

KINETICS MODELING OF WOOD TORREFACTION

Weight Loss Kinetics

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Keywords: Heat treatment, Modelling, Reaction kinetics, Thermo-degradation, Wood.

Abstract: Torrefaction is a thermal treatment step in a relatively low temperature range of 210–240°C, which aims to improve the dimensional stability and durability of wood. The weight loss kinetics for torrefaction of wood samples was studied using equipment specially conceived to measure mass losses during thermal treatment. Laboratory experiments were performed under nitrogen for heating rates of $1^{\circ}\text{C}.\text{min}^{-1}$. A mathematical model for the kinetics of the thermodegradation process was used and validated. Measurements of temperature distribution and anhydrous weight loss were performed on dry sample of poplar wood during pyrolysis in an inert atmosphere at 230°C. The mathematical formulation describing the simultaneous heat and mass transfers requires coupled nonlinear partial differential equations. These unsteady-state mathematical model equations were solved numerically by the commercial package FEMLAB. A detailed discussion of the computational model and the solution algorithm is given. Once the validity of different assumptions of the model had been analyzed, the experimental results were compared with those calculated by the model. Acceptable agreement was achieved.

1 INTRODUCTION

Nowadays the use of wood as building material is promoted. The heat treatment of the wood by mild pyrolysis is used to improve some of the characteristics of the final wood product, such as its durability and dimensional stability. This process substitutes the use of external chemical products, which enables the treated wood to remain an environmentally friendly product. It's an effective method to improve biological durability of wood (Shi et al. 2007). The heat treatment of the wood induces a chemical modification of the main wood constituents. The lignin polymer structure is modified, the ratio between the amorphous and the crystalline cellulose is also changed, hemicelluloses are strongly decomposed (Sinoven et al., 2002, Nguila et al., 2006, Nguila et al., 2007a, Gérardin et al., 2007), some products precursors of the charcoal appear (Nguila et al., 2007b). These chemical modifications confer with the new wood properties as the improved dimensional stability (Mouras et al.,

2002, Esteves et al., 2007), the improved fungal resistance (Kamdem et al., 2002, Hakkou et al., 2006).

The concept of thermal treatment to stabilise the wood structure has lead to the development of several treatment processes in some European countries. In the 70s, the research developed by the Ecole des Mines de Saint-Étienne (France) has worked out for the first time an industrial process named «Retified wood®». More recently, in the 90s, the forest industry in Finland has developed a new process; Thermowood®. Some others technologies have been developed such as the Netherlands process «PLATO® » and the Menz Holz's process OHT in Germany. The wood torrefaction is a heat treatment of ligno-cellulosic material carried out at temperatures up to 300 °C. Torrefaction can be carried out under different gaseous atmospheres. Nitrogen or hot gases released during the thermal treatment are employed most of time. Chemical reactions involved during torrefaction as well as final properties of the material depend strongly on

the treatment temperature and the duration of the process. During torrefaction, slow pyrolysis prevails: wood is thermally decomposed at a slow rate (Degroot et al., 1988). The anhydrous weight loss (AWL) resulting from the wood decomposition is representative for physical-chemical transformations of wood. The AWL matches to the advancement of the torrefaction process.

According to the treatment intensity, the conferred properties of the wood vary strongly. For high values of the treatment temperature and time, the fungal resistance becomes total. Recent studies have shown the direct relation between the anhydrous weight loss (AWL) due to thermo-degradation and the conferred wood properties (Hakkou et al., 2005, Welzbacher and Brischke, 2007). Hence, controlling the heat treatment process means to control precisely the AWL of the material. It requires a coupled model taking into account heat transfer and mass transfer due to thermo-degradation reactions inside wood sample.

The mechanism of wood thermo-degradation shows the presence of several phases when the temperature increases. 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 about 250-300°C, the lignin and cellulose decompose to give three products: gas, tar and char. This decomposition leads to an anhydrous weight loss, representative for wood chemical transformation. Properties of heat-treated wood depend on the mass losses (Nguila et al., 2009). Hence, controlling the quality of the heat treated wood means to control precisely mass loss during the treatment. Therefore, the knowledge of the kinetic schemes of the wood thermo-degradation is required.

The aim of this study is to develop a tool allowing predicting the temperature profiles in the wood and the associated AWL during the treatment. A two-stage semi-global kinetic model is used here to describe the wood thermo-degradation. Numerous experiences of heat treatment at 240°C under nitrogen were realized with five wood species. The curves of the instantaneous mass loss and temperature were recorded. The experimental data were used to determine the model parameters. Finally, a comparison between the experimental data and the numerical results was realized.

2 MATERIAL AND METHODS

Heat treatment is carried out on wood panels of large sections, dried in the steam room at 105°C until their mass stabilization. The panel's dimensions are 25 x 11 x 2.5 cm³ respectively in the longitudinal, tangent and radial directions. The wood specie used in the present study has the Poplar (*Populus nigra*).

Heat treatment has been carried out under nitrogen by conduction between two metallic heating plates placed on a precision balance. The instantaneous weight and temperatures at the surface and in the middle of the sample are recorded. The heat treatment phase consists of three successive thermal stability areas. The first one is kept at 105°C in order to verify the mass stability (anhydrous mass). The second one (165°C) is useful for the thermal homogenization of the panel. The last one corresponds on the thermo-degradation operating temperature.

3 MATHEMATICAL FORMULATION

Wood is a complex material whose thermo-degradation involves series of chemical reactions with coupled heat and mass transfer. This section is devoted to the mathematical formulation of the mentioned transfers in the wood porous media introducing as well the heat effects due to the reactions of polymer decomposition, as the obtaining of volatiles and non-degradable solid products. The following simplifying assumptions are used for the mathematical formulation:

- the wood sample has a rectangular form characterised by its length L , width l and thickness e , respectively in the longitudinal, tangent and radial directions. The sample thickness is very weak compared to the other dimension and the modelling can be represented in 1D.
- the convection transfer occurring because of the formation of volatiles inside the wood material during the heat treatment is neglected.
- the dimensions of the sample are considered invariable; the formation of fissures and cracks is neglected.
- the wood physical and thermal properties respectively the specific heat C_p and the wood thermal conductivity λ are considered as a linear function of the temperature.

$$C_p = 1112 + 4.85(T - 273) \quad (1)$$

$$\lambda = 0.13 + 0.0003 (T - 273) \quad (2)$$

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

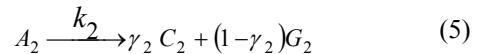
$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) + H_p \frac{\partial \rho}{\partial t} \quad (3)$$

where: $\rho = m(t)/V$ is the averaged anhydrous wood density, T is the local temperature, H_p is reaction enthalpy. The instantaneous sample weight $m(t)$ is detailed after on by the Eq. (11), the sample volume V is considered invariable.

The process of the wood heat treatment involves several reactions that of polymer degradation and synthesis giving numerous reaction products (Weiland et al., 1998, Nguila et al., 2009). Consequently, mathematical modelling describing the wood thermo-degradation is a simplified approximation of the real phenomena. However, the knowledge of kinetic schemes describing the thermo-degradation process is required for elaboration of predicting tools allowing the control of wood heat treatment.

Numerous mechanisms have been published to provide a rational explanation of the wood thermo-degradation and the associated heat effects. Three main approaches could be distinguished: the first one considers the wood as a single homogeneous element (Di Blasi and Branca, 2001, Rath et al. 2003, Sadhukhan et al., 2008), the second one takes into account the decomposition of the essential wood compounds: cellulose, hemicelluloses and lignin (Rousset et al., 2006), the third one considers the existence of three fractions (pseudo-compounds) which decomposition obeys different laws (Grioui et al., 2006). It is usually assumed that the reaction kinetics follows an Arrhenius law with two parameters: activation energy and kinetic constant.

The mechanisms adopted in this work, is based on a two-stage, semi-global multi-reaction kinetic model of wood mild pyrolysis where the wood is subdivided into three pseudo-components A_1 , A_2 , A_3 , as it was previously proposed by Grioui et al. (2006). Each pseudo-component is characterised by a specific kinetic law of decomposition and its mass fraction, respectively α_1 , α_2 and α_3 , such as $\alpha_3 = 1 - \alpha_1 - \alpha_2$. At a temperature level lower than 200°C occurs the elimination of some volatile wood compounds. At the temperature range 165 to 240 °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 . The proposed kinetic scheme is given by the Eq. (4-5):



The mass fractions of the non-degradable solid γ_2 and γ_3 depend on the temperature.

The assumption that the kinetic of all the involved reactions is described by first order laws the mass balance equations can be written respectively as follows:

$$\frac{dm_{A_1}}{dt} = -k_1 m_{A_1} \quad (6)$$

$$\frac{dm_{A_2}}{dt} = -k_2 m_{A_2} \quad (7)$$

$$\frac{dm_{C_2}}{dt} = k_2 \gamma_2 m_{A_2} \quad (8)$$

where m_{A_1} , m_{A_2} and m_{C_2} are respectively the mass of the constituents A_1 , A_2 and C_2 ; k_1 and k_2 are the reaction rate constants obeying the Arrhenius low such as :

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

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

where, k_{01} and k_{02} are the pre-exponential factors; Ea_1 and Ea_2 are the activation energies. The instantaneous total mass of the sample is equal to:

$$m(t) = m_{A_1}(t) + m_{A_2}(t) + m_{A_3}(t) + m_{C_2}(t) \quad (11)$$

The resolution of the Eq. (3-10) requires the determination of 8 parameters: the pre-exponential factors k_{01} , k_{02} , and activation energies Ea_1 , Ea_2 , the mass fraction fractions α_1 , α_2 and γ_2 ; the reaction enthalpy H_p . These parameters have been obtained by minimizing an error function between the experimental data and simulation results. The number of parameters to determine is large and the optimization procedure becomes difficult. The error function to minimize over both thermal and mass measurements is given be the Eq. (12):

$$\begin{aligned} error &= \frac{1}{n_1} \sum_{i=1}^{n_1} \frac{2|T_{\text{exp}}(i) - T_{\text{calculated}}(i)|}{(T_{\text{exp}}(i) + T_{\text{calculated}}(i))} + \\ &+ \frac{1}{n_2} \sum_{j=1}^{n_2} \frac{2|ML_{\text{exp}}(j) - ML_{\text{calculated}}(j)|}{(ML_{\text{exp}}(j) + ML_{\text{calculated}}(j))} \end{aligned} \quad (12)$$

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 the 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:

$$AML = (m_0 - m(t))/m_0 \quad (13)$$

m_0 is the anhydrous wood weight before heat treatment.

The experiences are carried out in such a way, allowing the determination of the model parameters over two stages. At the first 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 the reaction enthalpy of the first reaction is negligible. The three parameters relative to the first reaction (Eq. 4) are then determined: α_1 , k_{01} and Ea_1 . The second 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 H_p . A random algorithm has been used, and the minimum and maximum values of each parameter have been initialised according to the values available in the literature (Di Blasi and Lanzetta, 1997, Grioui et al., 2006, Rousset et al., 2006).

The governing equations are solved numerically with the commercial package, FEMLAB (Cosmol, 2000). 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 using the method described are in Table 1.

Table 1: Kinetic parameters used in the numerical simulation for the poplar.

α_1	0.08
α_2	0.12
$E_{a1}(\text{kJ.mol}^{-1})$	118.5
$E_{a2}(\text{kJ.mol}^{-1})$	119.0
$k_{01}(\text{s}^{-1})$	4.10^7
$k_{02}(\text{s}^{-1})$	6.10^8
γ	0.07
$H_p(\text{kJ.mol}^{-1})$	123.0

4 RESULTS AND DISCUSSION

To verify the final prediction of the model, experi-

ences have been carried out using poplar wood during 20 hours under heat treatment temperature of 230°C. The heat treated rate has been fixed to $1^\circ\text{C}.\text{min}^{-1}$. Experimental and numerical results of the surface et centre temperatures and the averaged weight loss are shown on Fig. 1-3. It can be observed that the increase of the treatment temperature enhances the AML. A good agreement is observed between the experience and the numerical simulation.

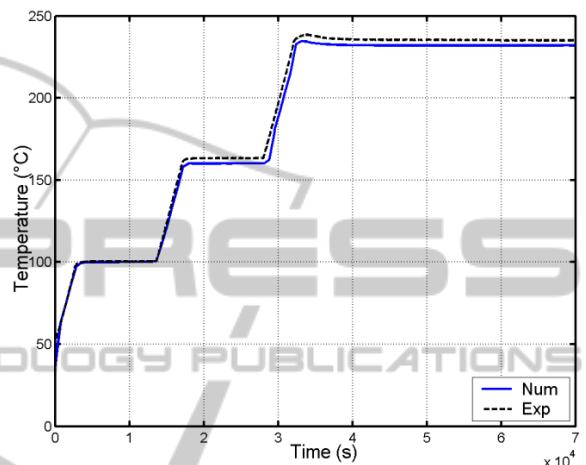


Figure 1: Time evolution of surface temperature: Poplar ($1^\circ\text{C}.\text{min}^{-1}$, $T_{max} = 230^\circ\text{C}$).

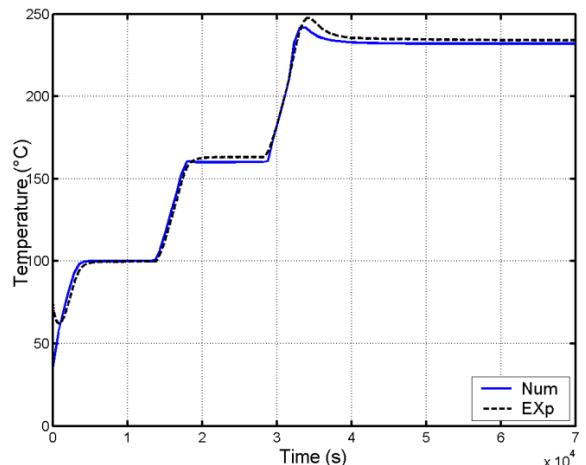


Figure 2: Time evolution of center temperature: Poplar ($1^\circ\text{C}.\text{min}^{-1}$, $T_{max} = 230^\circ\text{C}$).

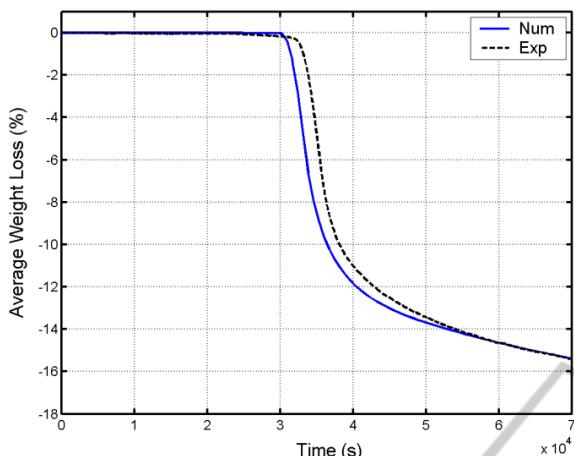


Figure 3: Time evolution of average weight loss: Poplar ($1^{\circ}\text{C}.\text{min}^{-1}$, $T_{\max} = 230^{\circ}\text{C}$).

5 CONCLUSIONS

The kinetics for the pyrolysis of wood was investigated. Based on laboratory experiments performed with the described device, a mathematical model for the kinetics of the pyrolysis process was proposed and validated. This model incorporates the reaction pathway that was developed by Grioui et al. (2006) for the description of the transformation of wood subject to heat. This model allows the computation of internal profiles of temperature and average weight loss. The Femlab software was used to solve the system of partial differential equations. This work includes a validation section that shows the ability of the model to accurately predict the internal profiles of temperature and weight loss in the experimental configuration. Comparison of the simulated temperature profiles and average weight loss with experimentally measured values showed reasonable agreement.

Further studies may allow accurate modeling of wood torrefaction mainly by taking into account thermodegradation of lignin and accurate thermophysical properties. This model can be used in the design of industrial pyrolysis installations

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