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WOOD THERMODEGRADATION: EXPERIMENTAL ANALYSIS AND MODELING OF MASS LOSS KINETICS

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In memoriam of Dr. Manfred SCHWANNINGER

ABSTRACT

In this study, heat treatment was carried out in a relatively low temperature (230°C). Mass loss kinetics was studied using equipment, specially conceived to measure sample's mass during the thermal treatment. Laboratory experiments were performed for heating rates of 1°C min^{-1}. Mathematical model for kinetics of pyrolysis process was used and validated. During the pyrolysis of dry wood samples under inert atmosphere, measurements of temperature distribution and dynamic weight loss were performed. Five different wood species *Fagus sylvatica* (Beech), *Populus nigra* (Poplar), *Fraxinus excelsior* (Ash), *Pinus sylvestris* (Pine) and *Abies pectinat*a (Silver Fir) were investigated. The unsteady-state mathematical model equations were solved numerically using the commercial package Femlab 2.0. A detailed discussion of the computational model and the solution algorithm is given. The validity of different model assumptions was analyzed. Experimental results were compared with those calculated by the model. Acceptable agreement was achieved.

Keywords: Heat treatment, modeling, reaction kinetics, thermodegradation, wood.

INTRODUCTION

Wood is commonly used as building and engineering material. Unprotected wood exposed to outdoor conditions undergoes a variety of degradation reactions induced by diverse factors such as light, moisture, heat, oxygen, pollutants (Evans *et al.* 1992). Moisture contain promotes the fungal attack and leads to sever destruction of wood. In the past, wood preservation has been carried out by chemical treatments, some of them including components that are poisonous for environment and human health. Nowadays, heat treatment of the wood by mild pyrolysis is used as an alternative to chemically impregnated wood materials. It is an effective method to improve biological durability of wood (Finnish Thermowood Association 2003, Momohara *et al.* 2003, Shi *et al.* 2007). Wood heat treatment induces chemical modification of main wood constituents. Lignin polymer structure is modified (Zammen *et al.* 2000, Tjeerdsma and Militz 2005, Nguila *et al.* 2006, Nguila *et al.* 2007a, Esteves *et al.* 2008), the ratio between amorphous and crystalline cellulose is also changed (Fengel and Wegener 1989, Sivonen *et al.* 2002, Yildiz *et al.* 2006), hemicelluloses are strongly decomposed (Sivonen *et al.* 2002, Nuopponen *et al.* 2004, Gérardin *et al.* 2007), some products precursors of charcoal appear (Nguila *et al.* 2007b). These chemical

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modifications confer new properties: improved dimensional stability (Mouras *et al.* 2002, Esteves *et al.* 2007, Esteves *et al.* 2007b), better fungal resistance (Hakkou *et al.* 2006, Kamdem and Pizzi 2002, Mazela *et al.* 2003, Welzbacher *et al.* 2007), some color changes (Mitsui *et al.* 2001, Bekhta and Niemz 2003, Mitsui *et al.* 2003, Ayadi *et al.* 2003, Mitsui *et al.* 2004), mechanical properties modification (Santos 2000, Yildiz 2002, Unsal and Ayrilmis 2005), wood acquires a hydrophobic character (Mitsui *et al.* 2001, Bekhta and Niemz 2003, Mitsui *et al.* 2004, Hakkou *et al.* 2003, Pétrissans *et al.* 2003, Hakkou *et al.* 2005, Kocaefe *et al.* 2008). Even if wood heat treatment seems simple, there are numerous parameters that control this process. Different methods for wood thermal treatment have been developed in France, Finland, Netherlands and Germany since the middle of the last century (Finnish Thermowood Association 2003). In these processes, wood heat treatment by mild pyrolysis (temperature range between 160°C and 260°C) is performed under different process conditions (diversity in the process stages, choice of inert atmosphere (nitrogen or hot gases produced from the heat treatment), wet or dry process, use of oil etc. (Rapp 2001). Chemical reactions involved during mild pyrolysis as well as final properties of the material depend strongly on the treatment temperature and process duration. All through the heat treatment, wood is thermally decomposed at a slow rate (Degroot *et al.* 1988, Repellin and Guyonnet 2005). The resulting anhydrous mass loss (ML) is representative for physical and chemical wood transformations. Mass loss matches to the advancement of the heat treatment process.

Wood thermal degradation is a complex topic given that the material contains several fractions with different thermal behavior. Authors often distinguish a number of stages (Degroot *et al.* 1988, Repellin and Guyonnet 2005, Nguila *et al.* 2009). A phase of elimination of some volatile compounds takes place at temperatures lower than 200°C. For temperature range of 200-280°C, hemicelluloses are converted essentially into gases and acetic acid. This step corresponds to the wood roasting. At the temperature range of 250-300°C, lignin and cellulose are decomposed to give three products: gas, tar and char. Wood thermodegradation leads to an anhydrous mass loss, representative for wood chemical transformation. Properties of heat treated wood depend on the mass loss (Weiland *et al.* 1998). For this reason, controlling the quality of the heat treated wood means to control precisely the mass loss during the treatment. Thus, the knowledge of the kinetic schemes of wood thermodegradation is required.

The aim of this work is to build up a kinetic model which could be applied to the industrial wood heat treatment processes, and make recommendations concerning the operating temperature and treatment duration in order to obtain a required mass loss. Because of the quantity and the complexity of degradation and polymerization reactions occurring in the wood during the heat treatment (Candelier *et al.* 2011), the concept is a simplified approximation of real phenomena. Wood thermodegradation is described using a two-stage, semi-global kinetic model. Numerous experiences of heat treatment at 230°C under nitrogen were carried out for five wood species (Beech, Poplar, Ash, Pine and Fir). The instantaneous mass loss and temperature were recorded. Experimental data were used to determine model parameters. Finally, a comparison between experimental data and numerical results was proposed.

MATERIAL AND METHODS

Wood sample

Heat treatment is carried out on wood panels of large sections, dried in a steam room at 105°C until mass stabilization. Panel's dimensions are 250 x 110 x 25 mm^3 respectively in the longitudinal, tangential and radial directions. Two softwood species *Pinus sylvestris* (Pine) and *Abies pectinata* (Silver fir) and three hardwood species *Fagus sylvatica* (Beech), *Populus nigra* (Poplar), *Fraxinus excelsior* (Ash) were used in this study.

Heat treatment process

Wood species were thermally treated under nitrogen, by conduction between two metallic heating plates. The device was placed on a precision balance allowing recording of dynamic mass loss and instantaneous temperature. Experimental apparatus was more precisely detailed in a previous work (Chaouch *et al.* 2010). Instantaneous weight and temperatures (at the surface and in the heart of the sample) are recorded. The heat treatment consists of three successive thermal stability areas. The first one is kept at 105°C in order to verify the mass stability (the anhydrous mass). The second one (165°C) is useful for the thermal homogenization of the panel. The wood roasting was performed at 230°C.

Mathematical formulation

Wood thermodegradation is a complex set of degradation and polymerization reactions giving several reaction products (Nguila *et al.* 2009, Weiland *et al.* 1998). Knowledge of kinetic schemes describing the thermodegradation process is required for elaboration of predicting tools allowing controlling wood heat treatment. Mathematical modeling of occurring coupled heat and mass transfers are a simplified approximation of real phenomena. Variety of methods based on the thermal analysis of polymer thermodegradation has been developed. An overview of required measurement, kinetic analysis of solid state reaction leading the determination of the reaction order and parameterization of the reaction rate, method's advantages and drawbacks has been proposed in the literature (Liu and Fan 1999, Brown *et al.* 2000, Vyazovkin *et al.* 2011). There could be cited the isothermal and the constant heating rate methods (Freeman and Carroll 1958, Coats and Redfern 1964), the multiple heating rate model (Kissinger 1957). Modeling of polymer thermodegradation is often based on global kinetics, since trying to represent full complexity of the process makes no sense. Global kinetics uses the key steps in the overall mass loss process. There is an ongoing debate concerning the determination of the kinetic parameters of the global reactions of wood pyrolysis (Prins *et al.* 2006, Di Blasi and Lanzetta 1997, Rousset *et al.* 2006, Grioui *et al.* 2006). Models available in the literature usually assume that kinetics of all the thermodegradation reactions obey an Arrhenius low defined by its kinetic constant and activation energy (Koufopanos *et al.* 1991, Prins *et al.* 2006, Di Blasi and Lanzetta 1997, Rousset *et al.* 2006, Grioui *et al.* 2006).

The following section is devoted to the mathematical formulation of coupled heat and mass transfers in wood porous media introducing heat effects due to the reactions of polymer decomposition, production of volatiles and non-degradable solid products. Simplifying assumptions are used for the mathematical formulation:

- Wood sample has a rectangular form characterized by its length *L*, width *l* and thickness *e*, respectively in the longitudinal, tangential and radial directions. The sample thickness is very weak compared to the other dimension and modeling can be represented in 1D.
- Convection transfer occurring because of the formation of volatiles inside the wood material during the heat treatment is neglected, following the recommendations of Vyazovkin *et al.* 2011.
- Dimensions of the sample are considered invariable; formation of fissures and cracks is neglected.
- Wood physical and thermal properties respectively the specific heat *Cp* and the wood thermal conductivity λ are considered as a linear function of temperature (Koufopanos *et al.* 1991).

$$Cp(T) = 1112 + 4.85(T - 273) \tag{1}$$

$$\lambda(T) = 0.13 + 0.0003(T - 273) \tag{2}$$

The macroscopic conservation equation governing heat transfer phenomenon is given by:

$$\rho(t)\, Cp(T)\, \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda(T)\frac{\partial T}{\partial x}\right) + Hp\,\frac{\partial \rho(t)}{\partial t} \tag{3}$$

Where: $\rho(t)=m(t)/V$ is the averaged anhydrous wood density, T is the local temperature; Hp is the global reaction enthalpy. The instantaneous sample weight $m(t)$ is detailed by the Eq. (11). Sample's volume V is considered invariable.

Mechanism adopted in this work is based on a two-stage, semi-global multi-reaction kinetic model of wood mild pyrolysis. Actually; it is not possible to identify the exact mechanism of simultaneous degradation of wood main polymers (hemicelluloses, lignin, and cellulose). Then, wood is assumed to be subdivided into three pseudo-components A_1, A_2, A_3, as it was previously done by (Grioui *et al.* 2006). Each pseudo-component is characterized by a specific kinetic law of decomposition and a mass fraction: $\alpha_1 = m_{A1}/m_0$, $\alpha_2 = m_{A2}/m_0$ *and* $\alpha_3 = m_{A3}/m_0$ *such as* $\alpha_1 + \alpha_2 + \alpha_3 = 1$. m_{A1}, m_{A1}, m_{A3} and are the masses of pseudo constituents A_1, A_2, A_3 in the native wood (before treatment) and m_0 is the mass of the native anhydrous wood sample. At a temperature lower than 200°C occurs the elimination of some volatile wood compounds. At the temperature range of 165 to 230 °C, the degradation of A_1 prevails giving a gaseous product G_1. The thermo-degradation of A_2 leads to the production of a solid fraction C_2 and a gas product G_2. Proposed kinetic scheme is given by Eq. (4-5):

$$A_1 \xrightarrow{k_1} G_1 \tag{4}$$

$$A_2 \xrightarrow{k_2} \gamma_2 C_2 + (1-\gamma_2) G_2 \tag{5}$$

Mass fraction of non-degradable solid γ_2 depends on the operating temperature. With the assumption that kinetic of all involved reactions is described by a first order law, mass balance equations can be written:

$$\frac{\mathrm{d}m_{A_1}(t)}{\mathrm{d}t} = -k_1 m_{A_1}(t) \tag{6}$$

$$\frac{\mathrm{d}m_{A_2}(t)}{\mathrm{d}t} = -k_2 m_{A_2}(t) \tag{7}$$

$$\frac{\mathrm{d}m_{C_2}(t)}{\mathrm{d}t} = k_2\, \gamma_2\, m_{A_2}(t) \tag{8}$$

Where, $m_{A1}(t)$, $m_{A2}(t)$ and $m_{C2}(t)$, are the instantaneous mass of the constituents A_1, A_2 and C_2; k_1 and k_2 are the reaction rate constants obeying an Arrhenius low such as:

$$k_1 = k_{01} \exp\left(-\frac{Ea_1}{RT}\right) \tag{9}$$

$$k_2 = k_{02} \exp\left(-\frac{Ea_2}{RT}\right) \tag{10}$$

Where, k_{01} and k_{02} are the pre-exponential factors; Ea_1 and Ea_2 are the activation energies of global thermo degradation reactions of pseudo constituents A_1 and A_2. Instantaneous total sample mass is equal to:

$$m(t) = m_{A_4}(t) + m_{A_2}(t) + m_{A_3}(t) + m_{C_2}(t) \tag{11}$$

The resolution of the Eq. (3-10) requires the determination of 8 parameters: pre-exponential factors k_{01}, k_{02}, and activation energies Ea_1, Ea_2, mass fraction fractions α_1, α_2 and γ_2; reaction enthalpy Hp of the global process. In this work, kinetics parameters haven't been derived by classic thermal analysis (Brown *et al.* 2000, Vyazovkin *et al.* 2011) but numerically, by minimizing the error function between the experimental data and simulation results Eq. (12):

$$error_{global} = \frac{1}{n_1}\sum_{i=1}^{n_1}\frac{2\left|T_{\exp}(i) - T_{calculated}(i)\right|}{\left(T_{\exp}(i) + T_{calculated}(i)\right)} + \frac{1}{n_2}\sum_{j=1}^{n_2}\frac{2\left|ML_{\exp}(j) - ML_{calculated}(j)\right|}{\left(ML_{\exp}(j) + ML_{calculated}(j)\right)} \tag{12}$$

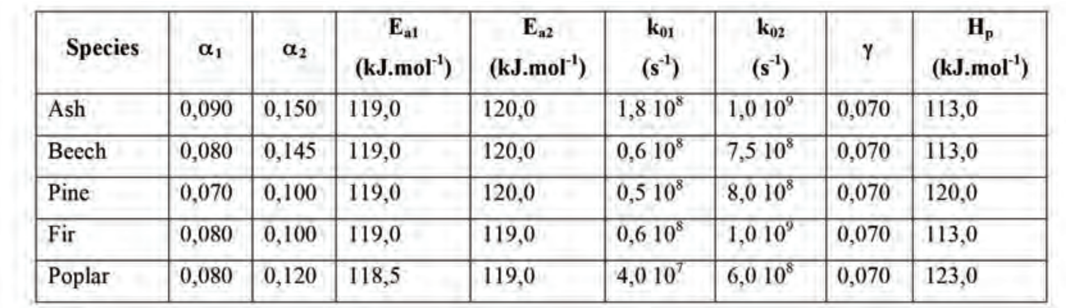
where n_1 is the number of data points of the temperature, $T_{exp}(i)$ is the experimental temperature, $T_{calculated(i)}$ is the calculated temperature on the *i*-th grid point, n_2 is the number of data points of the mass loss $ML_{exp}(j)$ and $ML_{calculated}(j)$ are respectively experimental and the calculated mass loss due to the thermo-degradation on the *j*-th grid point. The anhydrous mass lost is defined as follows:

$$ML = \left(m_0 - m(t)\right)/m_0 \tag{13}$$

Experiences are carried out in a way, allowing the determination of model parameters over two stages. At the second isothermal area at 165 °C, the reaction giving by the Eq. (5) can be neglected because of its very slow rate. It has been also considered that reaction enthalpy of this reaction is negligible. Three parameters relative to the first reaction (Eq. 4) are then determined: α_1, k_{01} and Ea_1. The third isothermal area at 230°C, corresponding to the heat treatment process, allows the determination of the five other parameters: α_2, γ_2, k_{02}, Ea_2 and Hp. Governing equations are solved numerically with the commercial package Femlab 2.0. This is designed to simulate systems of coupled non-linear and time dependent partial differential equations (PDE) in one-, two- or three- dimensions. The mesh convergence was verified with refined mesh sizes.

Time step of 360 s, 1866 nodes and 8080 elements mesh size were considered to be appropriate. The kinetic parameters obtained with this method are given in table 1:

Table 1. The kinetic parameters used in the numerical simulation for the five species.



Species	α_1	α_2	E_{a1} (kJ.mol^{-1})	E_{a2} (kJ.mol^{-1})	k_{01} (s^{-1})	k_{02} (s^{-1})	γ	H_p (kJ.mol^{-1})
Ash	0,090	0,150	119,0	120,0	1,8 10^8	1,0 10^9	0,070	113,0
Beech	0,080	0,145	119,0	120,0	0,6 10^8	7,5 10^8	0,070	113,0
Pine	0,070	0,100	119,0	120,0	0,5 10^8	8,0 10^8	0,070	120,0
Fir	0,080	0,100	119,0	119,0	0,6 10^8	1,0 10^9	0,070	113,0
Poplar	0,080	0,120	118,5	119,0	4,0 10^7	6,0 10^8	0,070	123,0

RESULTS AND DISCUSSION

In order to verify the final weight loss predicted by the model, experiments with a reaction time of 20 hours were carried out (including a drying period at 105°C, a stabilization phase at 165°C and the heat treatment at 230°C). The comparison between experimental data and simulation results was performed for five species. Results are shown in figure (1-5). Careful consideration of the experimental weight curves reveals that they do not become completely horizontal; the weight continues to decrease very slowly. Hardwoods (Figure 3-5) were shown to be more sensitive to thermodegradation than softwoods (Figure 1-2). Softwoods degradation products appear at slightly higher temperature. These physical phenomena were reproduced by the simulation; a good agreement was obtained.

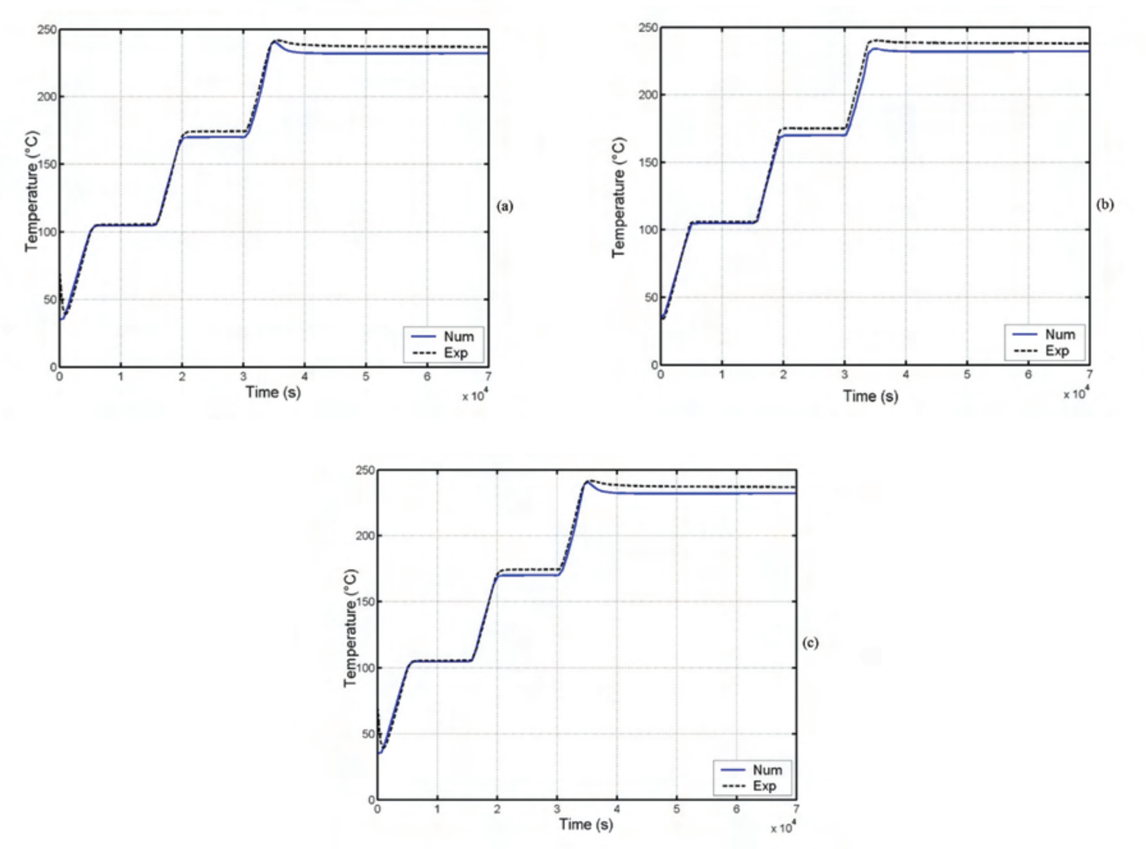


Figure 1. Fir -average mass loss (a), surface temperature (b), center temperature (c).

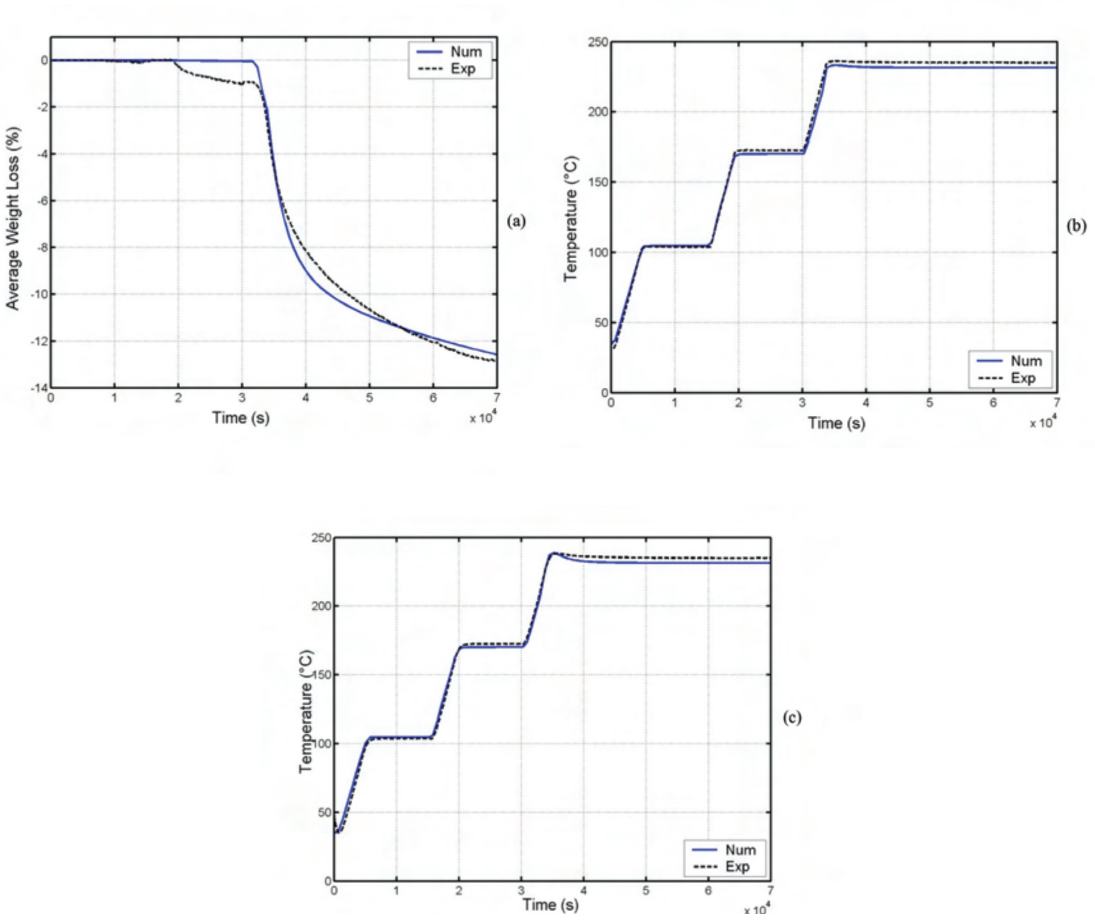


Figure 2. Pine - average mass loss (a), surface temperature (b), center temperature (c).

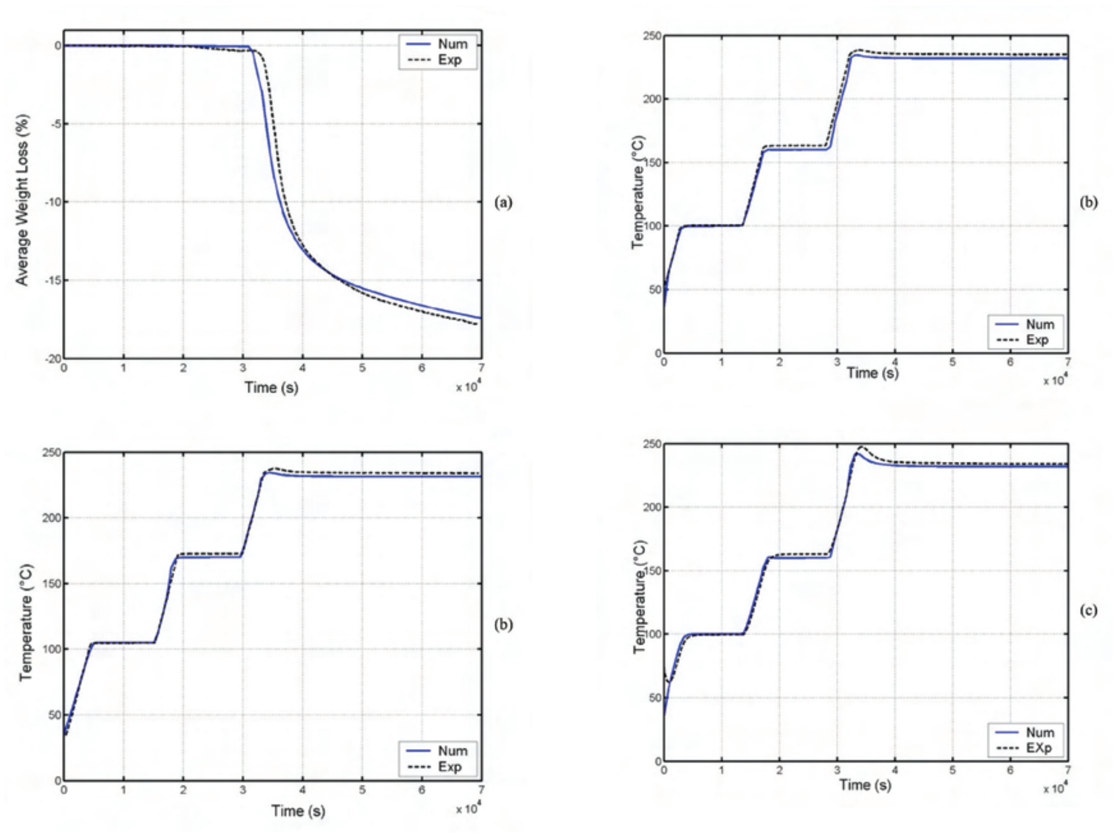


Figure 3. Poplar - average mass loss (a), surface temperature (b), center temperature (c).

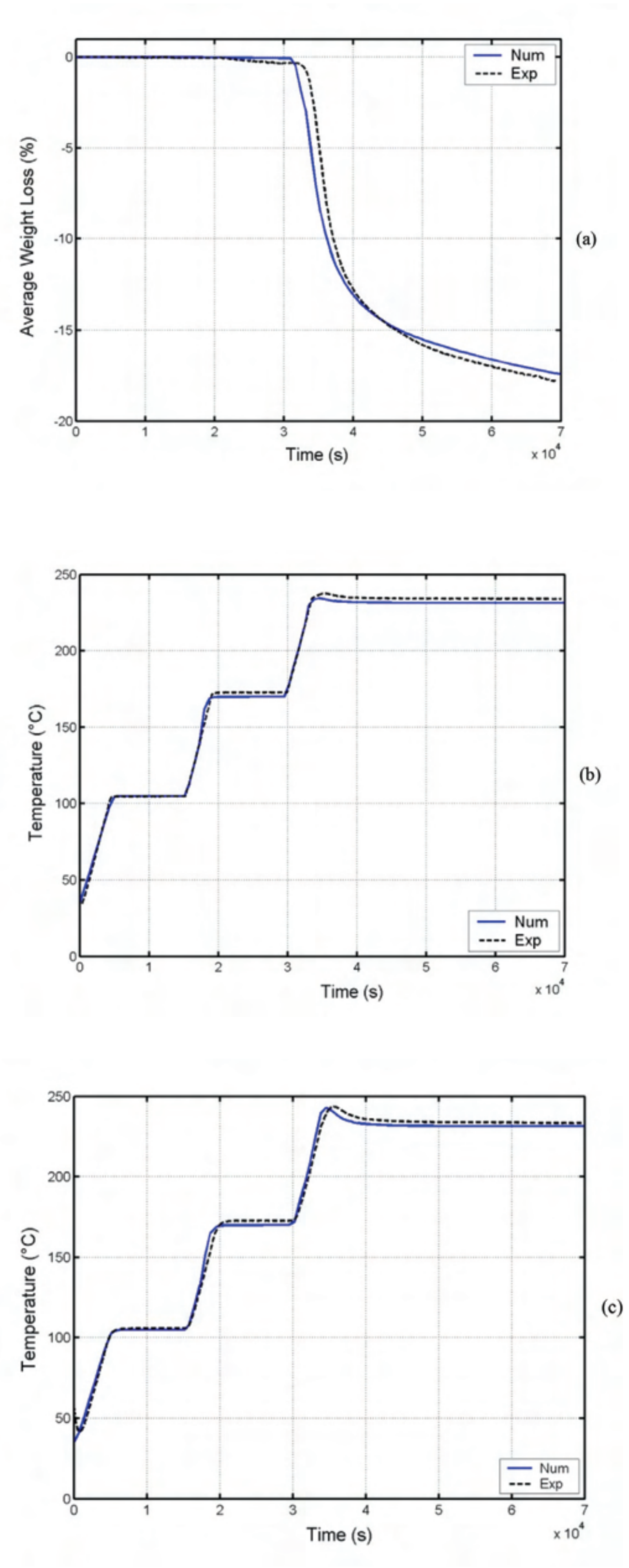


Figure 4. Beech - average mass loss (a), surface temperature (b), center temperature (c).

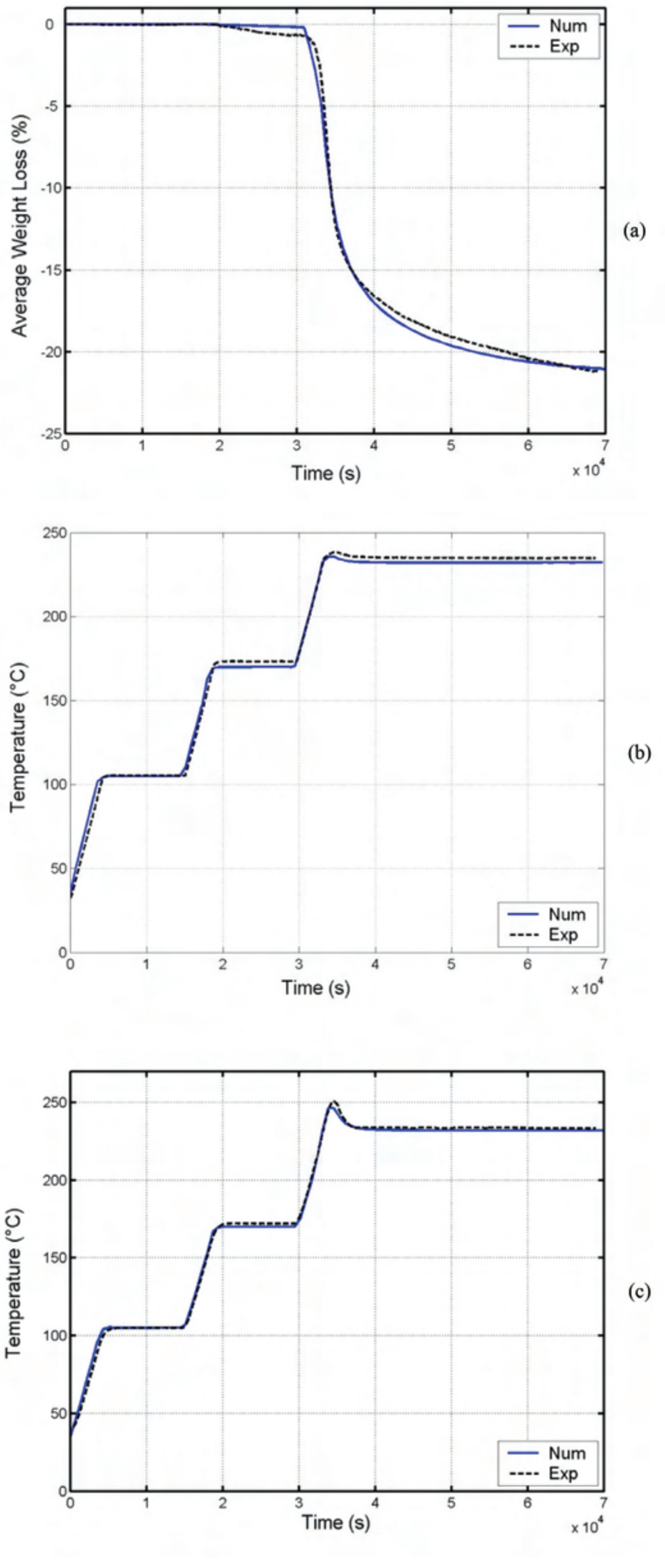


Figure 5. Ash - average mass loss (a), surface temperature (b), center temperature (c).

Concerning the observation of temperature evolution recorded data, it is important to pay attention on the existence of an exothermic peak. This temperature rising is more pronounced in the sample heart, it could be probably due to the heat produced by the reaction of wood thermodegradation which activates the exothermic degradation reactions, obeying themselves to the Arrhenius low. The temperature control of the heating plates attenuates this effect on the sample surface. The coupled consideration of integrated in the model heat and mass transfers allows a good representation of this exothermic phenomenon.

CONCLUSION

The kinetics of wood pyrolysis in a temperature of 230°C can be described accurately by the proposed two-step reaction mechanism. The model incorporates the reaction pathway that was developed by Grioui *et al.* (2006) describing wood transformation during the mild pyrolysis. The model allows the computation of temperature profiles and average weight loss. Femlab 2.0 software was used to solve the system of partial differential equations. This paper includes a validation section that shows the ability of the model to accurately predict temperature profiles and mass loss in the experimental configuration. Comparison between simulated results and experimentally measured values showed a good agreement.

This model requires a preliminary determination of the reaction kinetics parameter for each softwood or hardwood species. However, the model can be used as an accurate tool in the design of industrial pyrolysis installations.

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