the thermal degradation of wood at the cone calorimeter scale. Most  
52 of these studies have been carried out in an oxidative atmosphere [28, 5, 29, 30, 31, 32, 33, 34]. Under these  
53 conditions, oxidation reactions involving the gases (flame) and carbon (smouldering) increase the complexity  
54 of the problem. Therefore, it is necessary to limit these reactions and pay attention to pyrolysis by working in  
55 an inert atmosphere. Whereas, the study of wood degradation at the cone calorimeter in an inert atmosphere  
56 has been a subject of few prior investigations. In this area, the experimental study of Kashiwagi *et al.* [35] has  
57 for many years been the basis of numerous numerical works to develop a pyrolysis model. This study provides  
58 experimental data on mass loss rates and information on the in-depth temperatures for two heat fluxes: 25

59 and  $40 \text{ kW}\cdot\text{m}^{-2}$ . Swann *et al.* [36], on the other hand, has developed a new apparatus, Controlled Atmosphere  
60 Pyrolysis Apparatus II, which facilitates the collection of data on mass loss rate, temperature, and sample  
61 shape for materials exposed to radiant heating in a controlled atmosphere. However, this apparatus has  
62 not been applied in the study of wood pyrolysis. Lautenberger and Fernandez-Pello [37], Jia *et al.* [38]  
63 and Richter *et al.* [39] used data from Kashiwagi *et al.* [35] to validate their thermal pyrolysis model.  
64 Stoliarov *et al.* [40] proposed a specific calculation code, Thermakin, to investigate the thermal degradation  
65 of polymer materials. This code allows the analysis of the decomposition of various types of materials in  
66 different dimensions, ranging from 0D to 2D. Terrei *et al.* [41] have performed a new experimental setup  
67 allowing to study the wood thermal degradation at the cone calorimeter scale in an inert atmosphere. This  
68 study provides experimental data on mass loss rates and in-depth temperatures of spruce wood for three heat  
69 fluxes: 38, 49 and  $59 \text{ kW}\cdot\text{m}^{-2}$ . These measurements were used to validate their one-dimensional pyrolysis  
70 model with GPYRO [41]. More recently, Gong and Yang [42] have published an exhaustive review regarding  
71 the pyrolysis of commonly used solid combustibles.

72 In summary, wood pyrolysis has been investigated using a multiscale approach in the literature. In  
73 this approach, relatively simplified schemes are preferred to avoid lengthy calculation times. Numerous  
74 kinetic models, ranging from simpler to more complex and predictive, have been introduced in previous  
75 studies. Some of these models are mathematical, with the sole objective of fitting the experimental results.  
76 The others are physical models that describe the underlying chemical processes involved in wood thermal  
77 degradation, but they tend to be more complex and time-consuming. However, the ongoing challenge lies  
78 in formulating a simple kinetic model capable of accurately predicting mass loss and mass loss rate data  
79 while maintaining fidelity to the underlying chemical processes involved in wood thermal degradation. The  
80 present work addresses this challenge at the micro scale. At the bench scale, several wood pyrolysis models are  
81 available in the literature. However, the properties of these models are calibrated to fit the experimental data.  
82 In most cases, the large number of unknown properties in the model and the limited amount of experimental  
83 data result in non-intrinsic properties. Therefore, when the experimental setup is changed or scaled up, the  
84 reliability of the model decreases. This aspect is the main focus of this paper at a larger scale.

85 A global multi-reaction kinetic model of wood thermal degradation was proposed. This model was inspired  
86 from a two stages, semi global multi reaction kinetic model established to study the carbonisation of olive wood  
87 [43]. It divides the wood into three pseudo-components that are not considered to be the main components of  
88 wood: hemicellulose, cellulose and lignin. These pseudo-components degrade in a single step reaction, which  
89 allows a proper study of the kinetic aspects related to a variable temperature levels. The best set of the  
90 model kinetic parameters is then determined by an optimisation method. A comparison between numerical  
91 and experimental evolutions of the mass loss and the mass loss rate for the different heating rates obtained

92 from TGA showed a good agreement. At larger scale, cone calorimeter tests were then carried out in an  
93 inert atmosphere at two heat fluxes (38 and 49 kW · m<sup>-2</sup>). Mass loss and in-depth temperatures at twelve  
94 different positions were measured. A 1D-pyrolysis model was developed by coupling the kinetic model with  
95 the mass and energy conservation equations. All the properties of the model were taken from literature or  
96 determined through experimental measurements, except for the thermal conductivity above 200 °C. This  
97 particular property was estimated by fitting the mass loss data obtained from cone calorimeter tests. To  
98 validate the model at this scale, an additional experiment was conducted using a different heat flux of 25  
99 kW · m<sup>-2</sup>, which was not used to optimize the model parameters. The latter model shows good efficiency in  
100 predicting the experimental results obtained from the cone calorimeter tests.

## 101 2. Study at the micro scale

102 This section presents the experimental and numerical studies conducted at the micro scale to evaluate the  
103 thermal degradation of wood in an inert atmosphere, with a primary focus on chemical aspects. Two wood  
104 species, beech and spruce, were used for the tests. These species have chemical compositions representative  
105 of the typical standards for the hardwood and softwood categories, respectively [15].

### 106 2.1. Thermogravimetric analysis

107 The degradation studies were performed using a STA 449 f3 Jupiter thermobalance in an inert atmosphere  
108 of nitrogen at a flow rate of 20 mL · min<sup>-1</sup>. The tests were conducted using approximately 50 ± 3 mg of  
109 wood powder with a thickness of less than 0.1 mm. Before each test, the samples were dried at 105 °C for  
110 24 hours to remove moisture. During the experiments, the sample was heated from the ambient temperature  
111 to 800 °C at five different heating rates of 5, 10, 20, 30 and 40 K · min<sup>-1</sup>. The mass of the wood sample and  
112 the furnace temperature were continuously recorded. For each experiment, mass loss and normalised mass  
113 loss rate curves were plotted as a function of temperature. The mass loss represents the ratio of the sample  
114 weight ( $m$ ) to the initial weight ( $m_0$ ). The normalised mass loss rate curves were obtained numerically using  
115 the time derivative of the mass loss curves. In order to ensure good reproducibility of the experiments, at  
116 least two runs were carried out for each heating rate. Therefore, the reported experimental data correspond  
117 to the average of these tests, where the relative difference was less than 2 %.

118 Fig. 5a and Fig. 5b show the mass loss curves, for beech and spruce wood, respectively, under nitrogen  
119 atmosphere at five different heating rates 5, 10, 20, 30, 40 K · min<sup>-1</sup>. As can be seen in Fig. 5, the evolution  
120 of mass loss for both woods is similar regardless the heating rate. Even if the beech and spruce samples  
121 were pre-dried, the mass loss curves show a minor decline in mass before reaching 150 °C. This decrease is  
122 attributed to the evaporation of bound water still present in the wood. It is important to note that oven

123 drying at 105 °C can only remove free water and not bound water from the wood samples. Furthermore, about  
 124 70 % of the initial mass of beech and 65 % of the initial mass of spruce was found to be degraded between 240  
 125 and 400 °C, while 10 % of the initial mass of beech and 20 % of the initial mass of spruce was lost between 400  
 126 °C and 800 °C. The mass of the residue remaining at the end of the experiment was approximately 19 % and  
 127 21 % of the initial mass for beech and spruce, respectively. The analysis of Fig. 5 does not allow to clearly  
 128 identify all the steps of the thermal degradation of beech and spruce wood under inert atmosphere. In this  
 129 sense, Fig. 6a and Fig. 6b show the normalised mass loss rate curves, for beech and spruce wood respectively  
 130 at five different heating rates 5, 10, 20, 30, 40 K · min<sup>-1</sup> under nitrogen atmosphere. For both woods, it was  
 131 noticed that the pyrolysis process is characterised by two regions: main devolatilization and continuous slight  
 132 devolatilization. The main pyrolysis process develops from about 240 °C to 400 °C at low heating rates (5,  
 133 10 and 20 K · min<sup>-1</sup>) and 430 °C at high heating rates (30 and 40 K · min<sup>-1</sup>). In this region, there are two  
 134 peaks: a peak of approximately 305 °C at low heating rate and 350 °C at high heating rates. This peak is  
 135 mainly related to hemicellulose decomposition. Another peak was observed at a higher temperature around  
 136 345 °C for low heating rates and 380 °C for high heating rates and is essentially related to the cellulose  
 137 decomposition. The continuous slight devolatilization region occurred above 430 °C. This region corresponds  
 to the slow degradation of lignin, which decomposes in both regions without characteristic peaks [44].

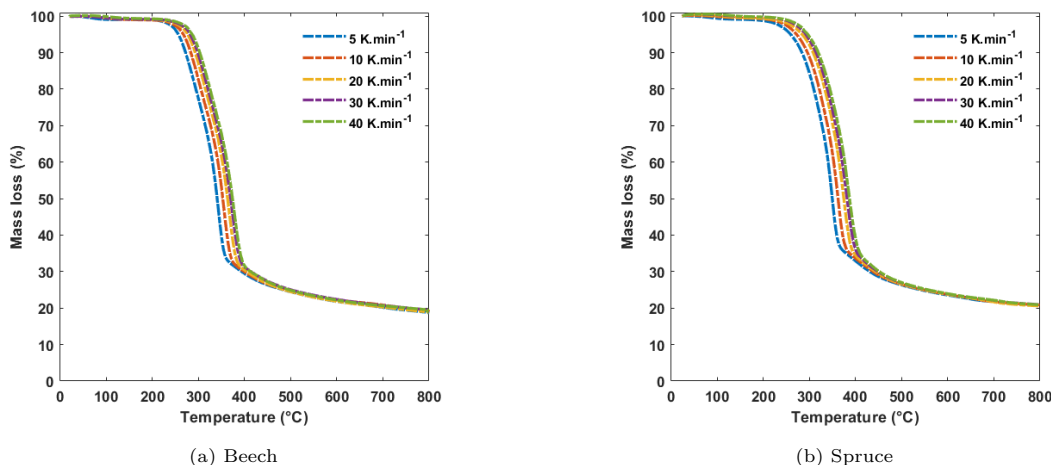


Figure 5: Normalised mass loss of beech and spruce wood in nitrogen atmosphere at five heating rates with TGA.

138

139 In order to quantify the effect of the heating rate on the degradation process characteristics of beech and  
 140 spruce wood, the same parameters as those introduced by Gronli *et al.* [18] were evaluated and reported  
 141 in Table 2. The initial degradation temperature  $T_{initial}$  was considered to be the temperature at which the  
 142 solid mass fraction is equal to 0.975. The parameter  $T_{final}$  was obtained when the normalised mass loss rate  
 143 curve represents an inflection point at a temperature of about 400 °C. The temperature of the first peak was



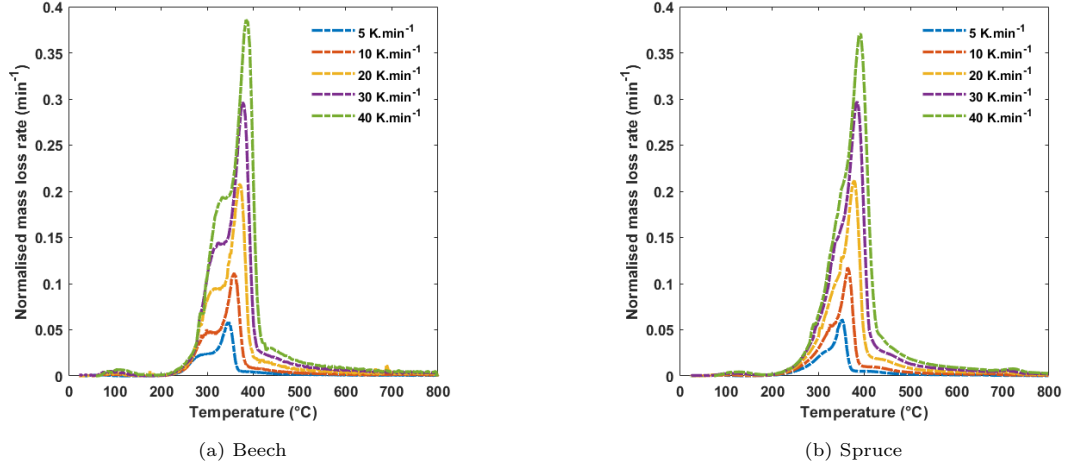


Figure 6: Normalised mass loss rate of beech and spruce wood in nitrogen atmosphere at five heating rate with TGA.

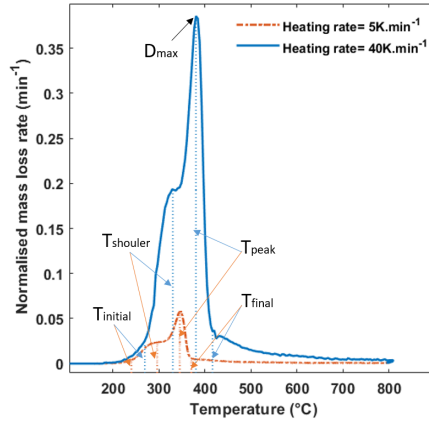


Figure 7: Normalised mass loss rate of beech with characteristic temperature for rates of 5 and 40  $\text{K} \cdot \text{min}^{-1}$ .

144 defined as  $T_{shoulder}$ . The temperature  $T_{peak}$  was the temperature at which the maximum peak is reached.  
 145 The maximum normalised mass loss rate was called  $D_{max}$ .  
 146 As the heating rate increased from  $5 \text{ K} \cdot \text{min}^{-1}$  to  $40 \text{ K} \cdot \text{min}^{-1}$  for beech and spruce wood, all the characteristic  
 147 temperatures ( $T_{initial}$ ,  $T_{final}$ ,  $T_{shoulder}$ ,  $T_{peak}$ ) became successively higher especially  $T_{shoulder}$  and  $T_{peak}$ ,  
 148 as shown in Table 2. The whole decomposition process was shifted towards higher temperatures and the  
 149 normalised mass loss rate increases. The shift of the normalised mass loss rate curves at higher temperature  
 150 is clearly shown, for example, by the normalised mass loss rate curves of beech wood for 5 and  $40 \text{ K} \cdot \text{min}^{-1}$   
 151 reported in Fig. 7. The maximum normalised mass loss rate  $D_{max}$  showed an increasing trend up to about  
 152  $0.39 \text{ min}^{-1}$  for both species as the corresponding temperature increased from  $342 \text{ }^\circ\text{C}$  to  $380 \text{ }^\circ\text{C}$  for beech and  
 153 from  $350 \text{ }^\circ\text{C}$  to  $392 \text{ }^\circ\text{C}$  for spruce wood. This can be interpreted on the basis of heat transfer limitations.  
 154 Indeed, at a low heating rate, the sample has more time to establish a uniform temperature within it. On

155 the other hand, at a high heating rate, the sample has less time to establish a uniform temperature within  
 156 it: heat transfer within the sample takes time, and the temperature at the core of the wood is not exactly  
 157 the same as that of the reactor. In such a case, the kinetic aspect competes with the heat exchange aspect  
 158 within the sample [45]. Therefore, the low heating rate results were used to evaluate the kinetic parameters  
 159 for a proposed model. In this case, the temperature gradients in the samples are smaller and the process is  
 160 controlled by the kinetics.

161 The mass loss and normalised mass loss rate curves for beech and spruce wood at the heating rate of 5  
 162  $\text{K} \cdot \text{min}^{-1}$  are shown in Fig. 8a and Fig. 8b, respectively. It can be seen that the evolution of mass loss is  
 163 similar for both woods and they differ only in the mass of the residue remaining at the end of the experiment.  
 164 The normalised mass loss rate of beech shows a clear shoulder peak in the first stage of the normalised mass  
 165 loss rate curve at around 300 °C, which is not obviously noticeable in the normalised mass loss rate curve of  
 166 spruce, possibly due to its lower hemicellulose content compared to beech [18]. However, the differences in the  
 167 corresponding degradation characteristics for beech and spruce at different heating rates are not exceedingly  
 168 large. The characteristic parameters are quantitatively similar for both cases at different heating rates, as  
 169 shown in Table 2. It is therefore worth looking for a common pyrolysis mechanism.

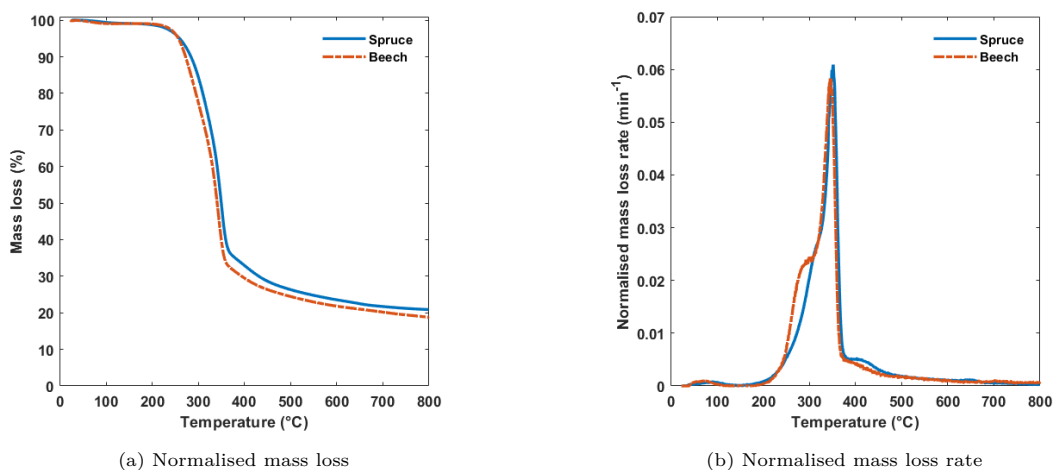


Figure 8: Mass loss and normalised mass loss rate curves of beech and spruce under a heating rate of 5  $\text{K} \cdot \text{min}^{-1}$ .

## 170 2.2. Kinetic model

171 As mentioned in the introduction, several kinetic models for the thermal degradation of wood have been  
 172 proposed in the literature. Some describe the pyrolysis of wood in terms of a single component, while  
 173 others recommend dividing the wood into three components corresponding to the main components of wood  
 174 (hemicellulose, cellulose and lignin). Models of these two categories have advantages and drawbacks: more  
 175 or less complex, more or less predictive. However, the thermal degradation of wood cannot be considered as

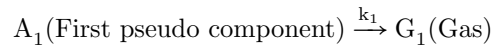
Table 2: Degradation characteristics parameters under different heating rate of beech and spruce wood.

Sample	Heating rate ( $\text{K} \cdot \text{min}^{-1}$ )	$T_{initial}$ ( $^{\circ}\text{C}$ )	$T_{final}$ ( $^{\circ}\text{C}$ )	$T_{shoulder}$ ( $^{\circ}\text{C}$ )	$T_{peak}$ ( $^{\circ}\text{C}$ )	$D_{max}$ ( $\text{min}^{-1}$ )
Beech	5	240	371	296	342	0.06
	10	249	387	300	357	0.11
	20	256	397	320	368	0.2
	30	263	412	331	374	0.29
	40	269	420	337	380	0.39
Spruce	5	234	380	317	350	0.06
	10	250	390	325	363	0.12
	20	260	407	342	376	0.2
	30	271	424	346	382	0.29
	40	277	430	350	392	0.4

176 a reflection of the sum of the thermal responses of its main components, since some inorganic components  
 177 catalyse the conversion process in an unpredictable variety of ways [46, 47]. Furthermore, the interaction  
 178 between the main components cannot be neglected, as shown by Hosoya *et al.* [48].

179 Based on the experimental results and on previous works, it was proposed to develop a global multi-reaction  
 180 kinetic model of wood degradation in order to properly follow the kinetic aspects related to the variable  
 181 temperature levels received by the sample. The model developed here is inspired from a two-stages, semi  
 182 global multi-reaction kinetic model established to study the carbonisation of olive wood [43] and then used  
 183 to study the isothermal degradation of wood panel and of its components [49].

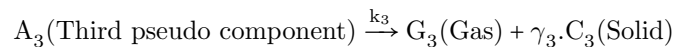
184 In the proposed model, wood is divided into three pseudo-components  $A_1$ ,  $A_2$  and  $A_3$ . These pseudo solids  
 185 cannot be assimilated to the main components, which are cellulose, hemicellulose and lignin. Each pseudo-  
 186 component corresponds to a specific kinetic law and a mass fraction  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$ , respectively of the initial  
 187 solid.  $A_1$ ,  $A_2$  and  $A_3$  degrade in a single stage reaction to give gas products  $G_1$ ,  $G_2$  and  $G_3$ , respectively,  
 188 and a non-degradable solid residue  $C_2$  and  $C_3$ . It is worth mentioning that there is no chemical difference  
 189 between  $C_2$  and  $C_3$ . At low temperatures ( $T \leq 300^{\circ}\text{C}$ ) only the degradation of  $A_1$  occurs and the product  
 190 is gaseous. Above this temperature, the transformation of the two pseudo-components  $A_2$  and  $A_3$  begins,  
 191 giving gaseous products  $G_2$  and  $G_3$  and non-degradable solids  $C_2$  and  $C_3$  respectively. The proposed kinetic  
 192 scheme is as follows:



193



194



195  $\gamma_2$  and  $\gamma_3$  correspond to the mass fractions of solid produced by the components  $A_2$  and  $A_3$  respectively.  
 196  $K_i$  is the rate coefficient which follows an Arrhenius-type law ( $K_i=K_{0i}.\exp(-E_i/RT)$ ). Assuming that the  
 197 kinetics of the three reactions are described by first order laws, the mass balance of the solid and slightly  
 198 volatile  $A_1, A_2, A_3, C_2$  and  $C_3$ , can be respectively written as:

$$\frac{dm_{A1}}{dt} = -K_1.m_{A1} \quad (1)$$

$$\frac{dm_{A2}}{dt} = -K_2.m_{A2} \quad (2)$$

$$\frac{dm_{A3}}{dt} = -K_3.m_{A3} \quad (3)$$

$$\frac{dm_{C2}}{dt} = \gamma_2.K_2.m_{A2} \quad (4)$$

$$\frac{dm_{C3}}{dt} = \gamma_3.K_3.m_{A3} \quad (5)$$

203 The total mass of the sample at the time t, is then described by  $m(t)$ , which is:

$$m(t) = m_{A1}(t) + m_{A2}(t) + m_{A3}(t) + m_{C2}(t) + m_{C3}(t) \quad (6)$$

204 The analytical resolution of the balance equations leads to the following equation:

$$\frac{m(t)}{m_0} = \gamma_2.\alpha_2 + \gamma_3.\alpha_3 + \alpha_1.\exp(-K_1.t) + \alpha_2.(1 - \gamma_2).\exp(-K_2.t) + \alpha_3.(1 - \gamma_3).\exp(-K_3.t) \quad (7)$$

205 Eq. 7 shows that the calculated mass of the sample according to this model during the thermal degradation  
 206 in an inert atmosphere depends on 11 kinetic and stoichiometric parameters ( $\alpha_1, \alpha_2, \alpha_3, E_1, E_2, E_3, K_{01},$   
 207  $K_{02}, K_{03}, \gamma_2$  and  $\gamma_3$ ). These parameters must be estimated as they cannot be measured or determined  
 208 experimentally. In practice, the least squares method was used to find the set of parameters that minimises  
 209 the total error  $E_{r1}$  (Eq. 8) and  $E_{r2}$  (Eq. 9) between the numerical and experimental mass loss and mass loss  
 210 rate respectively:

$$E_{r1} = \sum_{i=1}^X (m_{num}(i) - m_{exp}(i))^2 \quad (8)$$

$$E_{r2} = \sum_{i=1}^X (mlr_{num}(i) - mlr_{exp}(i))^2 \quad (9)$$

212 Where  $m_{num}$  and  $m_{exp}$  are respectively the numerical and experimental mass loss of the samples,  $mlr_{num}$  and  
 213  $mlr_{exp}$  are respectively the numerical and experimental normalised mass loss rate of the samples, and X is the  
 214 number of experimental points. The Levenberg-Marquardt algorithm was used in the optimisation. Initially,

215 the kinetic parameters provided by Grioui *et al.* [43] were utilized as a set of initial values for the estimation  
216 based on  $E_{r2}$  (Eq. 9). The resulting kinetic parameters were then used as initial values to minimize  $E_{r1}$   
217 (Eq. 8). This iterative process was repeated multiple times to obtain the optimal set of kinetic parameters  
218 that effectively fit the mass loss and mass loss rate curves simultaneously. To avoid heat and mass transfer  
219 limitations, the optimization process excluded the use of high heating rates (30 and 40  $\text{K} \cdot \text{min}^{-1}$ ). Instead,  
220 the optimization was performed for the slow heating rates: 5, 10, and 20  $\text{K} \cdot \text{min}^{-1}$  simultaneously. Indeed,  
221 employing the parameter estimation procedure on multiple experiments conducted under diverse conditions,  
222 such as various heating rates, while utilizing the same kinetic model and parameters, helped to circumvent  
223 the compensation effect [15]. The values of the kinetic parameters, obtained for beech and spruce wood, and  
224 the deviations between numerical and experimental are listed in Table 3.

225 The order of the reactions was kept constant and equal to one ( $n=1$ ). The introduction of higher order  
226 reactions in this model provides an excellent description of the experimental results. This was not done in  
227 accordance with the hypothesis that the reaction rate depends only on the amount of reactant present in  
228 the reactor [50]. The other parameters were estimated with constraints to ensure a successive degradation  
229 of the three components in the following order:  $A_1$ , then  $A_2$ , and finally  $A_3$ . The degradation of the first  
230 component, leading to the formation of gases, precedes that of the second and third components which lead  
231 to the formation of gases and char.

232 Details about the dynamics of the different pseudo-components and a comparison between predicted and  
233 measured mass loss and normalised mass loss rate at the three heating rates: 5, 10 and 20  $\text{K} \cdot \text{min}^{-1}$  for beech  
234 and spruce wood are shown in Fig. 9 and Fig. 10, respectively. In the case of beech, the reaction of the first  
235 pseudo-component  $A_1$ , which was completely converted to gas, started at 250 °C and was completed at 300  
236 °C approximately. The maximum mass loss rate of  $A_1$  occurred between 290 °C and 320 °C depending on  
237 the heating rate. As the heating rate is higher, the maximum mass loss rate occurred at a higher temperature  
238 as shown in the section 2.1. The decomposition of the second pseudo-component  $A_2$ , which leads to the  
239 formation of gas and non-degradable solid  $C_2$ , started at about 300 °C and was completed at about 400 °C.  
240 The maximum mass loss rate of  $A_2$  was proceeded between 340 °C and 370 °C. The final pseudo-component,  
241  $A_3$ , initiated its degradation into gas and  $C_3$  at approximately 420°C and concluded around 650°C. The  
242 maximum mass loss rate of  $A_3$  was between 500 °C and 600 °C. The char was completely obtained at about  
243 650 °C. For spruce, the decomposition of the first pseudo-component  $A_1$  started at about 230 °C and was  
244 completed at 300 °C. The maximum mass loss rate of  $A_1$  rate occurred between 320 °C and 340 °C depending  
245 on the heating rate. The decomposition of the second pseudo-component  $A_2$  started at about 300 °C and was  
246 accomplished at about 400 °C. The maximum mass loss rate of  $A_2$  was attained between 350 °C and 370 °C.  
247 The last pseudo-component  $A_3$  initiated to degrade at about 400 °C and was achieved at about 650 °C with

Table 3: Kinetic parameters estimated for the thermal degradation of beech and spruce wood.

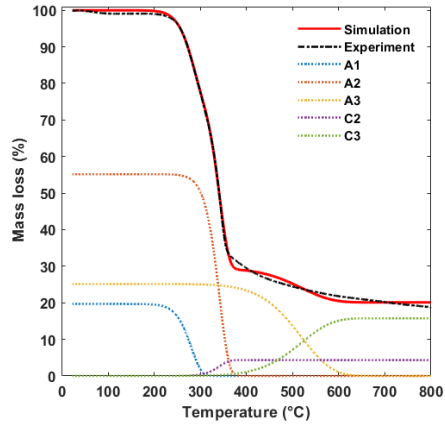
Sample	Reaction	E (kJ · mol <sup>-1</sup> )	K <sub>0<sub>i</sub></sub> (1/s)	α	γ	Mean NRMSE (%)
Beech	(1)	116	3.4 × 10 <sup>8</sup>	0.2	-	1.72
	(2)	155	5.52 × 10 <sup>10</sup>	0.55	0.08	
	(3)	80	2.37 × 10 <sup>2</sup>	0.25	0.63	
Spruce	(1)	105	2.1 × 10 <sup>7</sup>	0.16	-	1.21
	(2)	172	1.3 × 10 <sup>12</sup>	0.6	0.15	
	(3)	76.5	2.52 × 10 <sup>2</sup>	0.24	0.56	

248 a maximum mass loss rate between 500 °C and 600 °C. The char was fully formed at about 650 °C. As can be  
 249 seen, the simulated mass loss and the normalised mass loss rate for both species show a good agreement with  
 250 the experimental results for different heating rates. The performance of the kinetic mechanism was evaluated  
 251 using the Normative Root Mean Squared Error (NRMSE), between the experimental and predicted mass  
 252 loss, characterised by the following variable:

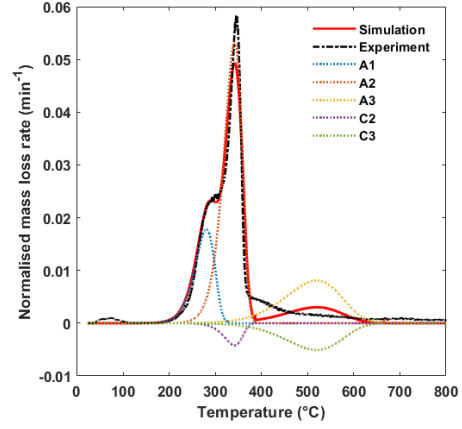
$$NRMSE(\%) = \frac{\sqrt{\frac{\sum_{i=1}^X (m_{num}(i) - m_{exp}(i))^2}{X}}}{\max_{i=1 \dots X} m_{exp}(i) - \min_{i=1 \dots X} m_{exp}(i)} \cdot 100 \quad (10)$$

253 For beech the total deviation for the mass loss curve is about 1.06, 1.4 and 2.7 % for 5, 10 and 20 K · min<sup>-1</sup>  
 254 respectively, leading to an average NRMSE of 1.72 %. For spruce, the overall deviation for the mass loss  
 255 curve is about 1.26, 1.27 and 2.1 % for 5, 10 and 20 K · min<sup>-1</sup> respectively, giving an average NRMSE of 1.21  
 256 %. For both species, the fit of the model to the experimental mass loss and mass loss rate curves was very  
 257 good from the ambient temperature to 400 °C. At temperatures above 400 °C, there is a slight discrepancy  
 258 between the experimental and simulated curves. This can be attributed to a delayed degradation of the third  
 259 pseudo-component. In addition, at higher temperatures, many reactions are likely to dominate which are  
 260 not described in detail in this model and which cause the discrepancy. The maximum peak of the mass loss  
 261 rate is slightly underestimated. This can be attributed to the presence of heat transfer phenomena and the  
 262 experimental procedures. In any case, the prediction by the present model is considered encouraging in terms  
 263 of the validity of the model itself.

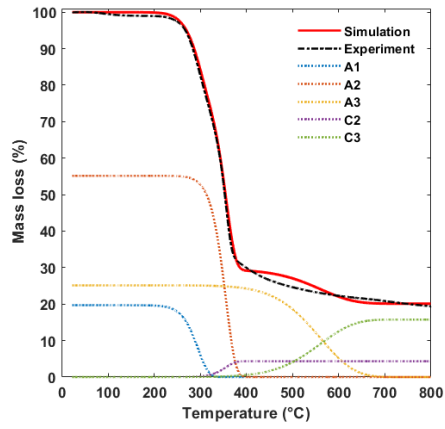
264 To validate the kinetic parameters obtained through optimisation, these parameters were employed to  
 265 predict mass loss and mass loss rates at elevated heating rates of 30 and 40 K · min<sup>-1</sup>. Despite these two  
 266 heating rates not being incorporated into the optimization process, the model demonstrates its efficacy in  
 267 predicting experimental mass loss and normalised mass loss rates for beech and spruce wood, as shown in  
 268 Fig. 11 and Fig. 12, respectively. Indeed, the NRMSE for beech is 3.3 % at 30 K · min<sup>-1</sup> and 3.5 % at 40  
 269 K · min<sup>-1</sup>. For spruce, it is 2.7 % at 30 K · min<sup>-1</sup> and 3.1 % at 40 K · min<sup>-1</sup>.



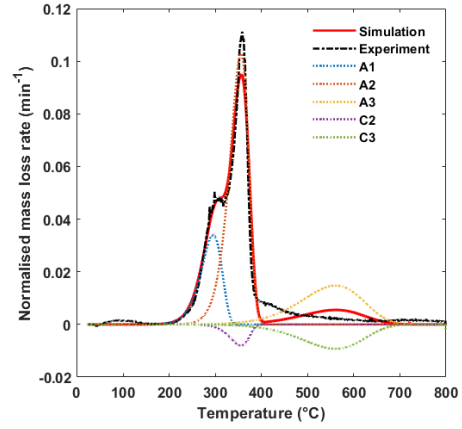
(a)  $5 \text{ K} \cdot \text{min}^{-1}$



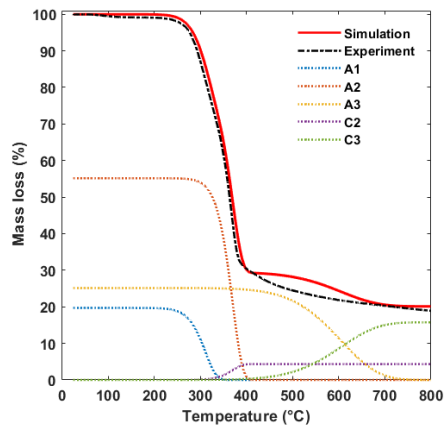
(b)  $5 \text{ K} \cdot \text{min}^{-1}$



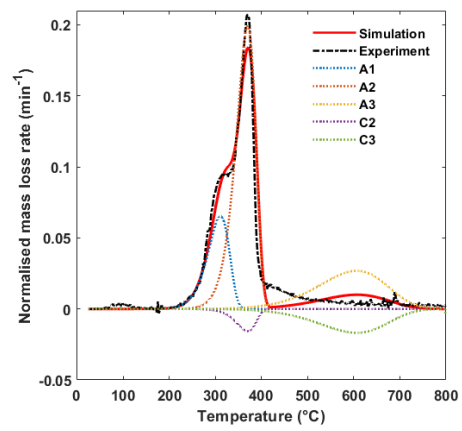
(c)  $10 \text{ K} \cdot \text{min}^{-1}$



(d)  $10 \text{ K} \cdot \text{min}^{-1}$



(e)  $20 \text{ K} \cdot \text{min}^{-1}$



(f)  $20 \text{ K} \cdot \text{min}^{-1}$

Figure 9: Comparison between the experimental and the numerical mass loss and normalised mass loss rate curves for beech wood at 5, 10 and 20  $\text{K} \cdot \text{min}^{-1}$ .

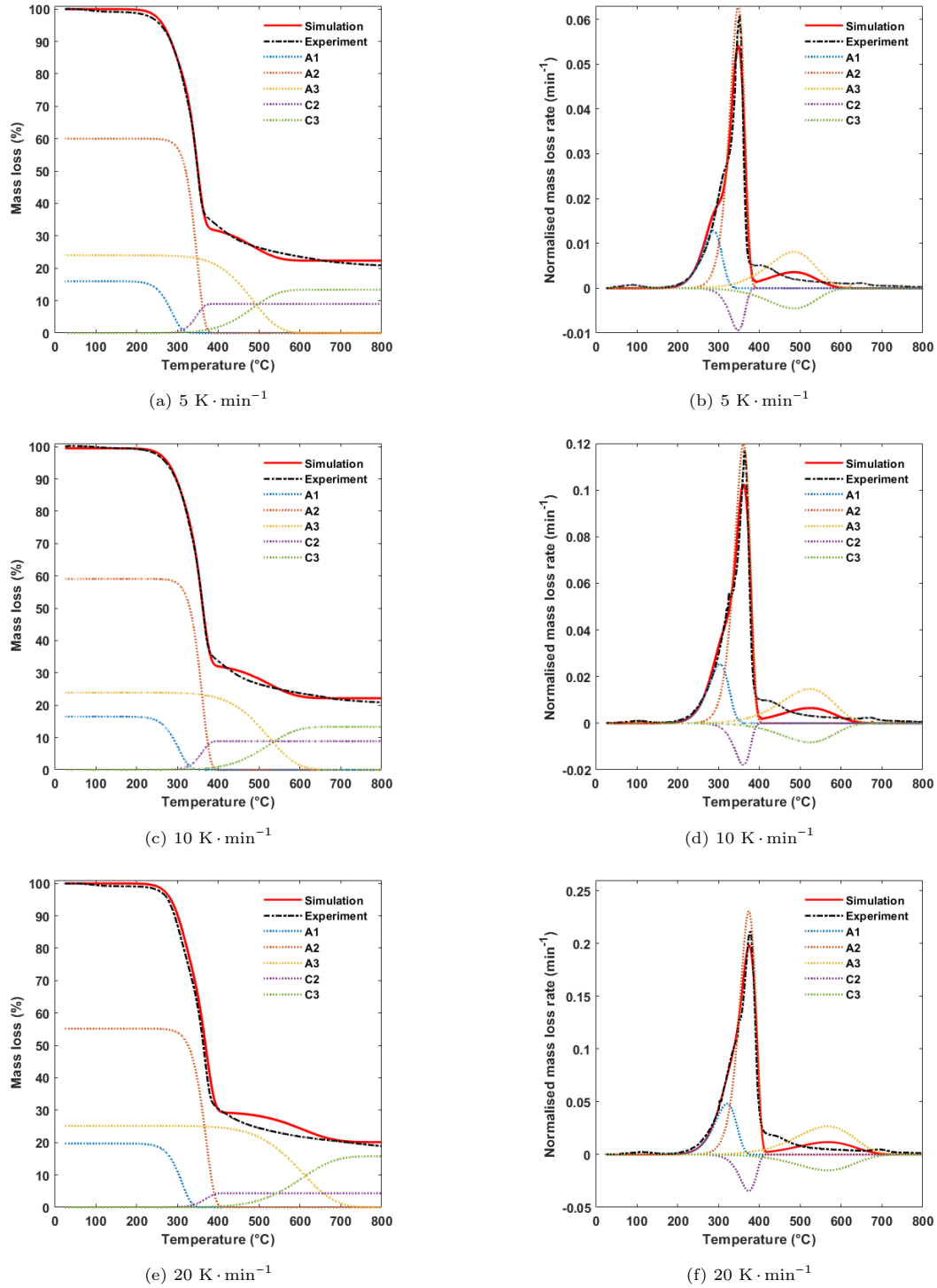


Figure 10: Comparison between the experimental and the numerical mass loss and normalised mass loss rate curves for spruce wood at 5, 10 and 20  $\text{K} \cdot \text{min}^{-1}$ .

### 270 3. Study at the bench scale

271 The objective of this section is to describe the thermal degradation of spruce and beech wood during  
 272 the cone calorimeter experiments under inert atmosphere. First, the experiments performed at the cone



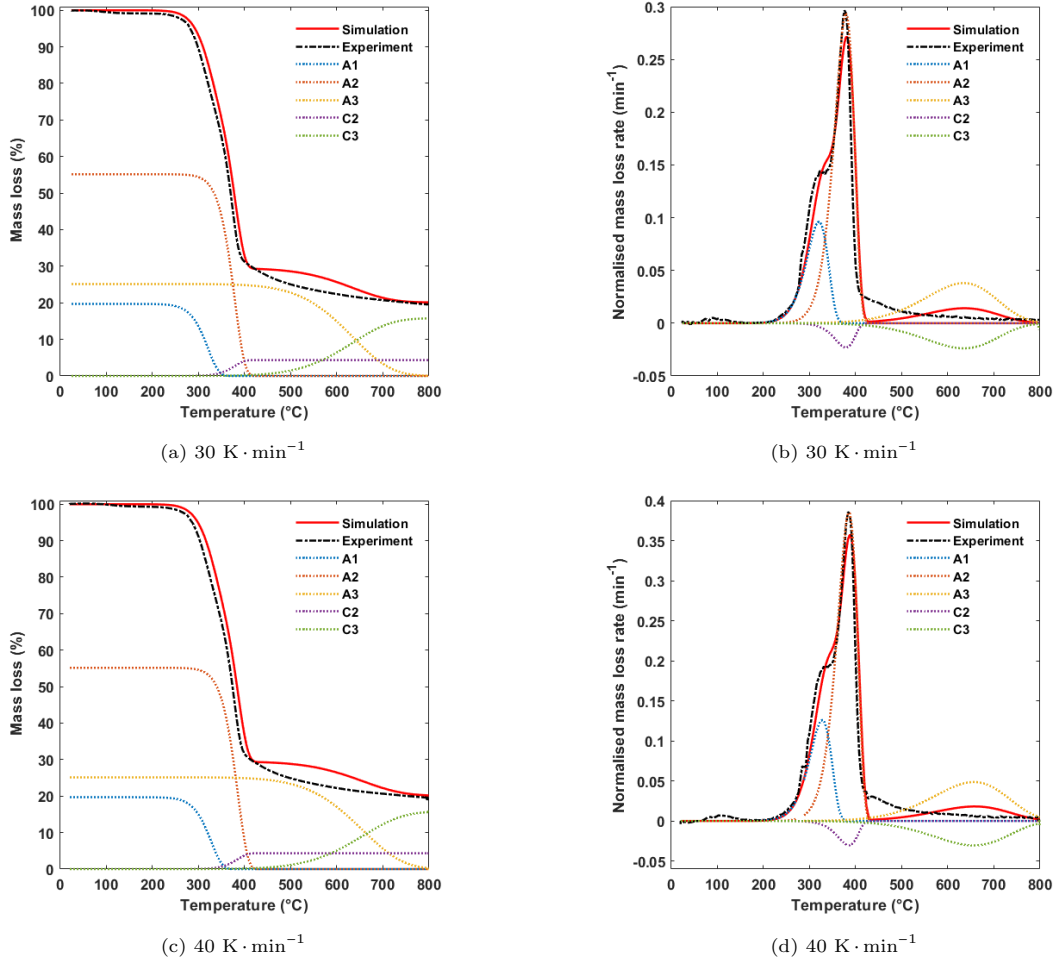


Figure 11: Comparison between the experimental and the numerical mass loss and normalised mass loss rate curves for beech wood at 30 and 40  $\text{K} \cdot \text{min}^{-1}$ .

273 calorimeter scale are briefly described. Then, the numerical model of pyrolysis at the cone calorimeter scale  
 274 is presented.

### 275 3.1. Cone calorimeter experiments

276 As a detailed description of the experimental apparatus has been reported by Terrei *et al.* [41], only a brief  
 277 description of the experimental setup is given here. The tests were performed in front of a cone calorimeter  
 278 oriented vertically. During the tests, the sample was placed in a stainless-steel chamber specifically designed  
 279 to study the wood thermal degradation under a controlled atmosphere. A sapphire window placed on the  
 280 front face of the chamber allows the heat flux from the cone to pass through. The chamber was inerted  
 281 by a continuous injection of argon at a flow rate of  $10 \text{ L} \cdot \text{min}^{-1}$ . A Testo 350 gas analyser was used to  
 282 determine the oxygen concentration. A test was started when the concentration of oxygen in the chamber  
 283 stabilised at around 3 %. This concentration was always less than 6 % during the tests. For each test, the

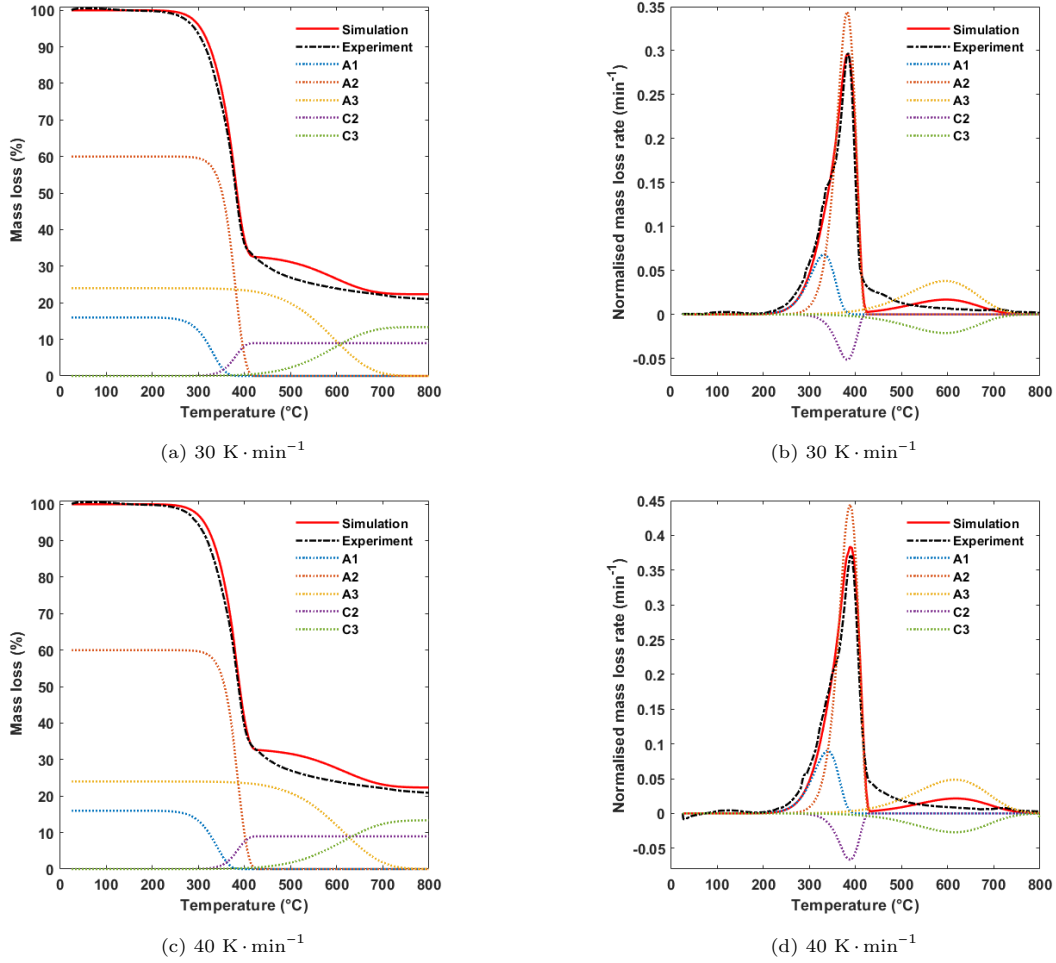


Figure 12: Comparison between the experimental and the numerical mass loss and normalised mass loss rate curves for spruce wood at 30 and 40 K · min<sup>-1</sup>.

284 wood sample was placed in a specific sample holder made of low density calcium silicate plates to limit the  
 285 thermal interactions with the edges and to ensure a 1-D heat transfer. The rear surface of sample is exposed  
 286 to free gas flow. The sample and its holder were then inserted into the chamber via the rear face, which  
 287 consists of a sliding door. Fig. 13 shows the experimental setup. The mass loss of the sample was measured  
 288 using a load cell with a precision of 0.1 g. The in-depth temperatures were measured using twelve thin wire  
 289 thermocouples embedded in the wood samples. Ten thermocouples were placed every 2 mm from 2 to 20 mm  
 290 depth from the exposed surface, one at a 30 mm depth and one at a 40 mm depth. Tests were conducted at  
 291 heat fluxes of 38 and 49 kW · m<sup>-2</sup> for 10 minutes. The samples used in the tests were square wood samples  
 292 of 100 × 100 × 50 mm<sup>3</sup>, dried at 105 °C for 48 hours prior to each test to remove moisture. The initial mass  
 293 of the samples tested was 180 ± 12 g and 300 ± 16 g for spruce and beech respectively. Terrei *et al.* [51]  
 294 have already performed the tests only for spruce wood. In this study, the experimental data on spruce wood  
 295 are identical to those presented in the study of Terrei *et al.* [51]. On the other hand, tests were carried out

296 using beech wood samples, with a few technical modifications. In these experiments, the flow rate of argon  
 297 was  $12 \text{ L} \cdot \text{min}^{-1}$  instead of  $10 \text{ L} \cdot \text{min}^{-1}$  to ensure an oxygen concentration less than 3% throughout all the  
 298 tests, and then to limit char oxidation as much as possible. In addition, a load cell with a precision of 0.01  
 299 g was used in order to provide a more reliable mass loss and mass loss rate. It is important to note that a  
 300 single test was conducted on a spruce wood sample using a purging flow rate of  $12 \text{ L} \cdot \text{min}^{-1}$ . It was observed  
 301 that the obtained mass loss rate is very similar to the mass loss rate obtained by Terrei et al. [51], who used  
 a purging flow rate of  $10 \text{ L} \cdot \text{min}^{-1}$ .

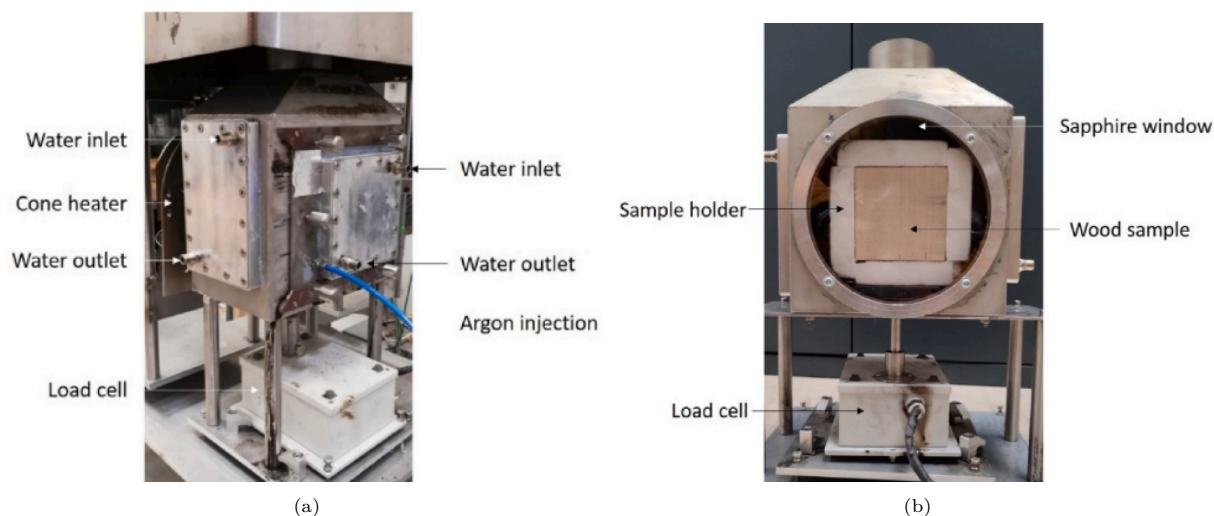


Figure 13: (a) Back and (b) front side of the experimental setup [41].

302

### 3.2. Modeling of the cone calorimeter experiments

304 In the literature, many software have been used to simulate the degradation of wood at bench scale, like  
 305 GPYRO, FDS and FireFoam. Previous works [52, 29] have shown the inadequacy of FDS to numerically  
 306 simulate cone calorimeter tests with kinetic parameters calculated from TGA data. Otherwise, many authors  
 307 [53, 39] have shown that GPYRO is able to well predict the thermal degradation behaviour of wood well.  
 308 However, in GPYRO, the evolution laws of the model thermal properties are imposed. Regarding FireFoam,  
 309 it is less commonly used in the literature compared to other software. In this paper, the modelling has been  
 310 written in MATLAB<sup>®</sup> environment, in order to develop a model with a good knowledge of the assumptions  
 311 and a good control of the evolution laws of all the properties. The modelling must focus on phenomena  
 312 that can predict what happens inside the sample, such as heat transfer, mass transfer, chemical reactions, as  
 313 well as the change in its thermophysical properties (conductivity, specific heat). The developed scheme and  
 314 its associated kinetic parameter, validated at TGA scale, were used as input data to simulate the thermal  
 315 decomposition of the spruce and beech wood at the cone calorimeter scale. The following assumptions were

316 made in the pyrolysis model:

- 317 1. The heat transfer was considered to be one dimensional since the wood sample seemed to degrade  
 318 uniformly from the exposed side.
- 319 2. The heat and mass transfer between the solid and gas phases were neglected.
- 320 3. The thermo-physical properties of the three pseudo-components  $A_1$ ,  $A_2$ , and  $A_3$  were equivalent to  
 321 those of dry wood.
- 322 4. The dimensions and shape of the wood sample remained constant and cracks and shrinkage were  
 323 neglected.
- 324 5. The heat of the three chemical reactions was supposed to be the same and was taken from the literature  
 325 [54].

326 Based on the above assumptions, the energy conservation equation for pyrolysis of the dry wood is described  
 327 as:

$$\frac{\partial}{\partial t} [T(\rho_s C_{p_s})] = \frac{\partial}{\partial x} \left( \lambda_s \frac{\partial T}{\partial x} \right) + Q_r'' \quad (11)$$

328 where:  $Q_r''$  is the sum of reaction heat of the three pyrolysis reactions, as follows

$$Q_r'' = k_1 \alpha_1 \rho_{A_1} \Delta h_1 + k_2 \alpha_2 \rho_{A_2} \Delta h_2 + k_3 \alpha_3 \rho_{A_3} \Delta h_3. \quad (12)$$

329 Here,  $\rho_s$  is the bulk density described as the sum of the constituents ( $A_1$ ,  $A_2$  and  $A_3$ ) and products ( $C_2$  and  
 330  $C_3$ ) densities as:

$$\rho_s = \alpha_1 \rho_{A_1} + \alpha_2 (\rho_{A_2} + \rho_{C_2}) + \alpha_3 (\rho_{A_3} + \rho_{C_3}) \quad (13)$$

331 where,  $C_{p_s}$  and  $\lambda_s$  are respectively the thermal capacity and conductivity of the wood sample.

332 For the resolution of Eq. 11, it was assumed that at  $t=0$ ,  $T=T_0$ , and that at  $t > 0$ , on the exposed side of  
 333 the sample ( $x=0$ ), the heat balance for the control volume with thickness ( $\Delta_x$ ) is as follows:

$$\frac{\partial}{\partial t} [T(\rho_s C_{p_s})] \Big|_{x=0} = \left( \alpha_{abs} q_e'' - q_{loss1}'' - \lambda_s \frac{\partial T}{\partial x} \right) / \Delta_x + Q_r'' \quad (14)$$

334 where  $q_{loss1}''$  is the heat balance of the control volume defined by:

$$q_{loss1}'' = \sigma \varepsilon (T_s^4 - T_0^4) + h (T_s - T_0) \quad (15)$$

Table 4: Values and correlations of thermophysical parameters used in the model.

Property	Correlation/Value	Ref.
Thermal conductivity ( $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )	$T < 200 \text{ }^\circ\text{C}$ , $\lambda_{spruce} = 0.102$	Measured
	$T > 200 \text{ }^\circ\text{C}$ , $\lambda_{spruce} = 0.102 + 1.2 \cdot 10^{-6}(T - 473)^2 + 3.7 \cdot 10^{-9}(T - 473)$	Optimised
	$T < 200 \text{ }^\circ\text{C}$ , $\lambda_{beech} = 0.138$	Measured
	$T > 200 \text{ }^\circ\text{C}$ , $\lambda_{beech} = 0.138 + 1.06 \cdot 10^{-6}(T - 473)^2 + 6.42 \cdot 10^{-9}(T - 473)$	Optimised
Specific heat ( $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ )	$C_{pwood} = 1112 + 4.85 \cdot (T - 273)$	[55]
	$C_{pchar} = 808.9 + 0.93 \cdot (T - 273)$	[56]
Density ( $\text{kg} \cdot \text{m}^{-3}$ )	$\rho_{spruce} = 360$	Measured
	$\rho_{beech} = 600$	Measured
Emissivity	$\varepsilon = 0.83$	[41]
Convective coefficient ( $\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ )	$h = 10$	[57]
Absorptivity	$\alpha_{abs} = \varepsilon = 0.83$	[41]
Reaction heat ( $\text{kJ} \cdot \text{kg}^{-1}$ )	$\Delta h_i = -100$	[54]

Moreover, for  $t > 0$ , at the back surface ( $x=L$ ) another heat balance for the control volume with a thickness of ( $\Delta_x$ ) is established:

$$\frac{\partial}{\partial t} [T(\rho_s C_{p_s})] \Big|_{x=L} = \left( \lambda_s \frac{\partial T}{\partial x} - q_{loss2}'' \right) / \Delta_x + Q_r'' \quad (16)$$

where  $q_{loss2}''$  is the heat losses by radiation and convection from the back surface and characterized by the following relation:

$$q_{loss2}'' = \sigma \varepsilon (T_b^4 - T_0^4) + h (T_b - T_0) \quad (17)$$

During wood pyrolysis, its thermo-physical properties such as thermal conductivity, specific heat, and density, change. The density of the sample was easily measured and then the variation in sample density was calculated by the model. The average initial density of the virgin spruce and beech samples was found to be 360 and 600  $\text{kg} \cdot \text{m}^{-3}$  respectively. In contrast, it was difficult to obtain the variation of the thermal properties of wood (thermal conductivity and specific heat) over large temperature ranges ( $> 200 \text{ }^\circ\text{C}$ ). In fact, above 200  $^\circ\text{C}$ , the properties of the original material are subjected to a large accompanying chemical reactions, and there are practical difficulties in determining material properties. Therefore, a wide range of different thermo-physical properties of wood were used in the literature. In addition, there is no clear trend in how the thermophysical properties vary in the modelling. Therefore, it was suggested that they should be chosen in such a way that the modelling results fit the experimental data well [24].

Fig. 14 shows the variations of the specific heat capacity of wood and char as a function of temperature reported in the literature. In most previous modelling studies, the heat capacity of wood and char were modelled as a linear function of temperature. In our case, the specific heat capacity of wood ( $C_{pwood}$ ) and char ( $C_{pchar}$ ) was supposed to vary according to the relations of Wenzl *et al.* [55] and Anca-Couce *et al.* [56] respectively. The specific heat capacity of the wood sample was then assumed to vary linearly between wood and char depending on the conversion factor  $\eta$ , the ratio between the current and initial density ( $C_{p_s} = (1 - \eta) \cdot C_{pwood} + \eta \cdot C_{pchar}$ ). It is worth mentioning that the choice of the specific heat of wood and

356 char are not the most sensitive parameters affecting the accuracy of the model, as reported by Haberle [24].  
 357 For thermal conductivity, Di Blasi [25] in their extensive review on the modelling of chemical and physical

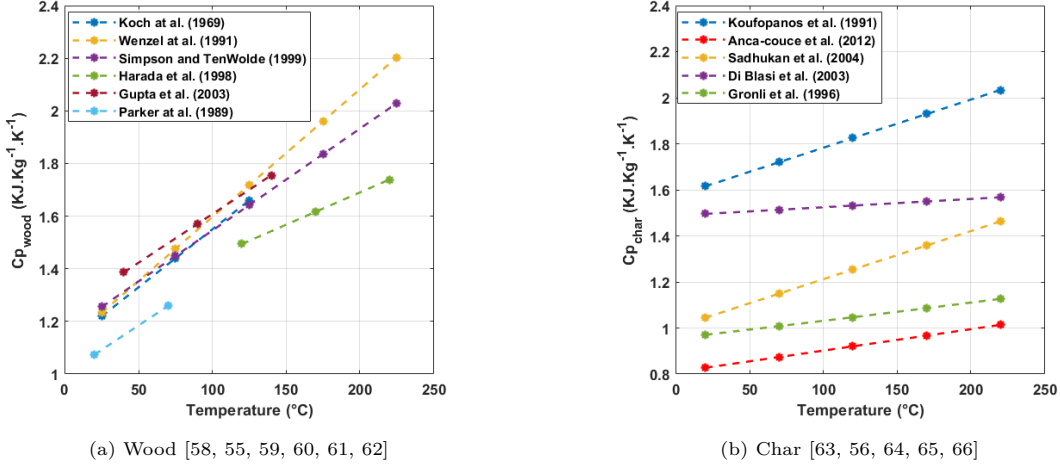


Figure 14: Specific heat capacities of wood and char available in literature.

357

358 processes of wood and biomass pyrolysis reported that among the wood properties, this property causes the  
 359 highest sensitivity of the model predictions. In the literature, thermal conductivity was assumed to be mainly  
 360 temperature dependent [60, 67]. In the present study, the thermal conductivity used was defined as follows:

- 361 1. Below 200 °C: the thermal conductivity of dry spruce and beech wood was measured in the laboratory  
 362 using the hot wire method and was found to be  $0.102$  and  $0.138 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  respectively [68].
- 363 2. Above 200 °C: the thermal conductivity of spruce and beech was assumed to vary as a function of  
 364 temperature as follows:

$$\lambda_{spruce} = 0.102 + a \cdot (T - 473)^2 + b \cdot (T - 473) \quad (18)$$

365

$$\lambda_{beech} = 0.138 + c \cdot (T - 473)^2 + d \cdot (T - 473) \quad (19)$$

366 Where  $a$ ,  $b$ ,  $c$  and  $d$  are four constants to be estimated. An inverse method was applied to the mass loss  
 367 measurements obtained from the cone calorimeter tests at  $38$  and  $49 \text{ kW} \cdot \text{m}^{-2}$  simultaneously using this  
 368 model. The Levenberg-Marquardt algorithm was used to minimise the following objective function:

$$E_r = \sum_{i=1}^X (m_{num}(i) - m_{exp}(i))^2 \quad (20)$$

369 Table 4 gives the thermal conductivity obtained by optimisation and the other properties used in the model.  
 370 Fig. 15 shows the thermal conductivity of spruce and beech wood from the current study side by side with the  
 371 available thermal conductivity from previous studies. For both species, the thermal conductivity increases  
 372 with temperature, which is quite logical. The thermal conductivity of beech is higher than that of spruce,

373 which is quite satisfactory taking into account the difference in density between the two species. Fig. 15 also  
 374 shows the large discrepancies in the thermal conductivity values used in the literature.

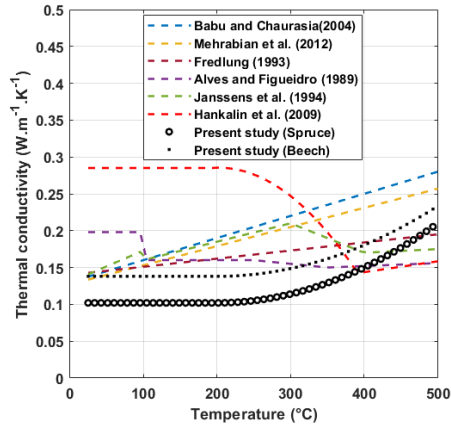


Figure 15: Thermal conductivity as a function of the temperature [69, 70, 71, 72, 73, 74].

375 Moreover, the emissivity of the wood surface was measured by Terrei *et al.* [41] and found to be 0.83.  
 376 The value for the convective coefficient of the solid surface was taken as  $10 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$  [57]. The heat and  
 377 mass conservation equations were numerically solved using a finite volume method written in a MATLAB<sup>®</sup>  
 378 code. The model allows the calculation of the temperature distributions within the sample, the mass loss  
 379 and the mass loss rate per unit area (MLRPUA).

#### 380 4. Results and discussion

381 This section presents the experimental and numerical results obtained at the cone calorimeter scale. Fig.  
 382 16 and Fig. 17 show the comparison between experimental and numerical temperatures at different depths  
 383 within spruce and beech wood samples respectively during their decomposition in front of the cone calorimeter  
 384 at  $38$  and  $49 \text{ kW} \cdot \text{m}^{-2}$ . It can be noticed that the experimental and predicted in-depth temperatures are  
 385 in good agreement for both species and heat fluxes. Although, the temperature predictions at depth (*i.e.*  
 386 from  $8 \text{ mm}$ ) were better than those near the surface. For  $38 \text{ kW} \cdot \text{m}^{-2}$ , it can be seen that the calculated  
 387 temperatures close to the surface for both species fit well the experimental data below  $400 \text{ }^\circ\text{C}$ . Above this  
 388 temperature, the simulation tends to underestimate the experimental evolution of near-surface temperatures.  
 389 In contrast, the simulation predicts very well the temperature evaluation in large depths. For tests at  $49$   
 390  $\text{ kW} \cdot \text{m}^{-2}$ , the simulation tends to slightly overestimate the experimental near-surface temperatures below  
 391  $500 \text{ }^\circ\text{C}$  for both species. Beyond this value, the simulation underestimates the experimental data. As for  
 392  $38 \text{ kW} \cdot \text{m}^{-2}$ , the model predicts very well the temperature evolution from  $8 \text{ mm}$ . In general, the numerical

393 results are in good agreement with the experimental results for low temperatures ( $< 350$  °C). For higher  
394 temperatures, and especially near to the exposed surface, there is some bias. This bias mainly caused by the  
395 low accuracy of measurements during the conversion of wood into char. As the wood undergoes pyrolysis  
396 and transforms into char, its porosity increases, leading to decreased thermal contact between the material  
397 and the thermocouple. Additionally, the ignorance of the effects of the volume shrinkage and cracks in this  
398 model could also be another source of the bias. However, the numerical temperatures were quite satisfactory.

399 Fig. 18 and Fig. 19 present the comparison between the mass loss and the Mass Loss Rate Per unit  
400 Area (MLRPUA) as a function of the time obtained by the model and those obtained from experiments  
401 performed at  $38$  and  $49$   $\text{kW} \cdot \text{m}^{-2}$  for spruce and beech wood respectively. It can be noticed that there is a  
402 good agreement between the calculated and the experimental results for both species, whatever the heat flux.  
403 The performance of the model was evaluated by calculating the NRMSE (Eq. 10), between the experimental  
404 and predicted mass loss. For spruce wood, the NRMSE is  $1.5$  and  $3.8$  % for  $38$  and  $49$   $\text{kW} \cdot \text{m}^{-2}$  respectively.  
405 For beech wood, the NRMSE is  $3.2$  and  $0.7$  % for  $38$  and  $49$   $\text{kW} \cdot \text{m}^{-2}$  respectively. Regarding the MLRPUA  
406 for both species, the numerical and experimental results are in good agreement for the quasi steady state.  
407 However, the numerical peak of the MLRPUA is overestimated at the beginning, especially for spruce. This  
408 bias may be due to an initial overestimation of temperatures from the near-surface thickness. To summarize,  
409 the model predict well the temperature profiles inside wood, the mass loss and the mass loss rate at the scale  
410 of the cone calorimeter. An additional experiment was conducted using a different heat flux of  $25$   $\text{kW} \cdot \text{m}^{-2}$   
411 with samples of spruce and beech wood. The results of this experiment were not used for optimising the  
412 model parameters. Instead, they were employed for model validation. The purpose of this experiment was to  
413 verify the predictive capability of the model and assess its performance when applied to conditions beyond  
414 those used for parameter optimisation. Fig. 20 shows the efficiency of the model in predicting mass loss and  
415 MLRPUA obtained from the experiments conducted at  $25$   $\text{kW} \cdot \text{m}^{-2}$  for spruce and beech wood. For spruce,  
416 the NRMSE is  $4.9$  %, while for beech, it is  $2.2$  %. So, despite the results under a heat flux of  $25$   $\text{kW} \cdot \text{m}^{-2}$   
417 not being utilised for optimising the model parameters, the model demonstrates its efficiency in predicting  
418 experimental mass loss and normalised mass loss rates for beech and spruce wood under this flux.  
419 These results validate the kinetic model developed at the micro scale in this study and show that the  
420 multi-scale approach is appropriate to model the wood pyrolysis at large scales.

## 421 5. Conclusion

422 In this work, the thermal degradation of beech and spruce wood has been investigated throughout the  
423 multi-scale approach. At the micro scale, the thermal degradation of spruce and beech wood was studied  
424 using a thermogravimetric analyser at five heating rates ( $5$ ,  $10$ ,  $20$ ,  $30$  and  $40$   $\text{K} \cdot \text{min}^{-1}$ ) under an inert



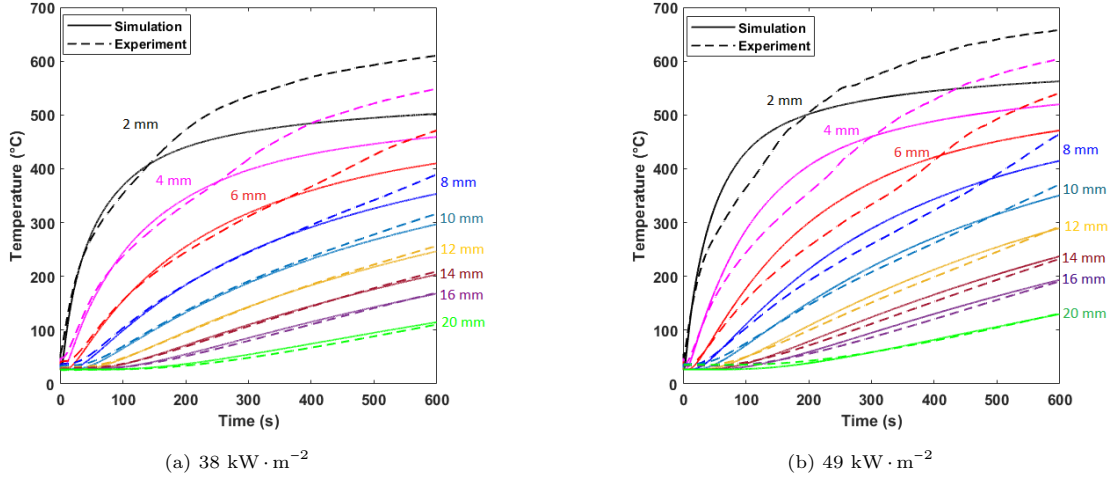


Figure 16: Comparison between the experimental and the numerical in-depth temperatures of spruce wood for 38 and 49  $\text{kW} \cdot \text{m}^{-2}$  heat fluxes.

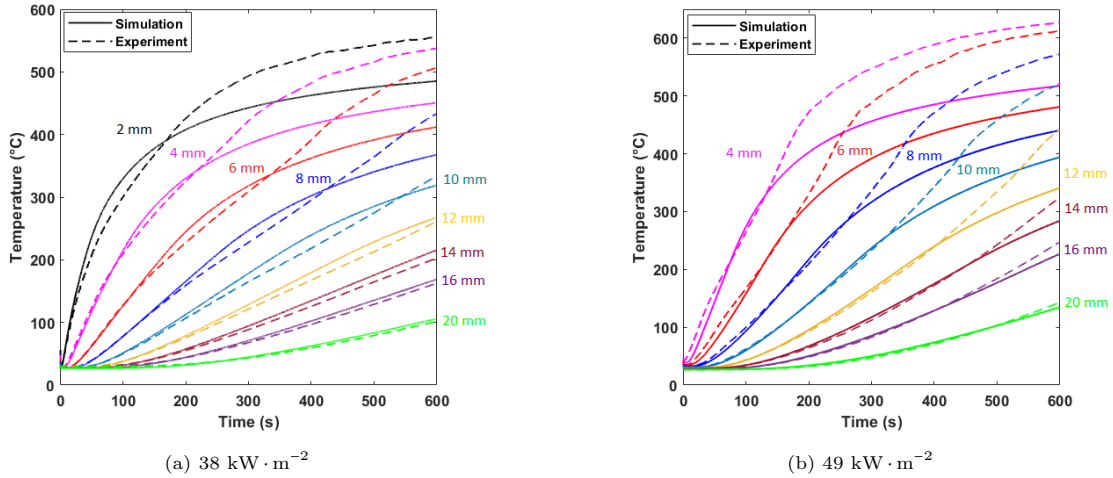
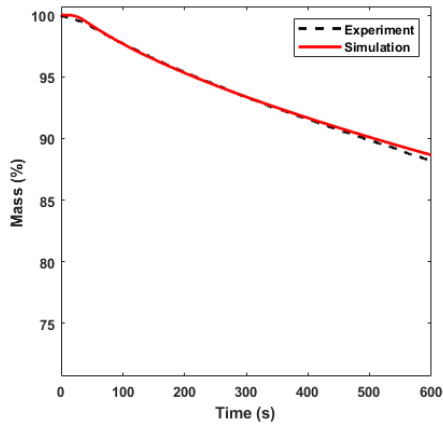
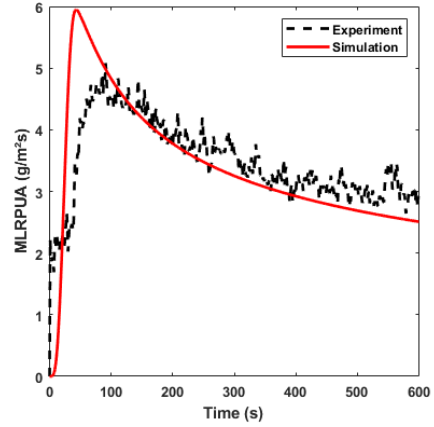


Figure 17: Comparison between the experimental and the numerical in-depth temperatures of beech wood for 38 and 49  $\text{kW} \cdot \text{m}^{-2}$  heat fluxes.

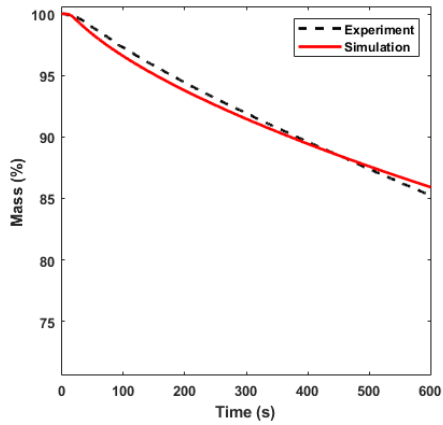
425 atmosphere. The results led to a suggested wood thermal degradation mechanism with global multi-reactions.  
 426 The associated kinetic parameters for both species were calculated by using the least squares method. The  
 427 results showed efficient predictions in agreement with experimental mass loss and mass loss rate for different  
 428 heating rates. At the bench scale, the model was completed by adding a heat and mass transfer model to  
 429 the kinetic mechanism. At this scale, the model was validated by comparing the predicted results with those  
 430 obtained from cone calorimeter tests. These tests were performed in a specific chamber, which was designed  
 431 to perform tests in an inert atmosphere. The wood samples (beech and spruce) were exposed to three heat  
 432 fluxes (25, 38 and 49  $\text{kW} \cdot \text{m}^{-2}$ ) for 600 s. The results predicted by the model were in good agreement  
 433 with the experimental measurements. Our perspective for the model developed in this study is to couple it



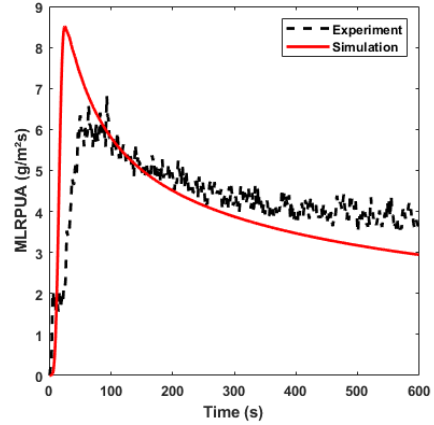
(a)  $38 \text{ kW} \cdot \text{m}^{-2}$



(b)  $38 \text{ kW} \cdot \text{m}^{-2}$



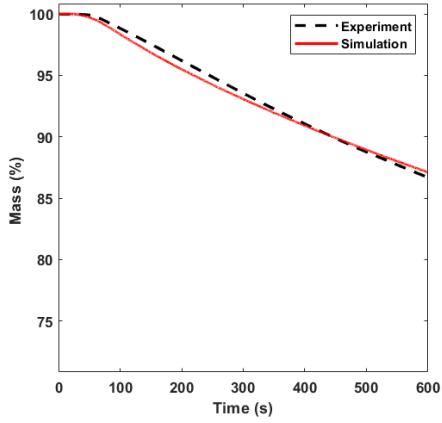
(c)  $49 \text{ kW} \cdot \text{m}^{-2}$



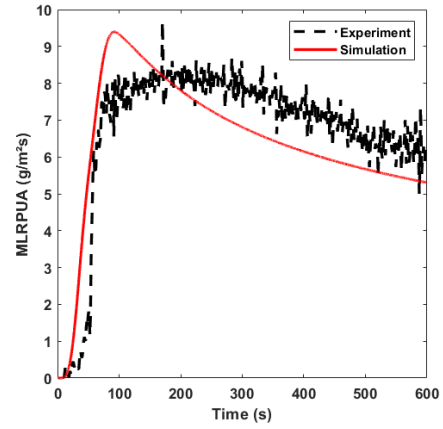
(d)  $49 \text{ kW} \cdot \text{m}^{-2}$

Figure 18: Comparison between the experimental and the numerical mass loss and MLRPUA for spruce wood for 38 and 49  $\text{kW} \cdot \text{m}^{-2}$  heat fluxes.

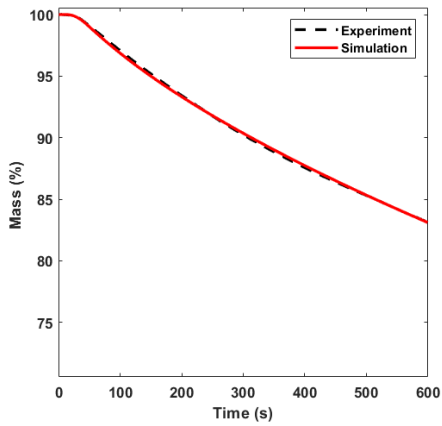
434 with a kinetic model of char oxidation as a function of oxygen concentration in order to model the thermal  
 435 degradation of wood in an oxidative atmosphere and at different intermediate oxygen concentrations.



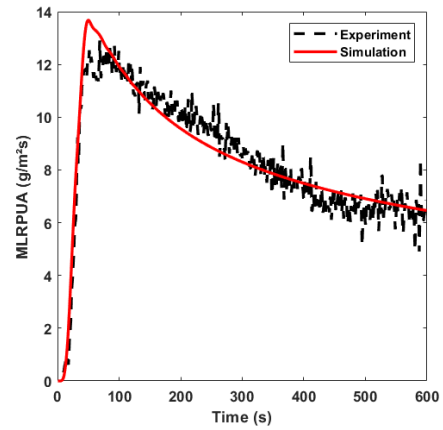
(a)  $38 \text{ kW} \cdot \text{m}^{-2}$



(b)  $38 \text{ kW} \cdot \text{m}^{-2}$

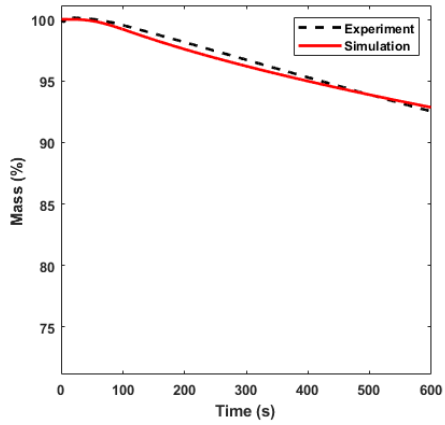


(c)  $49 \text{ kW} \cdot \text{m}^{-2}$

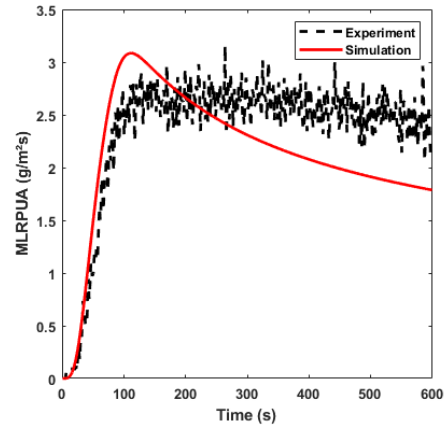


(d)  $49 \text{ kW} \cdot \text{m}^{-2}$

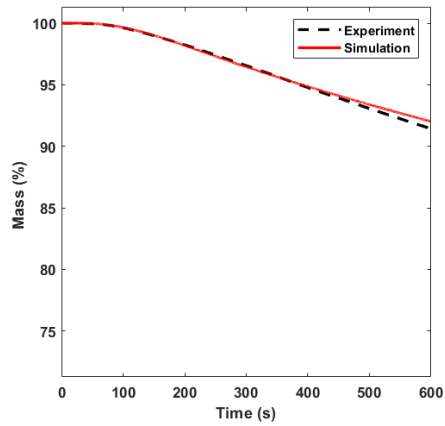
Figure 19: Comparison between the experimental and the numerical mass loss and MLRPUA for beech wood for 38 and 49  $\text{kW} \cdot \text{m}^{-2}$  heat fluxes.



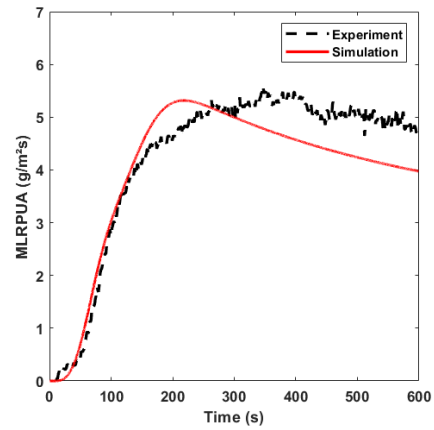
(a) Spruce



(b) Spruce



(c) Beech



(d) Beech

Figure 20: Comparison between the experimental and the numerical mass loss and MLRPUA for spruce and beech wood for  $25 \text{ kW} \cdot \text{m}^{-2}$  heat flux.

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