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ORIGINAL ARTICLE



## Influence of the heating rate on the thermodegradation during the mild pyrolysis of the wood

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### ABSTRACT

Wood constitutes a renewable and sustainable material, which raw utilization is limited because of the weak durability and dimensional instability. To improve shortcomings, a mild pyrolysis in the temperature range 200–300°C in oxygen-free atmosphere has been used for years. However, a significant lack of knowledge persists in the initial stage of the process. The purpose of this study is to investigate the influence of the heating rate on the wood thermodegradation pathway and the impact of this parameter on the conferred properties. The heating rate influences the total duration of the process and is strongly related to the power capacity of the heater. Experiments of thermal degradation were carried out at two different scales. Thermogravimetric analysis on wood powder allows to better understand the degradation scheme of biomass polymers. Experiments in a semi-industrial pilot-scale system on wood boards allow to transpose the process towards real conditions. Similar to industry practices, the heating rate has been varied between 0.2 and 1.0°C min<sup>-1</sup>. The results reveal noticeable differences in the degradation kinetics. A numerical tool has been tested to predict the advancement of the thermo-modification process. The observations are of interest for industrial applications.

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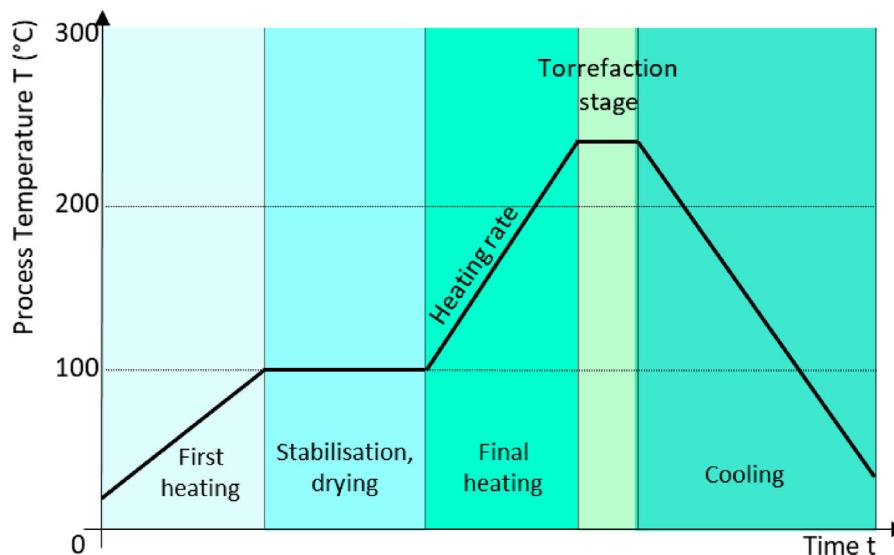
Heating rate; heat treatment; mass loss; mild pyrolysis; wood

## 1. Introduction

Wood is increasingly used in construction and furniture. However, even if the wood is a noble material, unprotected wood possesses several shortcomings, such as low fungal resistance, dimensional instability and hydrophilic character, resulting in a varying moisture content. Wood utilization requires the upgrading of its natural properties. In the past, chemical treatments have been applied to enhance wood's quality, some of them including components damaging for human health and the environment. Nowadays, "zero biocides directive" leads to the development of alternative methods to substitute chemical impregnation. Wood heat treatment by mild pyrolysis is a thermal modification process with a great ecological and economical importance which addresses the weaknesses of the raw material (Shi et al. 2007, Esteves and Pereira 2009, Chen et al. 2015, Candelier et al. 2016, Kumar et al. 2017, Chen et al. 2018). The method consists of holding the wood at temperatures in the 200–240°C range under inert conditions. The obtained product is referred to as heat-treated wood, thermally modified wood, torrefied wood, etc. Under the effect of the temperature, some biomass components are degraded, leading to a mass loss (ML), representative of the progress of the transformation. It has been reported in the literature that when

thermodegradation ML achieves 10–15% (Nguila et al. 2009; Chaouch et al. 2010) the process confers suitable new properties, such as a hydrophobic characteristic (Kumar et al. 2017, Chen et al. 2018), dimensional stability or good fungal resistance (Esteves and Pereira, 2009; Candelier et al. 2016). The increased energy density (Chen et al. 2015) is also an interesting characteristic, considering that, at the end of the life, heat-treated wood could be used for energy production by combustion, pyrolysis or gasification without the release of toxic molecules generated by added chemical products (paint, preservative, etc.).

Historically, since the 1980s, many technologies for wood thermochemical modification have been developed in Europe and all over the world. The most important processes implemented in Europe are Plato® (Netherlands), Thermo-wood® (Finland), and Retiwood (France). They vary with respect to operating conditions, heating media, and oven conception. Reviews on torrefaction processes and technologies were widely published (Bergman and Kiel 2005; Sun et al. 2011; Acharya et al. 2012) comparing the nature of the reaction in a low oxygen environment (nitrogen, steam, smokes, hot oil, pressurized water, vacuum), heating methods (convective vs. conductive), treatment intensity (temperature and residence time), and particle size (Militz 2002, Boonstra et al. 2007, Shi et al. 2007).



**Figure 1.** Temperature profile during the process of mild pyrolysis.

Each heat treatment process typically involves several stages that have been summarized in Figure 1. These stages are (1) the first heating to reach the stage of stabilization (for a temperature of approximately 100°C, the stabilization and drying stage take place to avoid cracks and other deformation of the wood), (2) the final heating to reach the target temperature (during this stage, the heating rate can be chosen), (3) the torrefaction stage (thermodegradation), and (4) cooling. The transition from one isothermal plate to another can be conducted with different heating rates. Their values depend on the objectives of the treatment (material production, energy pre-treatment), the heating process, the size of the wood board, etc. Recent studies reveal that this process parameter has an influence on the thermal degradation reactions (Neves et al. 2011; Collard and Blin, 2014; Bai et al. 2020). The degradation of wood polymers under the effect of the temperature is quantified by the ML. Previous studies have reported that ML is a good marker for the advancement of the thermal modification (Chaouch et al. 2010, Candelier et al. 2016, Lin et al. 2018) and have shown the strong relation between the ML and the final characteristics of the torrefied wood such as durability, dimensional stability, hydrophobic character, and mechanical properties.

This study is focused on the investigation of the influence of the heating rate on the biopolymer's degradation kinetics. The typical heating rate used in the industry to produce thermally modified wood is in the range of  $0.2\text{--}2.0\text{ }^{\circ}\text{C min}^{-1}$ , reaction temperatures are comprised between 180 and 240°C, and holding time lasts several hours to obtain a ML of 10–15% (Hakkou et al. 2006, Lin et al. 2018). In this study, heat treatment experiments were carried out under nitrogen at two different scales, (1) a thermogravimetric analyzer (TGA) treated wood powder and (2) a semi-industrial pilot-scale system operated with wood boards whose radial and transverse dimensions are close to those used in the industry. A hardwood species (Poplar – *Populus nigra*), common in European countries, with a low-cost value that needs to be

valorized, was chosen. The reaction temperature was 220°C. Several heating rates varying between 0.2 and  $1.0\text{ }^{\circ}\text{C min}^{-1}$  were applied. The mass yield curves as a function of time were recorded and analysed. A two-step reaction mechanism based on the Di Blasi and Lanzetta (1997) model was adopted to describe the dynamic ML. Experimental data provide information to fit the model's parameters. Model's equations were solved numerically by the commercial package MATLAB® software. Numerical results highlight the difference in the behavior according to the applied heating rate in the beginning of the process but show an encouraging accuracy to simulate the ML in the steady-state isothermal plate until the end of the treatment. The obtained results are relevant for the wood industry to estimate process duration and facilitate a business plan elaboration.

## 2. Materials and experiments

### 2.1. Material preparation

A hardwood species (poplar – *P. nigra*) was used in this study. Poplar is abundant in European forests but has low economic value. Mild pyrolysis is a way to upgrade its natural properties, improve the added value, and revive the local forest economy.

The basic characteristics of poplar wood (averaged density, chemical composition analysis, proximate analysis, elemental analysis) are determined and shown in Table 1. Averaged density was measured using a caliper ( $\pm 0.01\text{ mm}$ ) and a precision balance Scaltec SAC 51 ( $\pm 0.01\text{ g}$ ). Prior to each analysis, wood samples were dried in a convective oven at 105°C until mass stabilization. The chemical composition analysis was performed using the method developed by Milne et al. (1992) and Hames (2009).

In proximate analysis, volatile matter (E872-82) and ash (E1755) were measured and the fixed carbon (FC) content was calculated by difference ( $\text{FC\%} = 100\% \text{Ash\%} - \text{VM\%}$ ). The elemental analysis was conducted on a dry-ash-free basis

**Table 1.** The basic properties of raw poplar wood.

Poplar ( <i>Populus nigra</i> ) characterization	
Density (kg m <sup>-3</sup> )	324.00
Chemical composition analysis (wt%, dry basis)	
Hemicelluloses	22.54
Cellulose	50.11
Lignin	24.71
Extractives	2.63
Proximate analysis (wt%, dry basis)	
Volatile matter	84.75
Fixed carbon	14.71
Ash	0.54
Elemental analysis (wt%, dry basis)	
C	38.87
H	6.16
N	0.49
O (by difference)	54.48

by an elemental analyzer (PerkinElmer 2400 Series II CHNS/O). The weight percentages of C, H, and N were measured. The weight percentage of O was then calculated by difference, O (%) = 100–C–H–N.

*Samples for the thermogravimetric analysis:* Poplar samples were crushed with a grinder and sieved to particles of 0.5–1 mm diameter. The sieved wood samples were dried in an oven at 105°C for 24 h to provide a dry basis for analysis. Subsequently, the samples were placed in sealed plastic bags and stored at room temperature until experiments were carried out.

*Wood boards for semi-industrial pilot experiments:* The wood boards of poplar were cut into 60 cm<sup>3</sup> × 17 cm<sup>3</sup> × 2.2 cm<sup>3</sup> (length × width × thickness). Prior to experiments, the boards were dried in an oven at 105°C until mass stabilization.

## 2.2. Methodology

*Thermogravimetric analysis and procedure:* The thermodegradation behavior of poplar hardwood was analysed by a thermogravimetric analyzer (TGA 2 (LF), Mettler Toledo). The instantaneous weight of the sample over the course of analysis was detected and recorded at a frequency of 2 Hz. To ensure the quality of measurements and analyses, the temperature and weight in the TG were periodically calibrated using zinc (Zn), calibration weights, and sapphire glass, respectively. Prior to the experiments, the powdered woody samples were dried under 105°C in the oven for 24 h.

In Europe, the industries producing thermally modified wood operate in the temperature range of 200–240°C till reaching a controlled ML of treated wood at 8–10 wt% (Esteves et al. 2009, Sandberg and Kutnar, 2016). For this reason, the heat-treated experiments of woods were performed at 220°C. The temperature increased from room temperature to 105°C at a heating rate of 0.2°C min<sup>-1</sup>. An isothermal plate of 120 min is maintained to achieve mass stabilization in order to remove the moisture absorbed during the experiment's setting, and precisely determine the anhydrous woody mass. Anhydrous mass is then recorded. Subsequently, the temperature is raised to 170°C at the same heating rate and held for 120 min, like the industrial processes (Pétrissans et al. 2014). Finally, the temperature in the reactor is increased to 220°C at a heating rate of 0.2,

0.5, and 1.0°C min<sup>-1</sup>, respectively, and held for 1000 min. The treatment time of 1000 min was longer than that in industrial practice but it was necessary to observe detailed ML dynamics of the wood samples.

In each run, approximately 25 mg of sample were loaded into an Al<sub>2</sub>O<sub>3</sub> crucible (600 µL) and loaded onto the TG furnace. N<sub>2</sub> at a flow rate of 100 mL min<sup>-1</sup> was used as the carrier gas to provide an inert atmosphere.

The ML and *Solid yield* of a wood sample are expressed as follows:

$$ML = \frac{M_i - M_{\text{treated}}}{M_i} \quad (1)$$

$$\text{Solid yield} = \frac{M_{\text{treated}}}{M_i} \quad (2)$$

where  $M_i$  is the initial weight of the sample (dry basis) and  $M_{\text{treated}}$  is the instantaneous weight of the sample during the treatment. To ensure the repeatability of the results, all TGA were triplicated and the obtained difference was less than 2 wt%.

*Experimental pilot-scale reactor and procedure:* The experimental system for wood board heat treatment is represented in Figure 2. It can be considered as composed of a wood heat treatment unit, a control, and a recording unit.

In the wood heat treatment unit, the semi-industrial scale reactor is made of stainless steel with an outside diameter of 32 cm and length of 86.5 cm. Two boards of poplar with similar size are treated in each experiment. Heating is performed by conduction between three heating plates (length = 65 cm and width = 18 cm). A mass sensor connected to a computer is used to record the dynamic mass of wood boards during the experiments. The mass sensor's resolution is 0.1 g. K-type thermocouples are installed inside the heating plates and in the center of the wood samples. In the control and recording unit, a computer with a monitoring software is adopted to control and record the sample's temperature and mass during the treatment.

The temperature setting of the reactor is identical to the one used in the TGA. It has to be noted that 1.0°C min<sup>-1</sup> is the maximal heating rate for this device. The initial recorded point of all experiments began at 50°C for providing the basis of heat treatment, and the entire process took 2130 min. To ensure data accuracy, the instruments were calibrated prior to performing experiments. Moreover, the experiments of the present work were repeated at least twice. The ML data displayed were the average values, and the relative error of the ML between the two experiments was below 5%.

## 2.3. Model formulation

Thermal degradation of biomass during mild pyrolysis is a complex set of decomposition and polymerization reactions involving the main polymers: hemicelluloses, cellulose, and lignin (Brosse et al. 2010; Candelier et al. 2013; Lin et al. 2018). The kinetic analysis gives an insight into the thermal decomposition behavior of wood during the heat treatment (Bach and Chen, 2017; Wang et al. 2017). Globally, there are two basic ways to model wood degradation: using non-

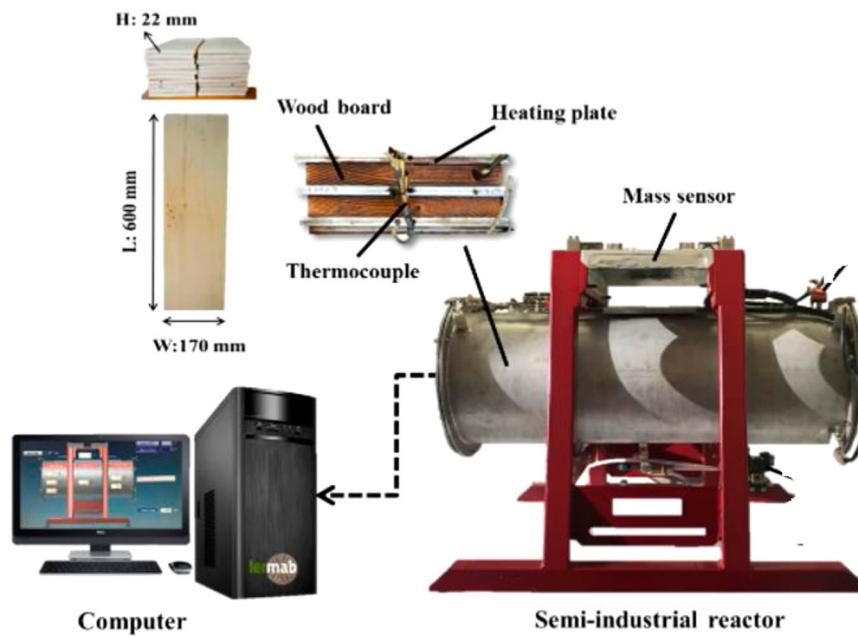


Figure 2. A schematic of the set-up system for wood heat treatment in vacuum.

isothermal or isothermal kinetics. For both of them, different models have been developed, such as one-step model (or called model-free) (Chen et al. 2014), two-step model (Chen et al. 2015), multi-step model (Cavagnol et al. 2013), and multi-component model (Bach and Chen, 2017; Wang et al. 2017).

The two-step kinetic model developed by Di Blasi and Lanzetta (1997) was chosen in this study because of its reliability, good results in the mild pyrolysis temperature range, and short calculation time. The two-step reaction scheme and the identification of the model's parameters have been demonstrated in detail in a previous publication (Silveira et al. 2018) and are summarized in Figure 3. Raw wood (A) is considered a homogeneous particle and is converted into a solid intermediate (B) and volatiles ( $V_1$ ) during the first step of the reaction scheme. Intermediate B then decomposes into solid residue C and volatiles  $V_2$ . At any moment, the mass of solid product is identified by the sum of masses of A, B, and C, while the total mass of volatiles is described by the sum of  $V_1$  and  $V_2$  (Bates and Ghoniem, 2012; Bach et al. 2016). The four reaction rate constants ( $k_1$ ,  $k_{V1}$ ,  $k_2$ , and  $k_{V2}$ ) are determined by fitting predicted curves to dynamic TGA mass yield. Assuming that the two steps of the reaction are first order, the rate equations for solids (A, B, and C) and volatiles ( $V_1$  and  $V_2$ ) are expressed as (Bates and

Ghoniem, 2012)

$$\frac{dm_A}{dt} = -m_A \times (k_1 + k_{V1}) \quad (3)$$

$$\frac{dm_B}{dt} = k_1 \times m_A - m_B \times (k_2 + k_{V2}) \quad (4)$$

$$\frac{dm_C}{dt} = k_2 \times m_B \quad (5)$$

$$\frac{dm_{V1}}{dt} = k_{V1} \times m_A \quad (6)$$

$$\frac{dm_{V2}}{dt} = k_{V2} \times m_B \quad (7)$$

In these equations,  $m_i$  is the mass of any pseudo-component ( $i = A, B, C, V_1$ , and  $V_2$ ). The rate constants obey the Arrhenius law:  $k_i(T) = A_i \exp\left(\frac{-Ea_i}{RT}\right)$ , in which  $A_i$ ,  $Ea_i$ ,  $R$ , and  $T$  are the pre-exponential factor ( $\text{mol}^{-1} \text{ s}^{-1}$ ), the activation energy ( $\text{J mol}^{-1}$ ), the universal gas constant ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ), and the absolute temperature (K), respectively.

Kinetic parameters are determined numerically using MATLAB<sup>®</sup> by identification with the experimental data over the whole curve. The solver of MATLAB<sup>®</sup> software is based on the Nelder–Mead optimization algorithm and is applied to minimize the root mean square of the difference between experimental and calculated mass yields, as expressed in the following:

$$\text{diff}^{(T)} = \sqrt{\sum_t \left( \frac{(Y_{sj}^{(T)})_{\text{exp}} - (Y_{sj}^{(T)})_{\text{cal}}}{(Y_{sj}^{(T)})_{\text{cal}}} \right)^2} \quad (8)$$

where  $(Y_{sj}^{(T)})_{\text{exp}}$  and  $(Y_{sj}^{(T)})_{\text{cal}}$  are the experimental and calculated solid yield at the data point  $j$ .

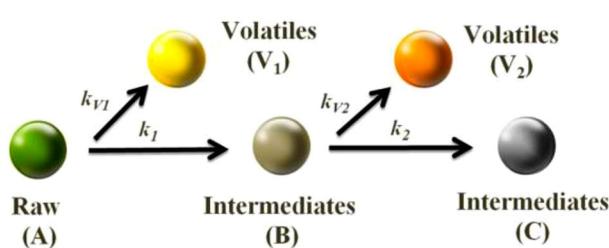


Figure 3. A schematic of the two-step kinetic model.

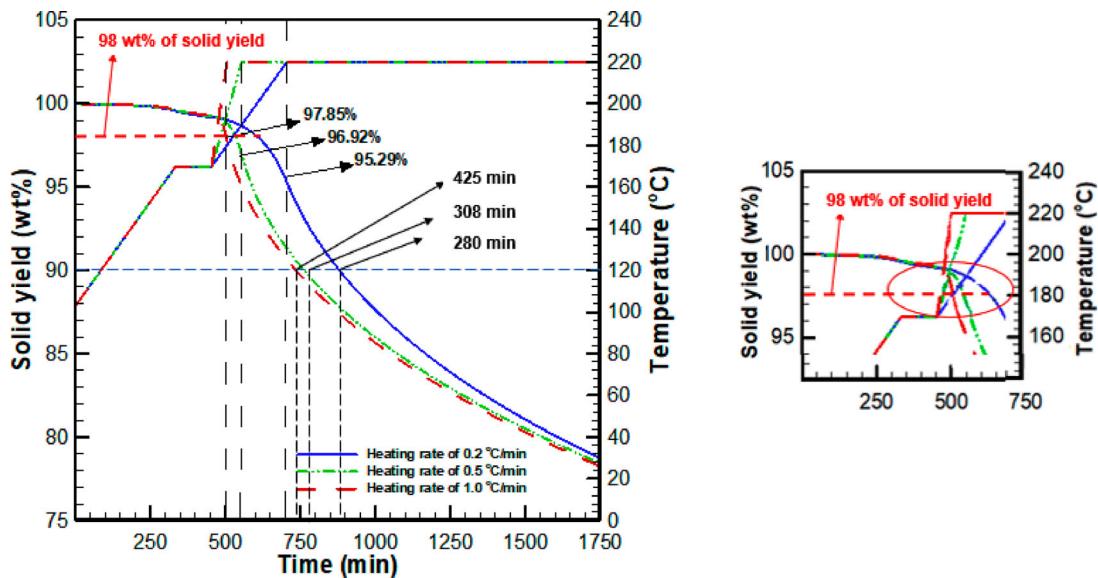


Figure 4. The poplar treated under heating rate of 0.2, 0.5, and  $1\text{ }^{\circ}\text{C min}^{-1}$  in the TGA.

### 3. Results and discussion

#### 3.1. Comparison of ML of poplar among three heating rates in TGA

The TGA results of powdered poplar sample treated under the heating rate of 0.2, 0.5, and  $1\text{ }^{\circ}\text{C min}^{-1}$  are displayed in Figure 4. The main differences among the three curves are in the heating stage from 170 to 220°C. The MLs throughout the post-drying intermediate heating, the duration to achieve the reaction isothermal plate, and the duration of the stationary isothermal torrefaction stage to achieve the target of 10% ML are summarized in Table 2 for all three cases. As it can be expected, the ML of powdered poplar in the intermediate heating is higher when treated with the lower heating rate in the TGA (4.71 ML% for  $0.2\text{ }^{\circ}\text{C min}^{-1}$ ), owing to its longer duration (200 min of difference between the three experiments). The results indicate that the sample treated with low-heating rate has sufficient time to degrade the extractives and light volatiles, and a part of hemicelluloses (Lin et al. 2019). The required duration of the isothermal stage is then slightly reduced (less than 1 h of difference). The total process duration of powdered wood remains more than 50% longer for the lowest heating rate.

On the temperature range between 170 and 220°C, it can be remarked that the shapes of the curves of different heating rates are slightly different (Figure 4). This observation suggests that thermochemical decomposition

reactions do not occur in the same way. It is not possible to achieve dynamic analyses of solid yield to follow the evolution of the wood composition. An indirect method has been proposed to better understand the thermal decomposition pathway. As basis for comparison, 98% of solid yield (2 wt% ML) was chosen. Time to reach this value was identified from experimental data. Thermogravimetric experiments were scheduled to reach the 2 wt% ML and samples were immediately pyrolysed until 800°C under nitrogen with a heating rate of  $20\text{ }^{\circ}\text{C min}^{-1}$ . The DTG was obtained as the derivative of each point of the TGA curve and plotted in Figure 5. The DTG curves are very similar. A weak shoulder at 300°C indicates the presence of hemicelluloses slightly higher for the faster heating rate ( $1.0\text{ }^{\circ}\text{C min}^{-1}$ ) where the residence time in this temperature range is shorter and hemicelluloses degradation is not complete.

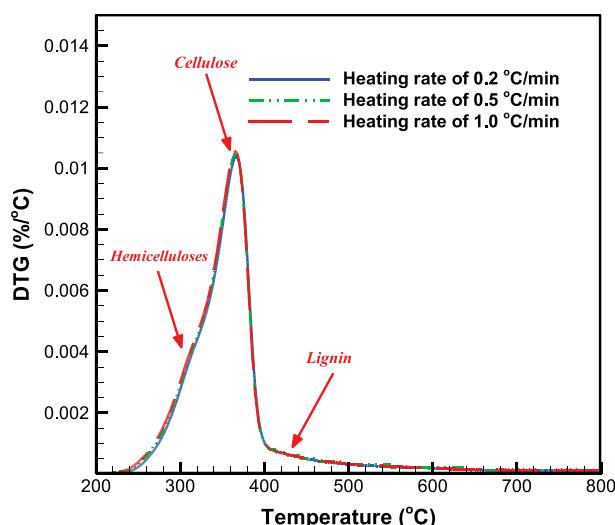


Table 2. The comparison of mass loss among three conditions in the TGA experiments.

Heating rate ( $^{\circ}\text{C min}^{-1}$ )	Duration (min)	Mass loss (%)	170–220°C	
			Time (min) to achieve 10% ML under 220°C	Total process duration (min)
0.2	250	4.71	175	425
0.5	100	3.08	208	308
1.0	50	2.15	230	280

Figure 5. Derivative thermodegradation analysis of pyrolysis of samples decomposed to 2 wt% ML under different heating rate.

Among the factors suggested to explain the differences in the 170–220°C range for the heating rates of 0.2, 0.5, and 1.0°C min<sup>-1</sup>, the values of activation energy for the cellulose pyrolysis reaction can be a probable one. The cellulose content in hardwood biomass is 39–54%, compared to hemicellulose (15–36%) and lignin (17–29%) (Chen et al. 2020). Therefore, observing the behavior of cellulose's pyrolysis is a lead to a better understanding of biomass degradation for hardwood. Observing experimental data, Chen et al. (2020) suggest that, for the pyrolysis of cellulose, a higher activation energy is needed when a small heating rate is applied. This corroborates the results found for the different heating rates, suggesting that at the lowest heating rate, more energy is needed for the cellulose pyrolysis reaction to occur. Thus, the time that the pyrolysis' decomposition starts at the heating rate of 0.2°C min<sup>-1</sup> is longer than the time that the reaction starts at the heating rates of 0.5 and 1°C min<sup>-1</sup>. This suggests that the lower heating rate creates conditions for slow pyrolysis at low-temperature pyrolysis reactions (Somerville and Deev 2020).

### 3.2. Comparison of ML of poplar boards among three heating rates in the pilot-scale reactor

Poplar boards were heat-treated in the pilot-scale reactor under heating rates of 0.2, 0.5, and 1.0°C min<sup>-1</sup>. The results are displayed in Figure 6 and show a similar tendency with the experiments conducted in the TGA. Compared to the ML of powdered poplar in TGA, the ML of poplar boards conducted in the pilot-scale reactor is lower. This can be explained first with the heat diffusion. The small particle samples have a good heat diffusivity whereas in the wood board, heat transfer is made by conduction from the heated surface to the sample's heart. Moreover, the wood powder offers a higher reaction surface to release the degraded volatiles. Furthermore, the isothermal durations required to reach 10% ML are shorter for poplar conducted in TGA due to the

**Table 3.** The mass loss comparison among three conditions in the pilot-scale reactor.

Heating rate (°C min <sup>-1</sup> )	170–220°C		Time (min) to achieve 10% ML under 220°C	Total process duration (min)
	Duration (min)	Mass loss (%)		
0.2	250	2.23	331	581
0.5	100	0.80	381	481
1.0	50	0.36	416	466

same reasons. In the case of the heating rate of 0.2°C min<sup>-1</sup>, the TGA has a shortest duration of 2.92 h to achieve 10% ML, which is almost 50% shorter than the results of pilot-scale reactor. This result is important for the development of the prediction tool to transpose the process to the industrial scale.

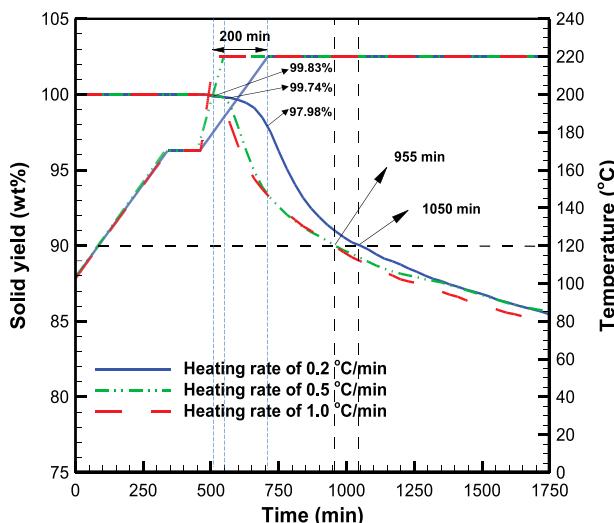
On the temperature profiles of the three heating rates, a significant difference of process is lying on the temperature range between 170 and 220°C. The comparison of ML between 170 and 220°C is calculated and given in Table 3. The lowest heating rate of 0.2°C min<sup>-1</sup> shows the highest ML of 2.23% in the heating-up zone similarly to the TGA experiments. The lower heating rate is also beneficial for heat conduction in the boards and the achievement of a thermal homogeneity. It may also enhance the thermodegradation under lower temperature and a longer duration. Consequently, in the zone foregoing the isothermal 220°C plateau, for heating rates of 0.5 and 1.0°C min<sup>-1</sup>, a lower ML is observed (0.80% and 0.36%, respectively). If the specific heat of the sample is assumed constant along the heat transformation process, then we could assume that the energy inputs from 170 to 220°C are the same for each heating rate. Thus, the results indicate that the high heating rate is more efficient for the wood heat treatment, which can save time and cost.

The isothermal duration required for each case to reach 10% ML is calculated and shown in Table 3. As the heating rate increases from 0.2 to 1.0°C min<sup>-1</sup>, the required durations are 5.52, 6.35, and 6.93 h, respectively. The results show that the lower heating rate can reach the desired ML in a shorter time than the higher heating rates. This once again indicates that the low-heating rate is more time-saving in the wood heat treatment. The possible reasons are already mentioned above. The ML at the end of the process for the three cases are 15.33%, 15.93%, and 16.39%, respectively, for the heating rate of 0.2, 0.5, and 1.0°C min<sup>-1</sup> (Figure 6).

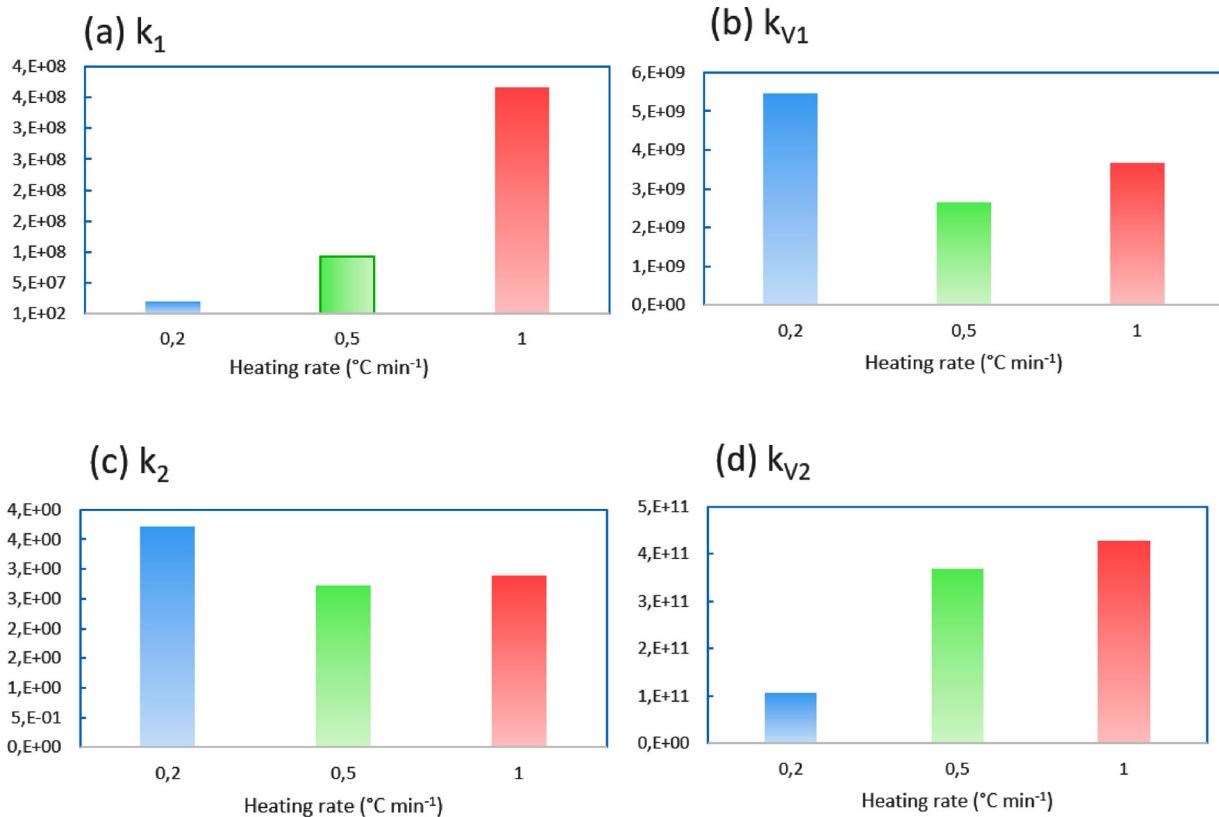
Therefore, the wood heat treatment with a low-heating rate of 0.2°C min<sup>-1</sup> is a promising process for the industrial application. However, the differences among the wood properties are still under investigation. It will be clearer after the mechanism and wood properties are explored in further planned studies.

### 3.3. Numerical analyses

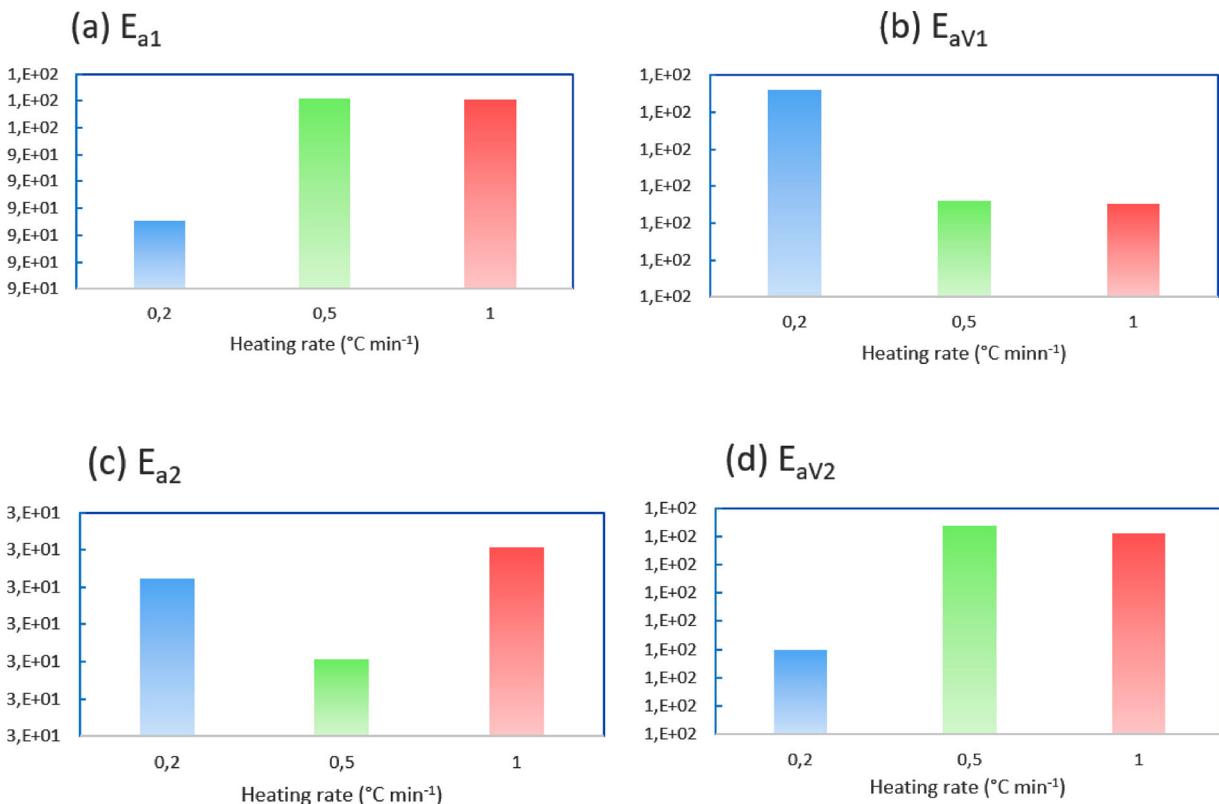
Kinetic parameters are determined for each heating rate individually. Pre-exponential factors  $A_i$  and activation energies  $E_{ai}$  were initialized using data from the literature



**Figure 6.** The temperature profiles and recorded solid yields under heating rate of 0.2, 0.5, and 1°C min<sup>-1</sup> in the pilot-scale reactor.



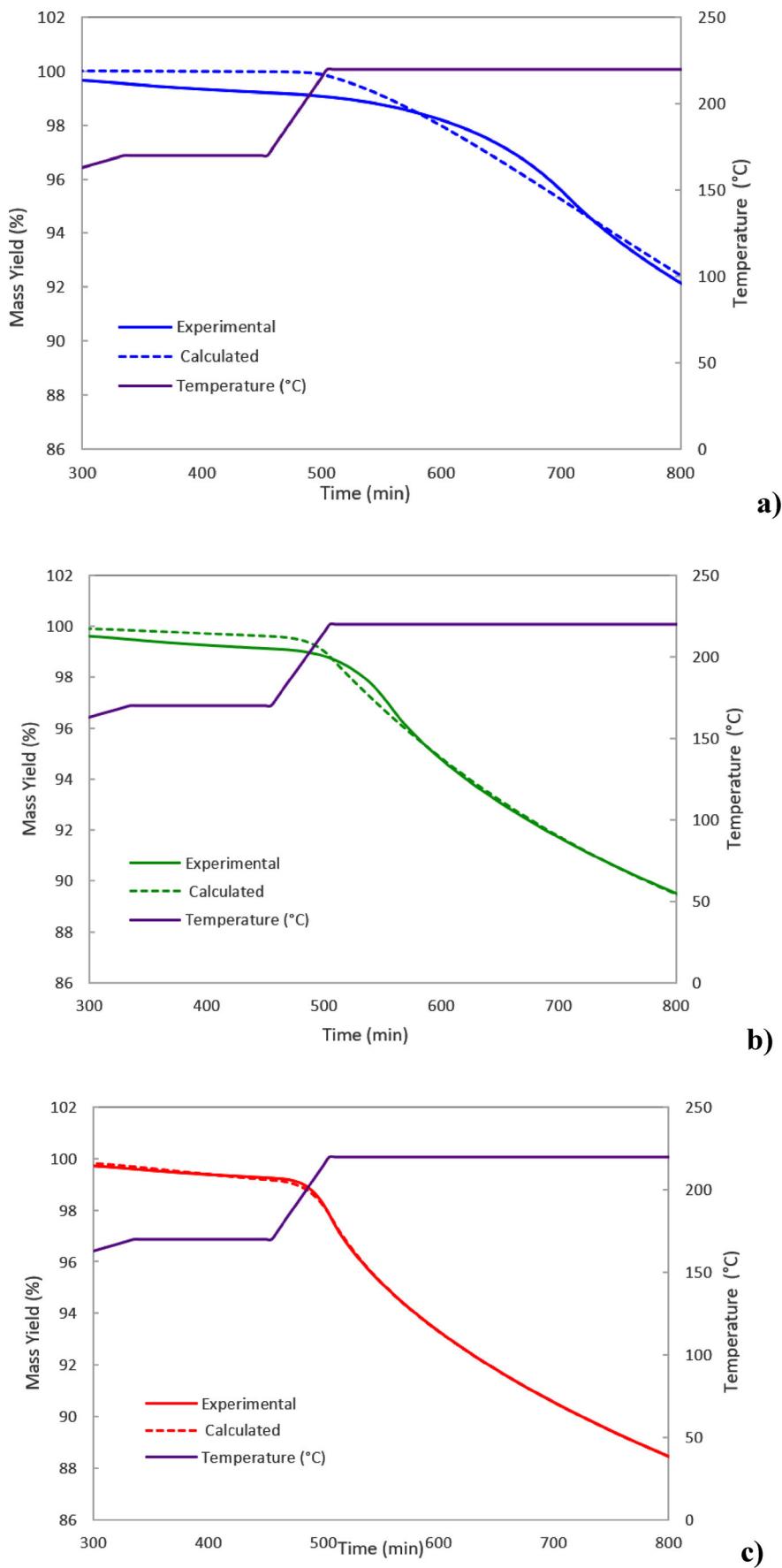
**Figure 7.** Pre-exponential factors determined for the heating rate. First-step reactions (a)  $k_1$  and (b)  $k_{V1}$  and second-step reactions (c)  $k_2$  and (d)  $k_{V2}$ .



**Figure 8.** Activation energies determined for the heating rate. First-step reactions (a)  $k_1$  and (b)  $k_{V1}$  and second-step reactions (c)  $k_2$  and (d)  $k_{V2}$ .

(Silveira *et al.* 2018) and upgraded by the minimization of  $\text{diff}^{(7)}$  (Equation 8) with admitted convergence criterion of  $10^{-4}$ .

Pre-exponential factors and activation energies obtained for each heating rate have been compared in Figure 7(a-d) and Figure 8(a-d). According to the main assumption that



**Figure 9.** Comparison between experimental (solid lines) and calculated (dashed lines) mass yields obtained with kinetic parameters determined for  $1.0^{\circ}\text{C min}^{-1}$  heating rate: (a) heating rate  $0.2^{\circ}\text{C min}^{-1}$ , (b) heating rate  $0.5^{\circ}\text{C min}^{-1}$ , (c) heating rate  $1.0^{\circ}\text{C min}^{-1}$ . Purple solid line indicates the temperature profile.

biomass is considered as a homogeneous particle decomposing following a first-order Arrhenius law, it could be expected that pre-exponential factors and activation energies do not depend on the temperature. However, an obvious gap is observed between the parameters obtained for the low-heating rate ( $0.2^{\circ}\text{C min}^{-1}$ ) and the higher ones 0.5 and  $1.0^{\circ}\text{C min}^{-1}$ . Pre-exponential factor, as well as the activation energy of the first decomposition reaction, is found to increase when the heating rate is increased. Volatile formation in the first stage is characterized by a higher pre-exponential factor and activation energy for the lowest heating rate ( $0.2^{\circ}\text{C min}^{-1}$ ). No noticeable trend can be reported for the second-step reactions. This first numerical step confirms the observation of TGA pyrolysis, suggesting that even if the biopolymers' degradation rate is comparable in the heating stage, polymers do not behave identically, and the assumption of uniform biomass decomposition doesn't reflect the reality. The results suggest that the decomposition pathway of biomass polymers at low temperature (slow pyrolysis) follows different pathways.

### 3.4. Numerical simulation of the solid yield dynamic evolution

The model based on Di Blasi and Lanzetta (1997) reaction mechanism was used to simulate the thermodegradation of the poplar-powdered wood. In order to verify the model robustness, kinetic parameters obtained for  $1.0^{\circ}\text{C min}^{-1}$  were used in the simulations. Calculated and TGA experimental profiles are plotted in Figure 9(a–c) in order to analyse the accuracy and weakness of the simulations. For a better readability of the figures, a zoom of the mass yields evolutions is presented in the heating stage, from  $170^{\circ}\text{C}$  until the 800th minute of the treatment. In Figure 9(a), the simulation uses the kinetic parameters determined for the respective experiment. It can be observed that a perfect match between experimental and numerical results is obtained. For Figure 9(b,c), where kinetic parameters come from the higher heating rate determination, as expected, a gap is observed in the sensitive stage of temperature rising, but in the steady-state isothermal plate, simulation overlaps with the experimental curve.

## 4. Conclusion and perspectives

This study investigates the effect of heating rate on the thermodegradation of poplar wood. The experiments are conducted in a pilot-scale reactor and a micro-scale TGA to provide a wide comparison. The results indicate that the heating rate has a significant effect on the wood degradation for both experiments under pilot-scale reactor and TGA, especially in the zone of post-drying intermediate heating. The observations indicate that the reaction scheme of degradation is not identical in the beginning of the process, but homogenizes during the isothermal treatment stage. A two-step kinetic model has been proposed and tested to describe wood dynamic degradation. Even if the numerical model does not allow to determine a unique set of kinetic parameters, this simple and robust reaction scheme gives

promising results to estimate the duration of the process to obtain a desired ML, representative of the final quality of the wood. In further studies, the model will be extended to consider the heat diffusion inside a large-scale sample as well as the heat effect of exothermic or endothermic reactions occurring during the thermal transformation.

## Disclosure statement

No potential conflict of interest was reported by the author(s).

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