A mathematical description of thermal decomposition and spontaneous ignition of wood slab under a truncated-cone heater

Qian Liu*, Dekui Shen*,†, Rui Xiao*, Huiyan Zhang*, and Mengxiang Fang**

*Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment,
Southeast University, Nanjing 210096, China
**The State Key Laboratory for Clean Energy, Zhejiang University, Hangzhou 310027, China

Abstract–A mathematical model of thermal decomposition together with the flammability limit is proposed to describe the pyrolysis and spontaneous ignition of wood slab subjected to the radiation from a truncated-cone heater. The prominent physical and chemical phenomena were considered in the model, involving heat transfer in a solid, heat consumed by thermal decomposition reactions, the evaporation of moisture, re-radiation from pore surfaces inside a solid and so on. The numerical solution allows the prediction of in-depth temperature profiles, evolution of volatiles, variation of thermal conductivity, apparent mass loss (solid conversion) and ignition time. The different densities for wood species and effect of moisture content and grain orientation on thermal conductivity are also considered in the model, producing a good prediction of surface temperatures. This gives birth to the reasonable prediction on ignition time of wood by employing fixed surface temperature (400 °C) as ignition criterion. However, the analysis of constituent fractions for the species associated with the multi-components kinetic scheme should be included in the mathematical model to give a more precise prediction on the apparent mass loss of solid.

Key words: Thermal Decomposition, Spontaneous Ignition, Model, Temperature, Ignition Time

INTRODUCTION

An accurate prediction of fire risk requires an adequate description of the initiation and development of a fire. Since wood contributes to the significant fuel load in building fires, the thermal decomposition and the sequent ignition of wood play an important role in the commencement and growth of fire. A large number of theoretical studies for describing the thermal decomposition and ignition of wood that have been published can be classified as: (1) simplified analytical studies that develope practical and useful formulae for variables such as temperature distribution and volatile mass efflux, and (2) detailed numerical studies that attempt to provide a comprehensive description of wood pyrolysis, including as many physical and chemical processes as possible (such as heat and mass transfer, thermal decomposition kinetics, heat consumption by reactions and variation of thermo-physical properties) [1].

Except the transient propagation of a constant temperature pyrolysis front into the solid, most existing analytical studies ignore many complicated physical and chemical processes, limiting their range of applicability and accuracy of the predictions [2,3]. Recently, some other complex phenomena during transient pyrolysis of wood were incorporated into the mathematical models, such as the heat loss/gain due to chemical reactions, structural changes as volume shrinkage and in-depth cracking, internal convective heat transfer between the volatiles and the solid matrix and the pressure build-up within the porous structure [4]. Obviously, it is not possible to provide a mathematical description of all the processes involved in pyrolysis

of wood. Ignition is the sequent process of pyrolysis, when flammability limit or ignition criterion (such as fixed surface temperature and critical mass loss rate) is reached [5]. Therefore, an ignition model is normally composed of the pyrolysis model discussed above and the fixed flammability limit. It was noted that most ignition models in the literature describe the piloted-ignition of wood, but spontaneous ignition has not been sufficiently reported.

A mathematical model together with the fixed flammability limit was proposed, in order to gain a better understanding of the mechanism of pyrolysis and spontaneous ignition of wood. The in-depth temperature profiles, evolution of volatiles and spontaneous ignition characteristics of solid were numerically predicted, considering the effects of moisture content, grain orientation, porosity and variation of thermal properties. The predictions were compared with the authors' previous experimental data, assessing the influencing mechanisms of the factors and the application of the proposed comprehensive model.

EXPERIMENTAL SETUP

The apparatus for investigating pyrolysis and ignition of wood was exactly introduced in a previous study, as well as the procedure and measurements for in-depth temperature, mass loss and ignition characteristics [6-8]. Willow, pear-wood, birch and white-pine were selected to be tested in the apparatus under the heat flux from 20 to 60 kW/m². The birch samples with moisture content from 3 to 36% were tested under 40 kW/m², and the larch samples with different grain orientation were tested under 20 and 40 kW/m². The experimental data was used to validate the predictions from the mathematical model.

†To whom correspondence should be addressed.
E-mail: 101011398@seu.edu.cn

MATHEMATICAL MODEL

In our previous experimental work, only the top side (surface) asbestos. The process for thermal decomposition and spontaneous ignition consists of complex phenomena involving a variety of physical and chemical processes, such as transient thermal conduction, mass transportation, structural changes, moisture evaporation and chemical reactions. The assumptions are listed and discussed based upon sound physico-chemical principles before the description of the mathematical model.

(1) The solid is assumed as a one-dimensional, thermally-thick, semi-infinite flat panel, since the solid is isolated from the surroundings except for the top surface and no difference between the measured surface temperatures at different position could be observed.

(2) To examine the relative importance of the convective heat transfer due to the outward flow of volatiles, the Péclet number was proposed by Kanury in 1970 [9] and quoted by Moghtaderi in 2006 [1]:

$$Pe = \frac{c_g m'' L}{\lambda} \tag{1}$$

where c_g and m'' represent the specific heat and the total mass flux of volatiles from the layer; λ and L represent the thermal conductivity and length of controlled volume. If $Pe \ll 1$, then convection effects will be small compared to the effects of conduction and, hence, the convective thermal transport of volatiles can be ignored. If, however, $Pe > 1$, the convection is not negligible and should be taken into account. For the present analysis m'' can be approximated at 22 g/m²s based on the data extracted from our experiments carried out in a truncated cone heater at heat flux levels of 15-70 kW/m². Using this value for volatile mass flux in conjunction with values of 0.1 W/mK and 1.03 kJ/kgK for the thermal conductivity of wood and the specific heat of volatiles, respectively, a value of 0.14 is obtained from Eq. (1). Therefore, the heat convection and mass transport of the gases and vapor inside the solid is ignored. The solid mass loss rate is equal to the volatiles' mass flux together with moisture evaporation.

(3) Drying of wood as an additional chemical reaction using an Arrhenius expression gave temperature rise continuously into and out of the drying plateau, especially for the moisture content below FSP [1]. The scheme matches experimental observations of temperature with pyrolyzing wood, which can be readily incorporated into the numerical pyrolysis model. Here, the evaporation of water inside wet wood is also described as a chemical reaction. Furthermore, no recondensation of water vapor inside the solid is considered due to assumption (2).

(4) Past studies [1,10] have shown that for temperatures below 600 °C the impact of shrinkage on predictions of the pyrolysis yield is negligible, and as such shrinkage can be ignored in the model. In this work, the temperature profiles in most cases are below 600 °C before the commencement of ignition, and thus the volume shrinkage of solid during the process of pyrolysis is neglected. However, the effect of structural property (porosity) on thermal conductivity of solid is considered and estimated in this model.

(5) The chemical reactions for pyrolysis of wet wood are described by the one-step multi-reactions scheme together with the kinetic parameters as shown in Table 2. The rate for the reactions is governed by the first-order Arrhenius Law.

(6) Heat losses by re-radiation and convection from the solid surface are included in the model.

(7) As known, ignition could only occur as the critical flammability limit was reached. With help of the given value of critical surface temperature with 285 °C for piloted ignition and 525 °C for spontaneous ignition, the pyrolysis model proposed by Bilbao was calculated and successfully correlated with the experimental data [11]. An average value for ignition temperature (surface temperature at the point of ignition) from our previous experiments on spontaneous ignition of wood is obtained as around 400 °C [12]. Therefore, the value of 400 °C is employed as the criterion for predicting the spontaneous ignition of wood.

Regarding the above assumptions, the energy conservation equation for pyrolysis of the wet wood could be reasonably described as:

$$\frac{\partial}{\partial t}[T(\rho_w c_w + \rho_c c_c + \rho_l c_l)] = \frac{\partial}{\partial x}\left(\lambda \frac{\partial T}{\partial x}\right) + Q_r'' \tag{2}$$

Where Q_r'' is described as the sum of reaction heat of the three pyrolysis reactions at the temperature T [6]:

$$Q_r'' = k_1 \rho_w [\Delta h_1^0 + (c_c - c_w)(T - T_0)] + k_2 \rho_w [\Delta h_2^0 + (c_g - c_w)(T - T_0)] + k_3 \rho_l [\Delta h_3^0 + (c_v - c_l)(T - T_0)] \tag{3}$$

The mass conservation equations for wood, char, volatile, liquid and vapor are listed as follows:

$$\frac{\partial \rho_w}{\partial t} = -(k_1 + k_2)\rho_w \tag{4a}$$

$$\frac{\partial \rho_c}{\partial t} = k_1 \rho_w \tag{4b}$$

$$\frac{\partial \rho_g}{\partial t} = k_2 \rho_w \tag{4c}$$

$$\frac{\partial \rho_l}{\partial t} = -k_3 \rho_l \tag{4d}$$

$$\frac{\partial \rho_v}{\partial t} = k_3 \rho_l \tag{4e}$$

According to assumption (4), the rate of pyrolysis reactions is governed by the first-order Arrhenius Law:

$$k = A \exp\left(\frac{-E}{RT}\right) \tag{5}$$

The boundary conditions are:

$$t = 0, \quad T = T_0 \tag{6}$$

$t > 0$, $x = 0$, the boundary condition is:

$$\lambda \frac{\partial T}{\partial x} = \alpha q_e'' - q_{loss}'' \tag{7}$$

$$q_{loss}'' = \sigma \varepsilon (T^4 - T_0^4) + h_{conv}(T - T_0) \tag{8}$$

$t > 0$, $x = L$, the boundary condition is:

$$\lambda \frac{\partial T}{\partial x} = q_b'' \tag{9}$$

where q_b'' is equal to zero as the bottom of the solid is adiabatic.

The effective conductivity (λ) was composed of two terms: the

solid conductivity (λ_s), and the conductivity caused by radiation from porosity of solid (λ_{rad}).

$$\lambda = \lambda_s + \lambda_{rad} \tag{10}$$

The values for solid conductivity used here were [13]:

For wood, $\lambda_w = 0.166 + 0.369X$ (W/mK) (11)

For char, $\lambda_c = 0.105$ (W/mK) (12)

where X is moisture content of wood. A variation for the solid thermal conductivity with solid conversion (η) was assumed as:

$$\lambda_s = \eta\lambda_c + (1-\eta)\lambda_w \tag{13}$$

$$\eta = \frac{\rho_c}{\rho_s} = \frac{\rho_c}{\rho_c + \rho_w} \tag{14}$$

The conductivity due to radiation from porosity is described as [14]:

$$\lambda_{rad} = \Phi(1-\Phi)\sigma\varphi_p d_p 4T^3 \tag{15}$$

where Φ is the porosity of solid, φ_p is the emissivity and d_p is the equivalent diameter of pores. The parameters used to solve the model were obtained either by using other experimental systems or from the literature (Table 1). The kinetic parameters for different pyrolysis reactions of wet wood are given in Table 2. Numerical solution allows the calculation of temperature profiles, evolution of volatiles and evaporated water in different layers inside solid. The ignition time could be easily predicted with the help of fixed surface temperature as ignition criterion.

Table 1. The summary of values and expressions for the thermo-physical properties of wood

Property	Value/expression	Ref.
Thermal conductivity	In text	
Specific heat (kJ/kg K)	$c_w = 1.95$	[13]
	$c_c = 1.39$	[13]
	$c_g = 2.4$	[18]
	$c_l = 4.18$	[19]
	$c_v = 1.58$	[13]
Porosity	$\phi = 1 - (\rho_w + \rho_c)/1500 - \rho_m/1000$	[14]
Emissivity	$\varepsilon = 0.78$	[20]
Emissivity of pore surface	$\varphi_p = 0.9$	[14]
Equivalent diameter of pores (m)	$d_p = 26.1 \times 10^{-6}$	[16]
Convective coefficient (W/m²K)	$h_{conv} = 10$	[5]
Average absorptivity	$\alpha = 0.95$	[21]

Table 2. The kinetic parameters for pyrolysis reactions and drying process

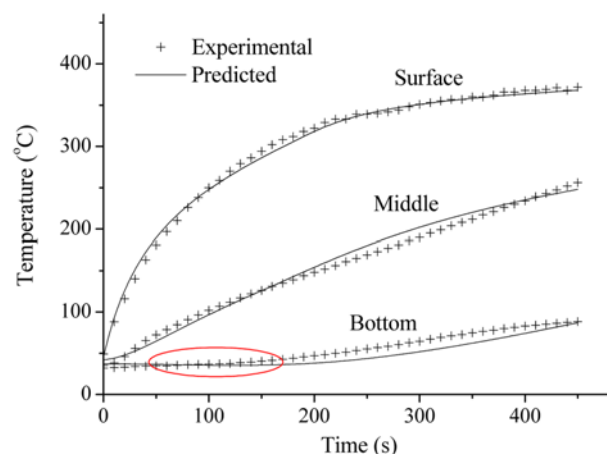| Reaction	A (1/s)	E (kJ/mol)	Ref.	ΔH_i^0 (kJ/kg)	Ref.
Pyrolysis reactions					
Wood $\xrightarrow{K1}$ Char	7.38×10^5	106.5	[22]	-420	[23]
Wood $\xrightarrow{K2}$ Gas	1.44×10^4	88.6	[22]	-420	[23]
Drying process					
Moisture $\xrightarrow{K3}$ Vapor	5.13×10^{10}	88	[24]	-2440	[19]

Fig. 1. The in-depth temperature distribution of willow under the heat flux of 20 kW/m².

RESULTS AND DISCUSSION

Once the external radiation is loaded on the surface of wood slab, the heat energy is transported into the solid and also consumed by the designated chemical reactions. The in-depth temperature profiles of willow under the heat flux of 20 kW/m² (Fig. 1) are predicted depending on the transient heat conduction theory coupled with the one-step multi-reactions scheme. The good agreement between most predicted results and experimental data could be observed, confirming the necessity of considering the reaction heat in the thermal-balanced equation. However, a slight decline of the predicted bottom temperature is observed within the red-circle zone, possibly due to the substantial heat consumed by decomposition reactions over the net heat transferred from the upper layer.

One of the important parameters to determine the net heat transferred into inner layers of solid is the thermal conductivity of surface layer, composed of three parts: solid part, moisture part and radiative part from pores. The variation of thermal conductivity of top layer of willow under heat flux of 20 kW/m² is shown in Fig. 2. The thermal conductivity of solid part related to the moisture content and solid conversion shows two significant declines during the
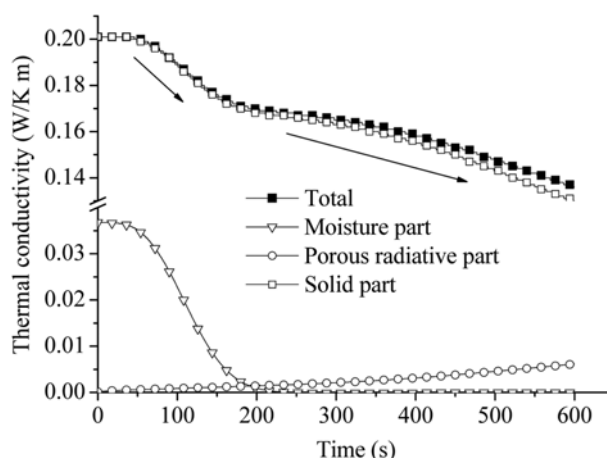

Fig. 2. The variation of thermal conductivity of top layer of willow under heat flux of 20 kW/m².
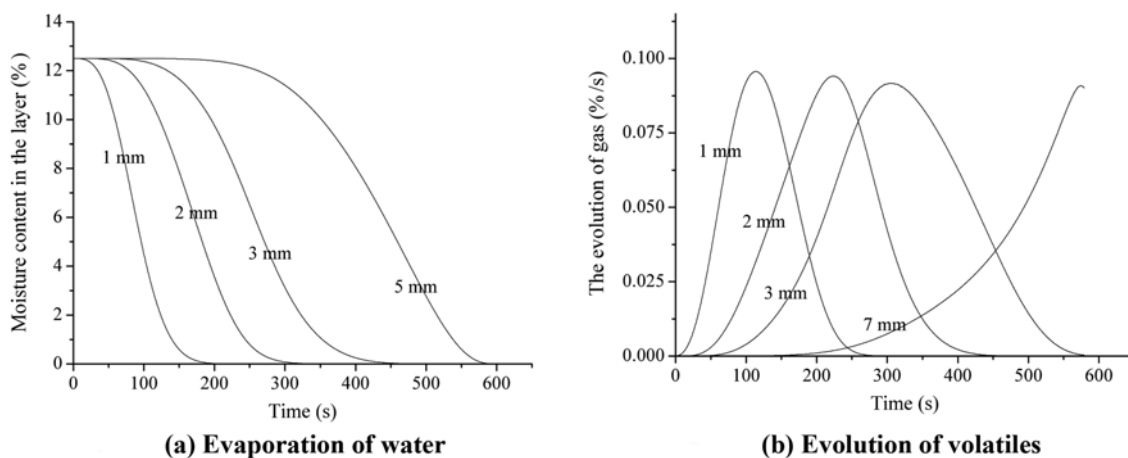
(a) Evaporation of water

(b) Evolution of volatiles

Fig. 3. The pyrolysis in different layers of willow under heat flux of 20 kW/m².

process. One is ascribed to the part of the decreased thermal conductivity of moisture part before 200 s, while the other one is mainly due to the gradually build-up of char with small thermal conductivity in the top layer. The radiative part of thermal conductivity ascribed to re-radiation from pores gives a remarkable increase during the process. However, the variation of total thermal conductivity shows a similar trend as that of solid part, since that of radiative part is not that pronounced.

The evaporation of moisture and evolution of volatiles in different layers of willow under the heat flux of 20 kW/m² are predicted and shown in Fig. 3(a) and Fig. 3(b). A pyrolysis front like a thermal wave is propagated from the top layer to the inner layers of solid during the thermal decomposition process. The above two processes were sustained longer for inner layers, due to the slow local temperature rise. Therefore, the predicted apparent mass loss rate reaches its peak value at around 300 s, when the decomposition of most top layers proceeds in a substantial extent (Fig. 4). The predicted apparent loss of willow under the heat flux of 20 kW/m² is not exactly consistent with the experimental data, showing the differences in three zones (Fig. 4). In the first zone, the experimental apparent mass loss mainly attributed to the water evaporation is larger than that predicted by the model. In experiments, most heat might be consumed to vaporize the moisture in the initial stage. The evapo-
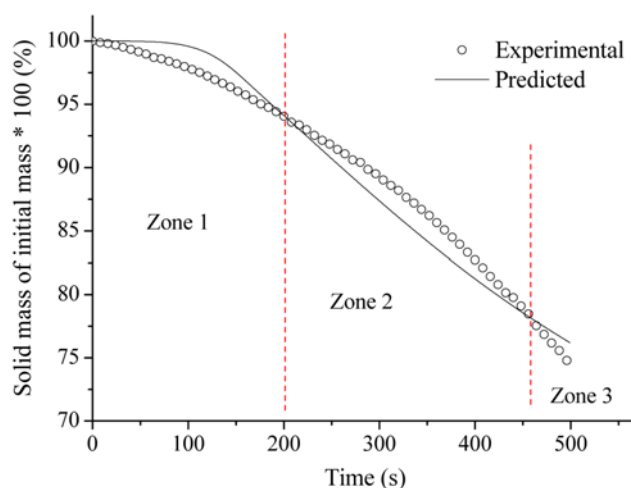

Fig. 4. The apparent mass loss of willow under heat flux of 20 kW/ m².

ration of water is determined by a chemical reaction in the model, rate of which is controlled by the local temperature rise. With the increased temperature of top layers, the apparent mass loss determined by the one-step multi-reaction scheme in the model gives
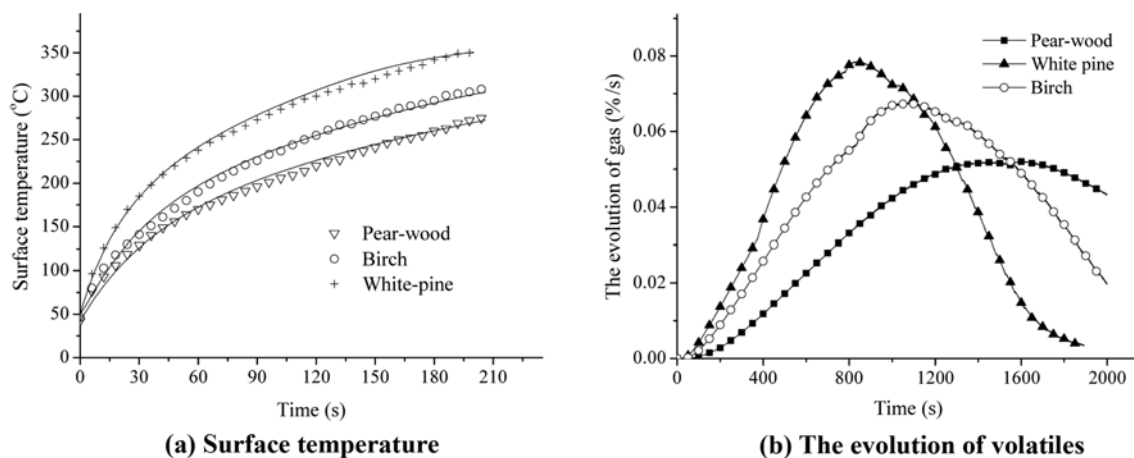

(a) Surface temperature

(b) The evolution of volatiles

Fig. 5. The comparison between experimental data and predictions for different wood species under heat flux of 20 kW/m².

an outstanding decrease over the experimental data in the second zone. The acceleration of experimental apparent mass loss in the third zone is possibly attributed to the structural changes (in-depth cracking), facilitating the heat transferred inside solid and enhancing the thermal decomposition reactions [7]. However, this phenomenon is not involved in the mathematical model, with regard to the assumption (4).

According to the transient thermal conduction theory, the density, specific heat and thermal conductivity play a very important role in the temperature variation during the pyrolysis of wood. The wood species are different in all the above three properties, among which density is considered to be the most significant one. The good agreement between the experimental and predicted surface temperature of three wood species confirms the significance to consider the different densities for wood species in the model (Fig. 5(a)). The differences in thermal conductivity and specific heat among wood species are not pronounced. This also gives an exact prediction on ignition time of three wood species under different heat fluxes, with the fixed surface temperature of 400 °C as ignition criterion (Fig. 6).

The one-step multi-reactions kinetic scheme with the same kinetic parameters produces similar variation of the predicted total evolu-tion of volatiles for the three wood species during the process (Fig. 5(b)). The discrepancy among them is mainly due to the different in-depth temperature histories of wood species, which is significantly determined by their densities. Actually, the chemical kinetics for thermal decomposition of wood is to a substantial extent related to its constituent fractions (cellulose, hemicellulose and lignin), except for that under high heat fluxes [8]. It is suggested that an analysis of constituent fractions for the wood species should be included in the mathematical model, although the surface temperature of different wood species is acceptably predicted.

Moisture content is estimated as another important factor influencing the thermal behavior of wood. The comparison between the experimental and predicted surface temperature of birch with different moisture contents under 15 kW/m² also confirms the above statement (Fig. 7(a)). The discrepancy between the experimental and predicted data is remarkable for that with moisture content of 36%, with regard to the temperature plateau around 100 °C due to the significant energy sink by evaporation of free water beyond FSP [1]. However, no significant difference between the experimental and predicted surface temperature of birch with different moisture contents could be observed under relatively high heat flux of 40 kW/m² (Fig. 7(b)), even for that of high moisture content of 36%. The energy consumed by evaporation of water, whether free water fraction or bound water fraction, only accounts for a small portion of the net heat energy absorbed from intensive external irradiance. This contributes to the equivalent effect on thermal conduction process as taking water-evaporation reaction heat into the thermal-balanced equation of surface layer. As a result, the predicted ignition time of birch with different moisture content under 40 kW/m² is in a sound agreement with the experimental data (Fig. 8). It could be summarized that the evaporation of water could be described as a chemical process under relatively high heat flux, while under low heat flux the evaporation of water beyond FSP should be described as a physical process.

The lag-effect of moisture content on predicted surface temperature rise is observed to be in accordance with that of experimental data (Fig. 7(a) and Fig. 7(b)). It should be clarified that the effect of moisture content on thermal conductivity of solid part is significant as described in Eq. (11). The total thermal conductivity of solid is significantly increased with the moisture content, dragging the tem-
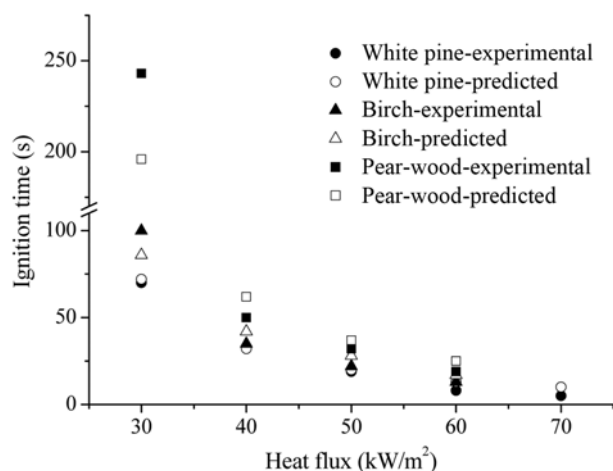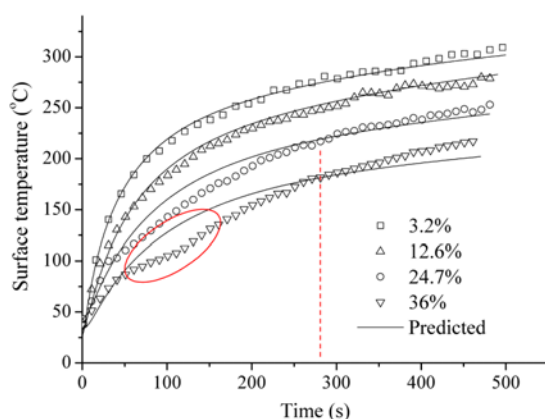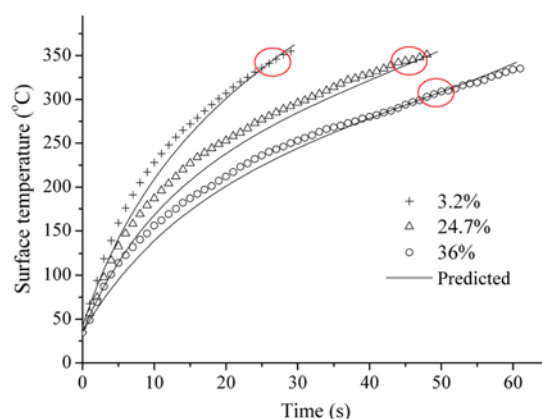

Fig. 6. The comparison between experimental and predicted ignition time for three wood species under different heat fluxes.

(a) Under heat flux of 15 kW/m²

(b) Under heat flux of 40 kW/m²

Fig. 7. The comparison between the experimental and predicted surface temperature of birch with different moisture contents.
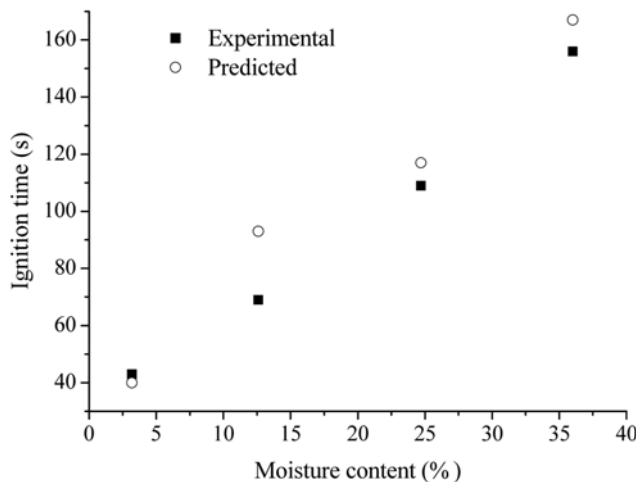
Fig. 8. The comparison between the experimental and predicted ignition time of birch with different moisture contents under heat flux of 40 kW/m².
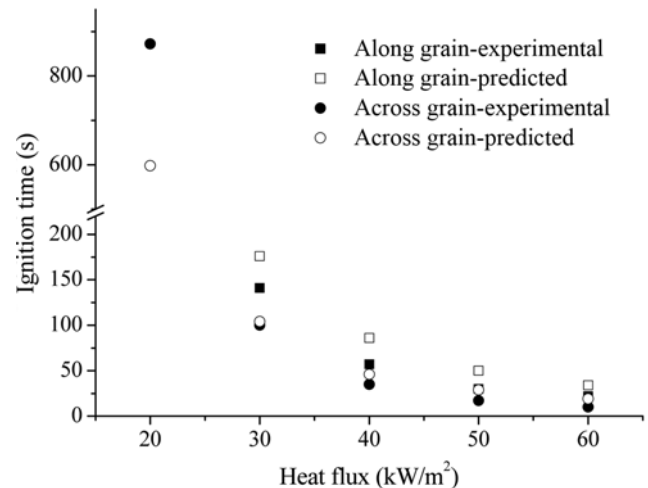

Fig. 10. The comparison between the experimental and predicted ignition time of larch with different grain orientations under different heat fluxes.

perature rise of the local layer. The effect of moisture content on the thermal conductivity is rather pronounced and should be considered in the model.
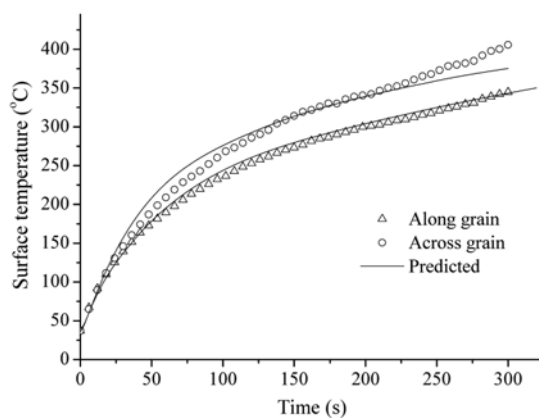
A literature survey shows that the thermal conductivity also depends on the orientation of the grain of wood. According to the Wood Engineering Handbook [15], the thermal conductivity of wood is approximately 2.0-2.8 greater along grain than perpendicular to grain. Fredlund [16] gives the range of ratios as between 1.75 and 2.25 in the study. In this work, it is assumed that the increase in thermal conductivity for the along-grain samples is typically 2.25 times greater than that of across-grain samples. The discrepancy in density and specific heat between samples of different grain orientations is not considered in the model. The agreement between experimental and predicted surface temperature of larch with different grain orientations is observed under both low and high heat fluxes (Fig. 9(a) and Fig. 9(b)). It confirms that the difference in thermal conductivity plays a significant role in the history of temperature rise for along-grain and across-grain samples. The predicted ignition time for larch with two grain orientations matches experimental data well, except for the across-grain sample under the heat flux of 20 kW/m² (Fig. 10). Since

the experimental ignition temperature for that under heat flux of 20 kW/m² is greatly more than 400 °C, the predicted ignition time is profoundly underestimated. The thermal conductivity of sample with different grain orientations is also related to the density and vessel distributions, which also influence the transportation of evolved volatiles and structural changes [7,17]. These characteristics should be further examined and considered in the comprehensive model.
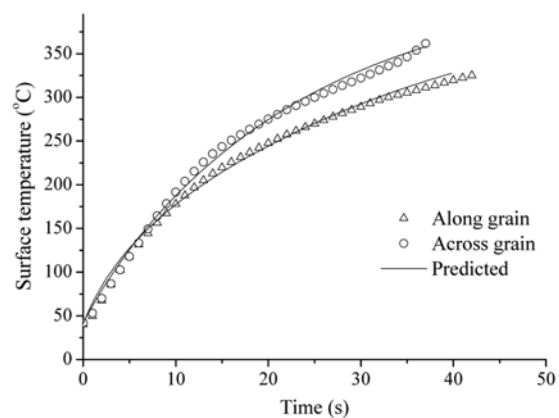
CONCLUSIONS

A mathematical model for thermal decomposition and spontaneous ignition of wood is proposed based on a set of restricted assumptions. Good agreement between the predicted and experimental temperature profiles is observed, confirming the necessity of considering chemical reaction heat in the thermal-balanced equation. The different densities for wood species are considered in the model, producing the good prediction of surface temperatures.

The total thermal conductivity of solid, composed of solid part and radiative part from pores in the model, plays an important role in prediction of temperature distribution. It gives two significant declines

(a) Under heat flux of 20 kW/m²

(a) Under heat flux of 40 kW/m²

Fig. 9. The comparison between the experimental and predicted surface temperature of larch with different grain orientations.

during the process, ascribed to the decrease of moisture part and the accumulated char fraction. The total thermal conductivity of solid is significantly increased with the moisture content, dragging the temperature rise of the local layer. Under low heat flux, the evaporation of water beyond FSP is better to be considered as a physical process. The effect of grain orientation on thermal conductivity is also included in the model, producing the prediction of surface temperatures and ignition time in good agreement with experimental data.

Although some complex physical and chemical phenomena need to be further specified and incorporated into the comprehensive model, most of the surface temperatures are exactly predicted by the proposed mathematical model. This gives birth to the reasonable prediction of ignition time of wood by employing a fixed surface temperature (400 °C) as the ignition criterion.

ACKNOWLEDGEMENT

NOMENCLATURE

T : temperature [K]
t : time [s]
x : distance from the upper surface [m]
L : thickness [m]
A : pre-exponential factor [1/s]
E : reaction active energy [J/mol]
R : universal gas constant [J/mol K]
c : thermal capacity [J/kg K]
K : reaction
k : reaction rate [1/s]
ΔH : raction heat [J/kg]
X : moisture content
d : equivalent diameter of pores
h_{conv} : thermal convective coefficient [W/m K]
Q_r'' : energy source [W/m K]
q_e'' : external heat flux per unit area [W/m^2]
q_{loss}'' : heat losses per unit area [W/m^2]
m″ : mass loss rate [kg/m^2 s]
Pe : Péclet number

Subscript

0 : initial or standard
i : reaction number
1 : char formation
2 : volatiles formation
3 : water evaporation
s : solid
c : char
g : volatile
l : liquid
v : vapor
w : wood

p : pore

Greeks

λ : thermal conductivity [W/m K]
ρ : density [kg/m]
α : average absorptivity
σ : stefan-Boltzmann constant [5.76* 10^{-8} W/m^2]
ε : emissivity
Φ : porosity of solid
φ : emissivity

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