







Modeling pyrolysis of wet wood under external heat flux

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Abstract

Experiments on the thermal decomposition of wet wood in air were carried out in this work. The samples (typically 100×100 mm exposed surface, 15 mm thick) of several species with moisture content from 5% to 30% were subjected to a uniform heat flux $20-70 \, \mathrm{kW \, m^{-2}}$. A one-dimensional pyrolysis model is proposed to examine the influence of heat flux, species and moisture content on the process of thermal decomposition of wet wood. Temperature profiles at different points and solid conversion are calculated and compared with experimental data. There is good agreement between the experimental and calculated results.

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1. Introduction

Wood and other cellulosic materials are widely used in buildings and increasingly utilized as renewable sources of energy. They also constitute a substantial fraction of the fuel load in many building fires. Thus, there have been many studies focused on their thermal behavior under high-temperature burning conditions. Thermal decomposition of wood, producing combustible gases, water vapor and char, plays an important role in the initiation of combustion and the subsequent fire behavior (i.e., flame spread and fire growth).

There are a great number of experimental and theoretical studies on the pyrolysis of cellulosic materials [1–25]. These studies have basically focused on the influence of heat flux, size, moisture content, chemical composition of the sample and structural variable on temperature distribution, solid conversion and evolution rate of the volatiles. Several literature reviews with different emphases on pyrolysis of cellulosic materials have been published [1–5], the latest one by Moghtaderi [5] dealing with theoretical studies of the pyrolysis of cellulosic materials. In his work, the previous pyrolysis models of solid fuel are broadly

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categorized into "thermal" and "comprehensive" models. While thermal models predict the conversion of solid fuel into products or charring rate based on a critical pyrolysis criterion and the energy balance [9,20,25], the comprehensive models describe the degradation of the fuel by a chemical kinetic scheme coupled with physical conservation equations for heat and/or mass transfer [8,11–19,21–24].

Meanwhile, the previous theoretical studies could be generally divided into two groups depending on solution methods used for the pyrolysis models: (1) simplified analytical studies that attempt to develop 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 by including as many physical and chemical processes as possible [9]. Except the transient propagation of a constant temperature pyrolysis front into the solid, most existing analytical studies ignore all physical and chemical processes, which limit their range of applicability and accuracy of the predictions [20,25]. On the other hand, numerical studies include physical and chemical processes, such as volatile heat convection, thermal decomposition kinetics, net decomposition exothermicity and variable thermophysical properties [6–8,10–11]. However, the effects of moisture content, variable char yield, shrinkage of sample volume and gas

Nomenclature		3	emissivity	
æ	(11)	$h_{\rm conv}$	thermal convectiv coefficient (Wm ⁻²)	
T	temperature (K)	Q_r''	energy source $(kW m^{-2}K^{-1})$	
t	time (s)	$q_{ m e}^{\prime\prime}$	external heat flux per unit area (kW m ⁻²)	
X	distance from the upper surface (mm)	$q_{ m loss}^{\prime\prime}$	heat losses per unit area (kW m ⁻²)	
L	thickness of the sample (mm)			
A	pre-exponential factor (s ⁻¹)	Subscript		
E	reaction active energy (J mol ⁻¹)		-	
R	universal gas constant (J mol ⁻¹ K ⁻¹)	0	initial or standard	
c	thermal capacity (J kg ⁻¹ K ⁻¹)	1	char formation	
λ	thermal conductivity (Wm ⁻¹ K- ¹)	2	volatiles formation	
ho	density $(kg m^{-3})$	3	water evaporation	
K	reaction	S	solid	
k	reaction rate (s^{-1})	c	char	
Δh	reaction heat (J kg ⁻¹)	g	volatile	
X	moisture content	1	liquid	
α	average absorptivity	V	vapor	
σ	Stefan-Boltzman constant	W	wood	

momentum have not been considered in most numerical studies.

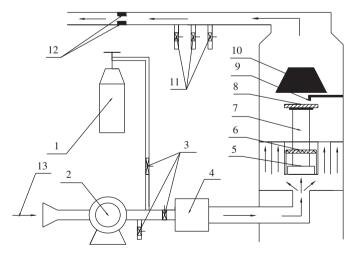
Recently, some numerical studies have added the influence of moisture content [13–16], structural changes [17–21] and gas movement inside the solid [22,23]. The purpose of this work is to obtain a wider knowledge of the influence of heat flux, species and moisture content on the process of wood pyrolysis (i.e., temperature distribution and volatiles mass efflux), but the effect of volume shrinkage and gas movement are neglected. Both experimental and theoretical studies have been conducted. Slabshaped wood was used in the experiments and the temperature at different points and the global solid conversion were examined. In the theoretical study, a pyrolysis model including the effect of moisture content was used to predict the temperature profiles and solid conversion and compared with experimental data.

2. Experimental system

The apparatus used for investigating pyrolysis and ignition of wood is shown in Fig. 1. The sample of wood was fixed in horizontal orientation by the sample holder and heated by a cone calorimeter (supplying heat flux from 0 to $80\,\mathrm{kW\,m^{-2}}$) inside a $580\times580\times460\,\mathrm{mm}$ refractory steel furnace.

Experiments on thermal decomposition of different species under an atmosphere of air were conducted in this work. One side of the samples (typically $100 \times 100 \, \text{mm}$ exposed surface, $15 \, \text{mm}$ thick) of several species was subjected to uniform heat flux from 20 to $70 \, \text{kW m}^{-2}$, and the other sides were isolated with asbestos. Samples of birch with different moisture content (about 5%, 15% and 26%) radiated by the heat flux of $40 \, \text{kW m}^{-2}$ were tested to investigate its effect on thermal degradation of wood.

Several thermocouples were placed at different points within the sample (1, 7 and 14 mm below the surface) to record the temperature along the centerline. Two thermocouples were placed in the vicinity of the center of solid surface at a depth of 1 mm, where no significant difference was observed between the two points. The continuous measurement of the mass of the solid was conducted by means of a precise electronic balance connected to the sample holder. The temperatures and the mass of the solid (plus the sample holder) were recorded every 1 s. .Runs were repeated if the recorded data in the experiment were considered to be unreasonable.



- 1. Nitrogen, 2. Electromotor, 3. Valves,
- 4. Gas mixing room, 5. Electronic balance,
- 6. Insulating board, 7. Specimen holder,
- 8. Sample 9. Electrical spark,
- 10. Cone calorimeter, 11. Electro magnetic valve,
- 12. Flowmeter, 13. Air

Fig. 1. Experimental system.

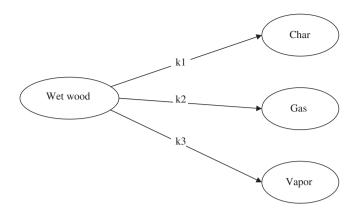


Fig. 2. The one-step multi reactions of pyrolysis of wet wood.

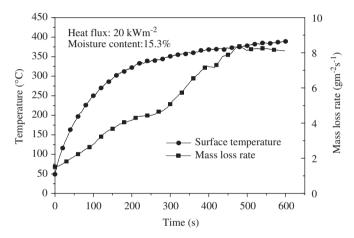


Fig. 3. Experimental data of thermal decomposition of birch under $20\,kW\,m^{-2}$ heat flux.

The surface temperature and mass loss rate of birch under 20 kW m⁻² is shown in Fig. 2. It was found that the wood sample began to lose its water of constitution as the temperature exceeded 100 °C. Solid weight loss was slow up to 240 °C and the evolved gases were not ignitable. The solid underwent glassy transition in this range. From 240 to 320 °C, the pyrolysis was thought to be endothermic and resulted in evolution of mixtures primarily composed of carbon dioxide and water vapor. From 320 to 450 °C, the wood specimen pyrolyzed rapidly and the rate of release of flammable volatiles was greatly released.

3. Description of the mathematical model

A wet wood slab, subjected to a radiant heat flux on one side is modeled. As the surface is heated (the other side is assumed to be adiabatic), the wood is first dried and then pyrolyzed by radiant and conductive heat transfer. Pyrolysis of wood to water vapor, gas and char forms a one-step, multi-global reaction scheme for pyrolysis of wet wood (Fig. 3). A small portion of the pyrolysis gases and water vapor move inward, while the greater portion pass

through the char layer and leave from the upper surface of solid.

The assumptions for the pyrolysis model of wet wood are listed as follows:

- (1) The wood slab is considered to be a one-dimensional, thermally thick, opaque and semi-infinite solid.
- (2) The heat and mass transport of the gases and vapor inside the solid is ignored. Pyrolysis gases and water vapor leave from the solid surface as soon as they are produced, and therefore the solid mass loss rate is taken as volatiles mass flux.
- (3) Evaporation of water inside the wet wood is reasonably taken account as a chemical reaction as the moisture content is below the fiber saturation point (FSP, commonly 30% [5]). There is no recondensation of water vapor inside the solid.
- (4) The chemical reactions for pyrolysis of wet wood are described by the first-order Arrhenius Law.
- (5) Heat losses by re-radiation and convection from the solid surface are included in the model.
- (6) Volume shrinkage of the solid is neglected during the process of pyrolysis.

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

$$\frac{\partial}{\partial t} [T(\rho_{\mathbf{w}} c_{\mathbf{w}} + \rho_{\mathbf{c}} c_{\mathbf{c}} + \rho_{\mathbf{l}} c_{\mathbf{l}})] = \frac{\partial}{\partial x} \left(\lambda_{\mathbf{s}} \frac{\partial T}{\partial x} \right) + Q_r'', \tag{1}$$

where Q_r'' is described as the sum of reaction heat of the three pyrolysis reactions at the temperature T:

$$Q_r'' = k_1 \rho_w [\Delta h_1^0 + (c_c - c_w)(T - T_0)]$$

$$+ k_2 \rho_w [\Delta h_2^0 + (c_g - c_w)(T - T_0)]$$

$$+ k_3 \rho_1 [\Delta h_3^0 + (c_v - c_1)(T - T_0)].$$
(2)

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

$$\frac{\partial \rho_{\mathbf{w}}}{\partial t} = -(k_1 + k_2)\rho_{\mathbf{w}},\tag{3a}$$

$$\frac{\partial \rho_{\rm c}}{\partial t} = k_1 \rho_{\rm w},\tag{3b}$$

$$\frac{\partial \rho_{g}}{\partial t} = k_{2} \rho_{w}, \tag{3c}$$

$$\frac{\partial \rho_1}{\partial t} = -k_3 \rho_1,\tag{3d}$$

$$\frac{\partial \rho_{\mathbf{v}}}{\partial t} = k_3 \rho_1. \tag{3e}$$

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

$$k = A \exp\left(\frac{-E}{RT}\right). \tag{4}$$

The boundary conditions are

$$t = 0, \quad T = T_0, \tag{5}$$

t>0, x=0, a heat balance for the control volume with a height of (Δx) is obtained, similar to the boundary condition for Bilbao's model [13]:

$$\frac{\partial [T(\rho_{w}c_{w} + \rho_{c}c_{c} + \rho_{l}c_{l})]}{\partial t}$$

$$= \left(\alpha q_{e}'' - q_{loss}'' - \lambda_{s}\frac{\partial T}{\partial x}\right)/\Delta x + Q_{r}'', \tag{6a}$$

$$q''_{loss} = \sigma \varepsilon (T^4 - T_0^4) + h_{conv}(T - T_0).$$
 (6b)

t>0, x=L, another heat balance for the control volume with a height of (Δx) is established:

$$\frac{\partial [T(\rho_{\rm w}c_{\rm w} + \rho_{\rm c}c_{\rm c} + \rho_{\rm l}c_{\rm l})]}{\partial t} = \left[\lambda_{\rm s}\frac{\partial T}{\partial x} - q_{\rm b}^{"}\right]/\Delta x + Q_{\rm r}^{"},\tag{7}$$

Table 1 Kinetic parameters for pyrolysis reactions and drying process

	$A \\ (s^{-1})$	$\frac{E}{(kJ \text{mol}^{-1})}$	Ref.	$\Delta H_i^0 (kJ kg^{-1})$	Ref.
Pyrolysis reactions Wood $\xrightarrow{k1}$ Char Wood $\xrightarrow{k2}$ Gas	7.38×10^5 1.44×10^4	106.5 88.6	[30] [30]	-420 -420	[27] [27]
Drying process Moisture $\xrightarrow{k3}$ Vapor	5.13×10^{10}	88	[29]	-2440	[28]

Table 2 Values and correlations of physical parameters used in the model

Property	Correlation/value	Ref.	
Thermal conductivity (Wm ⁻¹ K ⁻¹)	$\lambda_{s} = \eta \lambda_{c} + (1 - \eta) \lambda_{w}$ $\lambda_{c} = 0.105$ $\lambda_{w} = 0.166 + 0.369 X$	[12] [12]	
Specific heat $(kJkg^{-1}K^{-1})$	$c_{w} = 0.16010.3694$ $c_{w} = 1.95$ $c_{c} = 1.39$ $c_{g} = 2.4$ $c_{1} = 4.18$ $c_{v} = 1.58$	[12] [12] [32] [28] [12]	
Emissivity Convective coefficient (Wm ⁻² K ⁻¹) Absorptivity	$\varepsilon = 0.78$ $h_{\text{conv}} = 10$ $\alpha = 0.95$	[31] [26]	

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

The thermal conductivity value was obtained from those corresponding to wood and char. The values used here were [12]:

for wood,
$$\lambda_{\rm w} = 0.166 + 0.369 X \, ({\rm Wm}^{-1} {\rm K}^{-1}),$$
 (8a)

for char,
$$\lambda_c = 0.105 \, (Wm^{-1}K^{-1}),$$
 (8b)

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

$$\lambda_{\rm s} = \eta \lambda_{\rm c} + (1 - \eta) \lambda_{\rm w},\tag{9a}$$

$$\eta = \frac{\rho_{\rm c}}{\rho_{\rm s}} = \frac{\rho_{\rm c}}{\rho_{\rm c} + \rho_{\rm w}}.\tag{9b}$$

The parameters utilized to solve the model were obtained either by using other experimental systems or from the literature. The kinetic parameters for different pyrolysis reactions of wet wood are given in Table 1, specific heat for wood, char, gas, liquid and vapor are given in Table 2, and the initial density and moisture content of the sample was measured experimentally for different species (Table 3).

Moreover, the average absorptivity of wood, independent of the species, was approximately one under the cone calorimeter as obtained by Wesson [33]. The emissivity value of wood slabs, 0.78, was given by Costa [31] and considered to be constant during the experiment. The value for convective coefficient of the solid surface was taken as $10 \, \mathrm{Wm}^{-2} \mathrm{K}^{-1}$ from the literature [26].

The model allows calculations of the temperature distributions, solid conversion and evaporated water at different points in the sample. Using the results, global conversion of the solid could be calculated and compared with experimental data. This will be discussed in next section.

4. Results and discussion

The numerical model was used to examine the impact of heat flux, species and moisture content on the process of pyrolysis of wood. The temperatures and solid conversion of wood were calculated from the above pyrolysis model and compared with the experimental data.

The temperatures at different points of a birch sample under 20 kW m⁻² heat flux were calculated and compared with the experimental data (Fig. 4). As the slab is heated,

Details of the samples used in the experiments of thermal decomposition of wood

Species	Mongolian oak	White birch	Aspens	Spruce	White pine	Masters larch
Density (kg m ⁻³)	888	740	582	469	360	469
Moisture content (%)	14.9	15.3	14.4	14.1	14.6	14.2

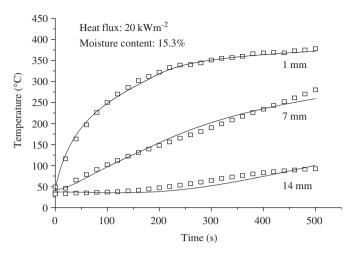


Fig. 4. Comparison between experimental data and calculated results on temperature distribution of birch under $20\,kW\,m^{-2}$ heat flux.

the surface temperature is gradually increased and the wood is simultaneously dried and pyrolyzed. Due to the temperature gradient, temperatures at different depths increased in sequence and the thermal wave of pyrolysis propagates into the solid.

Moreover, no drying plateau could be found at approximately 100 °C at different depths inside the solid (Fig. 4), which is not consistent with the results of Bilbao [13]. This may be caused mainly by the nonuniform heat flux used in Bilbao's work. Thus, the drying process of wet wood is described by a one-step chemical reaction in this model. The solid conversion and water evaporation at different points of the solid were calculated and using the results, total solid conversion was obtained and compared with the experimental data in Fig. 5. It can be seen that the calculated temperatures and total solid conversion match the experimental data very well.

The influence of heat flux on the process of wet wood pyrolysis was also studied by using this model. The surface temperature of birch under four different heat fluxes (20, 20, 40 and 60 kW m⁻²) were predicted and compared with experimental data (Fig. 6). As the heat flux increased, the surface temperature was increased more steeply due to the higher temperature gradient. Meanwhile, it is seen that the calculated surface temperature at the low heat flux matches the experimental data better than that at relatively high heat fluxes. This is mainly because the materials were not opaque at the high heat flux and the effect of diathermancy of solid should be considered [34,35]. Moreover, it was found by Moghtaderi [36] that there was no obvious drying behavior during the process of pyrolysis of wet wood or before piloted ignition of wet wood for heat fluxes higher than 25 kW m⁻². And as the brief process of pyrolysis of wet wood can be observed under higher heat fluxes, the model proposed in this paper was more valid and precise for the pyrolysis of wet wood under relative low heat fluxes (lower than $40 \,\mathrm{kW}\,\mathrm{m}^{-2}$).

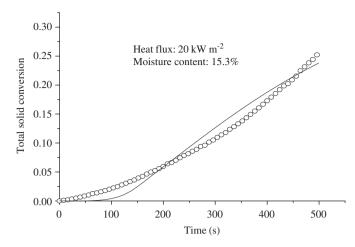


Fig. 5. Comparison between experimental and calculated total solid conversion of birch under $20\,\mathrm{kW}\,\mathrm{m}^{-2}$ heat flux.

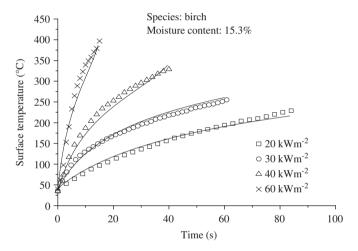


Fig. 6. Comparison between experimental and calculated surface temperature of birch under four different heat fluxes.

The experimental results shows that the temperature profiles are also affected by wood species and moisture content, and the surface temperature was calculated and compared with the experimental data (Figs. 7 and 8). As the solid fuel is heated, the material properties, including density, specific heat, thermal conductivity, thermal diffusivity, void fraction, permeability and so on, all continuously change with time. Depending on the transient conduction law, the former four properties (especially thermal diffusivity) play significant role in temperature variation during the process of wood pyrolysis. The differences of surface temperature between the wood species are mainly due to their different thermal diffusivities. In the study of Fredlund [24], it was described that the thermal conductivity of wood varied with moisture content, temperature, density, emissivity and the type of gases enclosed in the material. There is a good agreement between the calculated and experiment data, as the effect of

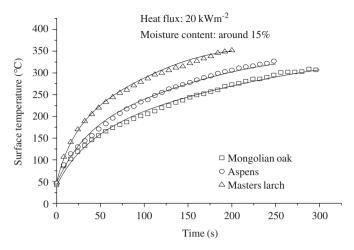


Fig. 7. Comparison between experimental and calculated surface temperature for three different species under $20\,kW\,m^{-2}$ heat flux.

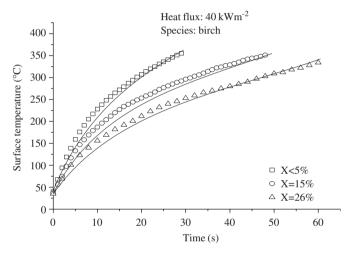


Fig. 8. Comparison between experimental and calculated surface temperature of birch for three different moisture content under $40\,\mathrm{kW\,m^{-2}}$ heat flux.

moisture content and solid conversion on thermal conductivity is considered in this model.

Finally, the effect of moisture content on pyrolysis of wood will be discussed. As stated by some investigators [5,13,23], solid fuels of wood-based materials naturally contain moisture existing in two basic forms: (i) bound or hygroscopic water, and (ii) free or capillary water. The former is found in the cell wall bonded to the hydroxyl groups inside the solid, and the latter is present in the liquid form in the void of wood. Moreover, FSP is defined by the saturation of the cell walls at a certain relative humidity of surrounding air, as additional water beyond FSP exists only in the form of free water.

When moist wood is subjected to external heat flux, it first undergoes initial drying process as surface temperature reaches a temperature near 100 °C. Most of the energy is consumed by heating and evaporating the free water portion of total moisture content. With drying proceeding,

the total moisture content of the surface drops to the level close to FSP, and then, an evaporation front moves into the solid, leaving behind a zone with a moisture content below FSP. While ahead of the evaporation front the moisture is in the form of free water, behind the front moisture exists in the form of water vapor. And the water vapor mixed with volatiles flows out of the solid, affecting the progress of pyrolysis. Therefore, the moisture content has an important effect on the pyrolysis behavior of wood.

The surface temperatures of birch with different moisture content are calculated by using this model and compared with experimental data (Fig. 8). It could be found that the surface temperature rise was slowed down as the moisture content of solid increased. This could be explained because a large portion of energy was consumed by evaporating the water (higher or lower than FSP) for higher moisture content, and thus, small portion of energy was transferred into the solid. Consequently, the temperature profiles and pyrolysis rates at different points were all modified by the moisture content.

Moreover, there is a good agreement between the calculated and experimental data, as some discrepancies could be observed mainly due to the ignorance of the heat and mass transport of water vapor and recondensation of the vapor inside solid in this model. It is confirmed by Moghtaderi [5] that this pyrolysis model of wet wood ignores free water and is applicable to the samples with moisture contents below the FSP having similar longitudinal and transversal dimensions. The restrictive assumptions are removed in a moisture–vapor equilibrium pyrolysis model of wet wood [21].

5. Conclusions

The influence of heat flux, species and moisture content on thermal decomposition of wet wood has been experimentally and theoretically studied in this paper. Depending on the above discussions, the following conclusions are obtained:

- (1) Wood sample begins to lose its water of constitution as the temperature exceeds 100 °C. Solid weight loss is slow up to 240 °C and the evolved gases are not ignitable. From 240 to 320 °C, pyrolysis results in evolution of mixtures primarily composed of carbon dioxide and water vapor. From 320 to 450 °C, the wood specimen begins to pyrolyze rapidly and flammable volatiles are released.
- (2) No drying plateau was found at approximately 100 °C at different depths inside the solid, as there is no obvious drying behavior during the pyrolysis of wet wood for heat flux higher than 25 kW m⁻² [35]. The calculated results match experimental data very well except that under higher heat flux the effect of diathermancy of the solid should be considered under the high heat fluxes. Thus, this model was more valid and precise for the pyrolysis of wet wood under relative low heat flux.

- (3) The presence of moisture content slowed down the surface temperature rise due to the consumption of large portion of energy. Temperature profiles and pyrolysis rates at different points in the solid were all modified by the moisture content. And it was found that this pyrolysis model was applicable to the samples with moisture content below FSP.
- (4) The discrepancies observed between the calculated and experimental data may be caused by two domains:

 (i) input parameters for calculation of the model, and
 (ii) the restrictive assumptions for the model, including the ignorance of heat and mass transfer of volatiles and vapor inside the solid and volume shrinkage. So, the effect of gas movement inside solid, void fraction and volume shrinkage should be taken account for the development of the pyrolysis model of wet wood.

Appendix A

A.1. Description of the energy source Q''_r in the model

Q'' is the sum of the reaction heat of the three pyrolysis reactions of wet wood. The standard reaction heat ΔH_R^0 is defined as dispersion of the enthalpy between resultants and reactants under standard conditions (the pressure is $10^5 \, \text{Pa}$ and temperature is $298 \, \text{K}$):

$$\Delta H_R^0 = \sum_{i=s} M_i \, \Delta h_{fi,298}^0 - \sum_{i=r} M_j \, \Delta h_{fj,298}^0, \tag{A.1}$$

or

$$\Delta H_R^0 = \sum_{i=s} m_i \, \Delta h_{mi,298}^0 - \sum_{i=r} m_j \, \Delta h_{mj,298}^0, \tag{A.2}$$

where M_i , M_j , m_i , m_j are the mol and mass of resultants and reactants, respectively. $\Delta h_{fi,298}^0$ and $\Delta h_{fi,298}^0$ are the standard resulting heat for resultants and reactants per unit mol, and $\Delta h_{mi,298}^0$ and $\Delta h_{mj,298}^0$ are the standard resulting heat for resultants and reactants per unit mass, respectively. Substituting the mass variation of wood, char, gases, moisture and water vapor in pyrolysis reactions into Eq. (A.2) gives

$$\Delta H_R^0 = (k_1 \rho_{\rm w} \Delta h_{mc,298}^0 + k_2 \rho_{\rm w} \Delta h_{mg,298}^0 + k_3 \rho_1 \Delta h_{mv,298}^0) - (k_1 \rho_{\rm w} \Delta h_{mw,298}^0 + k_2 \rho_{\rm w} \Delta h_{mw,298}^0 + k_3 \rho_1 \Delta h_{ml,298}^0).$$
(A.3)

Combining the right-side term of Eq. (A.3) gives

$$\Delta H_R^0 = k_1 \rho_{\rm w} (\Delta h_{mc,298}^0 - \Delta h_{mw,298}^0) + k_2 \rho_{\rm w} (\Delta h_{mg,298}^0 - \Delta h_{mw,298}^0) + k_3 \rho_{\rm l} (\Delta h_{mv,298}^0 - \Delta h_{ml,298}^0) = k_1 \rho_{\rm w} \Delta h_1^0 + k_2 \rho_{\rm w} \Delta h_2^0 + k_3 \rho_{\rm l} \Delta h_3^0.$$
 (A.4)

Actually, it is known that the reaction heat varies with temperature and surrounding pressure. In this model, the variation of the surrounding pressure was ignored, but the effect of temperature on the reaction heat was considered. Similar to Eq. (A.2), the reaction heat for the pyrolysis system at the temperature T could be described as

$$\Delta H_R^T = \sum_{i=s} m_i \, \Delta h_{mi,T} - \sum_{i=r} m_j \, \Delta h_{mj,T}. \tag{A.5}$$

Eq. (A.5) was differentiated by T, giving

$$\frac{\mathrm{d}\,\Delta H_R^T}{\mathrm{d}\,T} = \sum_{i=s} m_i \frac{\mathrm{d}\,\Delta h_{mi,T}}{\mathrm{d}\,T} - \sum_{j=r} m_j \frac{\mathrm{d}\,\Delta h_{mj,T}}{\mathrm{d}\,T}.\tag{A.6}$$

Because the pressure was constant for the reaction system, Eq. (A.6) could be reduced as

$$\frac{\mathrm{d}\,\Delta H_R^T}{\mathrm{d}\,T} = \sum_{i=s} m_i c_i - \sum_{i=r} m_j c_j. \tag{A.7}$$

Integrating Eq. (A.7) from T_0 to T gives

$$\Delta H_R^T - \Delta H_R^0 = \int_{T_0}^T (\sum_{i=s} m_i c_i - \sum_{j=r} m_j c_j) dT.$$
 (A.8)

Substituting the mass variation of wood, char, gases, moisture and water vapor in pyrolysis reactions into Eq. (A.8) gives

$$\Delta H_R^T - \Delta H_R^0 = \int_{T_0}^T \left[(k_1 \rho_w c_c + k_2 \rho_w c_g + k_3 \rho_l c_v) - (k_1 \rho_w c_w + k_2 \rho_w c_w + k_3 \rho_l c_l) \right] dT.$$
 (A.9)

Thus

$$\Delta H_R^T - \Delta H_R^0 = k_1 \rho_{\rm w} (c_{\rm c} - c_{\rm w}) (T - T_0) + k_2 \rho_{\rm w} (c_{\rm g} - c_{\rm w}) (T - T_0) + k_3 \rho_1 (c_{\rm v} - c_1) (T - T_0).$$
 (A.10)

Substituting Eq. (A.4) into Eq. (A.10) gives

$$\Delta H_R^T = k_1 \rho_{\rm w} [\Delta h_1^0 + (c_{\rm c} - c_{\rm w})(T - T_0)] + k_2 \rho_{\rm w} [\Delta h_2^0 + (c_{\rm g} - c_{\rm w})(T - T_0)] + k_3 \rho_{\rm l} [\Delta h_3^0 + (c_{\rm v} - c_{\rm l})(T - T_0)].$$
 (A.11)

The sum of reaction heat of the three pyrolysis reactions Q_r'' at the temperature T, energy source in the model, is equal to ΔH_R^T :

$$Q'' = \Delta H_R^T = k_1 \rho_{\rm w} [\Delta h_1^0 + (c_{\rm c} - c_{\rm w})(T - T_0)]$$

$$+ k_2 \rho_{\rm w} [\Delta h_2^0 + (c_{\rm g} - c_{\rm w})(T - T_0)]$$

$$+ k_3 \rho_{\rm l} [\Delta h_3^0 + (c_{\rm v} - c_{\rm l})(T - T_0)].$$
(A.12)

A.2. Energy conservation for the boundary layers

The slab-shaped wood is considered to be inert, opaque, semi-infinite but finite thickness board in this model. The illustration of energy conservation for boundary layers in the model is described in Fig. 9. The physical domain discretized into layers (one-dimensional cells) of finite size (Δx) . It is observed that the energy conservation consists of

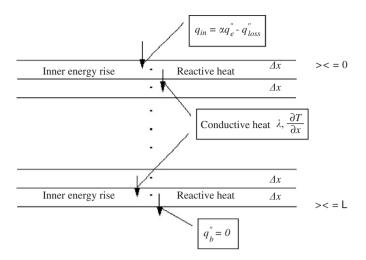


Fig. 9. Illustration of the energy conservation for boundary layers.

inner energy rise, external heat-in, conductive heat and energy source. The boundary conditions are:

for
$$x = 0$$
,
$$\frac{\partial [T(\rho_{w}c_{w} + \rho_{c}c_{c} + \rho_{l}c_{l})]}{\partial t}$$
$$= \left(\alpha q_{e}'' - q_{loss}'' - \lambda_{s}\frac{\partial T}{\partial x}\right)/\Delta x + Q'', \tag{A.13}$$

for
$$x = L$$
,
$$\frac{\partial [T(\rho_{w}c_{w} + \rho_{c}c_{c} + \rho_{l}c_{l})]}{\partial t}$$
$$= \left[\lambda_{s}\frac{\partial T}{\partial x} - q_{b}''\right]/\Delta x + Q''. \tag{A.14}$$

Then, the partial differential equations describing the model are discretized on the grid layers, resulting in a system of strongly coupled algebraic equations. Because of that, all unknowns could be evaluated by iteration on these algebraic equations.

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