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Modelling Self-Heating and Self-Ignition Processes during Biomass Storage

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Abstract: A mathematical model was developed to predict the self-heating and self-ignition processes of relatively dry biomass during storage, considering in detail the effects of moisture exchange behaviour, low-temperature oxidation reaction and associated heat and mass transfer. Basket heating tests on fir pellets and powder at temperatures of 180–200 °C were conducted to observe the heating process and determine the kinetics of low-temperature chemical oxidation for model validation. As a result, it was demonstrated that the developed model could reasonably represent the self-heating and spontaneous combustion processes of biomass storage. Furthermore, the numerical study and model sensitivity analysis revealed that reasonably describing the low-temperature oxidation and associated heat and mass transfer process with reliable estimations of kinetic and thermophysical parameters of the biomass material is necessary for predicting the self-ignition, considering the effect of water exchange behaviour is essential to predict the self-heating process even for relatively dry biomass, such as pellets, with the moisture content up to 15–20%.

Keywords: biomass; storage; self-heating; spontaneous combustion; modelling

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1. Introduction

As an important renewable energy source, biomass is utilised on large scales for heat and power generation and biofuel production. However, due to the low energy density and the regional and temporal distribution, a logistic chain—including the storage, transportation and handling of a bulk mass of biomass—is essential to ensure a stable supply of feedstock for bioenergy conversion systems [1]. To achieve higher energy density and reduce supply chain costs, raw biomass can be pre-dried, milled and compressed into pellets, which have been an important form of solid commercial biofuels and are widely used for heat and power production [2].

During the storage, as well as transportation and handling, biomass in piles or heaps generates heat due to physical processes related to moisture condensation and wetting, biological reactions associated with microbial degradation and chemical oxidation reactions [3–6]. As the thermal conductivity of biomass material is generally poor, the heat produced within the biomass pile may not be sufficiently dissipated to the surroundings. Consequently, the inner temperature rises, and the elevated temperature, in turn, enhances biological and chemical oxidation reactions and their heat generation, leading to a continuous increase in the temperature (i.e., a self-heating process occurs). The ongoing increase in the temperature may trigger spontaneous combustion [7], leading to economic losses and endangering the safety of operators [8]. Even if spontaneous combustion does not occur, a low degree of self-heating can cause losses of mass and energy and emissions of harmful greenhouse gases [9–12]. Therefore, it is highly important and necessary to prevent self-heating and self-ignition of biomass piles for efficient and safe management of biomass storage.

The self-heating of stored biomass materials involves various physical processes and biological and chemical reactions [3,5,9]. Moisture exchange behaviours and chemically oxidative reactions contribute heat to the self-heating process even for relatively dry biomass,

such as biomass pellets [13,14]. The involved reactions can occur in series or parallel, which is of great complexity, not to mention the heat and mass transfer processes involved as well. All of these determine that self-heating depends on the properties of the biomass material (e.g., moisture and particle size), the configuration of the pile (e.g., size and shape), and environmental conditions of storage (e.g., temperature and humidity) [3], making reasonable description and prediction of self-heating and spontaneous combustion processes challenging. Conventional prediction methods are based on basket heating experiments [15], but they only predict the tendency of a material to self-ignite. Moreover, the experimental temperatures are relatively high, and the spontaneous combustion and its prior process are measured rather than the occurrence and development of the self-heating process. Large-scale storage experiments can also be carried out to monitor the self-heating process [13,14]. However, the experimental design, environmental conditions, and especially the operating parameters are difficult to be manipulated, and the experiments are also time-consuming and costly. In contrast, the modelling approach can overcome the drawbacks of the experimental methods by establishing and solving mathematical models that couple the reactions and heat and mass transfer process to describe and predict the self-heating and spontaneous combustion processes [4,16].

For a long time, model description of the spontaneous combustion of solid fuels such as biomass and coal has been mainly based on the Frank-Kamenetskii (F-K) model of thermal explosion theory [4,17–19], which considers an Arrhenius form chemical reaction and neglects the consumption of reactants. Sidhu et al. [20] extended the F-K model by including the oxygen consumption and related mass transfer, and also the contribution of microbiological activity in heat generation. Based on this, Fu et al. [21] applied a model to consider the moisture exchange and transport processes to investigate the effect of ambient humidity variation on the self-heating process of a wood bark pile. Gray et al. [22] developed a model in which, in addition to chemical oxidation, water-mediated oxidation was taken into consideration for the storage of moist biomass. The heat generated through the evaporation and condensation of moisture was also included in the model, as well as the mass transfer processes of oxygen, liquid water and vapour. Krause et al. [16] further considered the complex chemical reactions of fuel decomposition and oxidation, and the momentum, heat and mass transport processes in a model to simulate the self-ignition process of a lignite stockpile. A similar model had been developed by Ferrero et al. [4] and employed to simulate the self-heating in a stockpile of pine wood chips, which included physical processes and chemical and biochemical reactions as heat sources [4,23].

Although the heat production mechanisms and transport processes are considered and integrated systematically, the state-of-art models have been limited in their applications due to the diversity of biomass, the variation in storage forms and the rationality of mechanistic models [3]. As a result, the models are far from making reliable predictions for the self-heating and spontaneous combustion processes of biomass piles. In the present work, a mathematical model was developed for describing the self-heating and self-ignition processes in the storage of relatively dry biomass such as wood pellets, taking into account the physical processes associated with water exchange and low-temperature chemical oxidation. Basket heating experiments on materials of wood pellets were conducted to determine low-temperature oxidation kinetics and measure the temperature evolution during the self-heating process, which were applied for model validation. A sensitivity analysis was also employed to evaluate model parameters' effects on prediction, including kinetics, material, and process parameters.

2. Modelling and Methods

2.1. Models and Its Numerical Solution

Biomass pellets have experienced pre-drying and temperatures of 100–170 °C during pelletisation, in which microorganisms colonising in biomass material are inactivated. The resulting pellets have a low moisture content (<10%), insufficient to support microbial activity and the heat production due to microbial activity is very limited [11,14]. Therefore,

the physical process related to water exchange (i.e., evaporation and condensation), low-temperature chemical oxidation reactions and associated heat and mass transfer processes are considered in modelling the self-heating and self-ignition processes of stored pellets and other relatively dry biomass, while the effect of microbial activity excluded.

The model is based on the energy and mass conservation of a porous solid system. The heat and mass transfer processes, coupled with the reactions and their heat effects, are considered to describe the self-heating processes within the biomass stockpile. The general formulas of the one-dimensional (1D) mathematical model are

$$\rho c_P \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + \sum S_{T_i} \tag{1}$$

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} + r_i \tag{2}$$

where T is the temperature, x is the position, t is the time, ρ, c_P, and λ are the bulk density, effective heat capacity and effective thermal conductivity of the bulk material, respectively, and C_i is the concentration of species i involved in the reaction including O_2, water vapour and liquid. D_i is the effective diffusivity of species i. In Equations (1) and (2), the left-hand side is the accumulation term of heat or mass, the first term on the right-hand side represents the thermal conduction or species diffusion, S_{T_i} is the heat source ($S_{T_{phy}}$ for the physical process of water exchange and $S_{T_{chem}}$ for low-temperature oxidation reactions), and r_i is the mass source of species i. The model assumes that the properties of biomass and gas are independent of temperature, and the mass loss of the biomass is negligible as compared to the total biomass mass. The heat and mass transport due to convection within the pores of biomass pile are not separately considered, while the thermal conductivity and gas diffusivities are appropriately increased to accommodate their effects [4]. For simplicity, the model is presented here in 1D form but can be extended to 2D or 3D applications by considering the configuration of the storage and heterogeneities of the stored biomass.

The stored biomass material can undergo the moisture exchange with the atmosphere inside the pores and the ambience through evaporation and condensation processes, leading to thermal effects and moisture transport, which are described by an Arrhenius-type model [4,16,22,24,25], given as

$$r_m = EV \cdot W \exp(-\frac{L_v}{RT}) - CD \cdot V \tag{3}$$

where r_m is the condensation adsorption rate or evaporation desorption rate; EV and CD are the pre-exponential factors of the evaporation and condensation process, respectively; W and V are the concentration of liquid water and vapour, respectively; L_v is the latent heat of water evaporation. Apparently, the water evaporation in Equation (3) is presented as a first-order reaction with regard to the local liquid water content, with an Arrhenius-type rate constant. At the same time, the vapour condensation is modelled as a first-order reaction with regard to the water vapour concentration in the gas phase, with a constant reaction rate constant.

Chemical oxidation contributing to the self-heating process covers a wide temperature range from close to room temperature, at which self-heating starts, to the ignition and even subsequent spontaneous combustion. It virtually involves various oxidative reactions, including oxidation, pyrolysis and hydrolysis, proceeding simultaneously or successively in the process [3], but it is often modelled with a global oxidative reaction rather than a mechanistic model [3,4,21]. Considering the effect of oxygen availability on the reaction, the low-temperature chemical oxidation of materials is described by a first-order global reaction with regard to the oxygen concentration [21,26]. The oxidation rate is denoted as

$$r = \rho A C_{O_2} \exp(-\frac{E}{RT}) \tag{4}$$

where A and E are the pre-exponential factor and activation energy of the dry oxidation reaction, respectively; however, moisture may catalyse or enhance the oxidative reaction. To account for this effect, a separate water-mediated oxidative reaction is additionally included in the model following the approach of Gray et al. [27], and its rate is expressed as

$$r_{wet} = \rho A_{wet} C_{O_2} \exp(-\frac{E_{wet}}{RT}) \quad (5)$$

where A_{wet} and E_{wet} are the pre-exponential factor and activation energy of the wet oxidation reaction, respectively.

The source terms of the energy and mass conservation equations of the self-heating model called as full model, are summarised in Table 1 (the first row). If the contribution of the water-mediated oxidation is negligible, the model is simplified as model 1. On the other hand, for dry biomass stored in a confined space, the effect of physical processes associated with moisture exchange can be ignored, and the heat mainly originates from low-temperature chemical oxidation. In this case, the model is simplified as model 2. Because the low-temperature oxidation and its heat release are generally weak, little oxygen is consumed during the self-heating process, and the effects of oxygen and its transport may be excluded. The model is then reduced to the classical F-K model (model 3) [19]. In the present work, the full model and its simplified models were compared to evaluate the effects of moisture behaviour and oxygen transport on the self-heating and self-ignition process.

Table 1. Mathematical model of heat and mass transfer and its source term.

	S_{Tchem}	S_{Tphy}	r_{O_2}	r_V	r_W
The full model	$Qr + Q_{wet}r_{wet}$	$L_v r_m$	$r + r_{wet}$	r_m	$-r_m$
Simplified model 1	Qr	$L_v r_m$	r	r_m	$-r_m$
Simplified model 2	Qr	-	r	-	-
Simplified model 3	$Q\rho A \exp(-E/RT)$	-	-	-	-

The models were solved by discretising Equations (1) and (2) based on the finite volume method (FVM) [28]. The discretised equations were then calculated through the tridiagonal matrix algorithm. The model inputs for the calculations include the physical properties and reaction kinetics of the biomass. Since the moisture-related physical processes and their kinetics are less dependent on the material, the literature data [22] were used. However, for low-temperature chemical oxidation, because the kinetic model is global and empirical rather than mechanistic [3], its kinetics are dependent on the material and its properties. Therefore, the kinetics determined by experimental measurements is required to ensure the accuracy of the model prediction.

2.2. Methods for Determining the Low-Temperature Oxidation Kinetics

The kinetics of the low-temperature oxidation is determined by the basket heating method [29] based on the F-K theory. Assuming that the heat-producing oxidation reaction inside a 1D sample follows the Arrhenius law and neglects the consumption of reactants and the effects of moisture, Equation (1) is simplified to be

$$\rho c_P \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + QA\rho \exp(-\frac{E}{RT}) \quad (6)$$

Accordingly, the transients F-K method [30,31] was applied to derive the kinetics of the oxidation reaction. Namely, the thermal conduction term in Equation (6) can be neglected if the temperature around the centre of the sample is uniform during heating, and Equation (6) becomes

$$\rho c_P \frac{\partial T}{\partial t} = QA\rho \exp(-\frac{E}{RT}) \quad (7)$$

Or

$$ln(c_P \cdot \frac{dT}{dt}) = ln(QA) - \frac{E}{R}\frac{1}{T} \quad (8)$$

Equation (8) is independent of the sample size. Therefore, the apparent kinetic parameters of the exothermic reaction can be determined by conducting experiments at multiple temperatures with only one sample size and then doing Arrhenius fitting for Equation (8). Additionally, the right-hand side of Equation (7) is, in fact, the heat release rate of the oxidation reaction at the determined temperature. Therefore, it can be used to represent the self-heating propensity, especially for comparison between different biomass materials.

Two transient F-K methods, i.e., the cross-point (CPT) method [30] and the heat release (HR) method [31], were developed with different assumptions used for neglecting thermal conduction. The CPT method assumes that the thermal conduction term can be neglected when the temperatures of the centre and its nearby are equal; the HR method takes the sample central temperature equal to the oven temperature to neglect the thermal conduction. Nevertheless, both methods are recommended by a standard [32] for determining the kinetics of low-temperature oxidation of granular materials, including biomass and evaluating the tendency to spontaneous combustion due to low-temperature oxidation. Moreover, the basket heating test monitors the evolution of the internal temperature of a sample stored at a constant ambient temperature. Therefore, it can also represent the process of self-heating developing into spontaneous combustion, which can be used for model validation.

2.3. Experiments on the Self-Heating Process of Biomass Pellets

Basket heating experiments on biomass materials were carried out following the standard procedure [32] to investigate the characteristics of the self-heating process of the samples and to measure the low-temperature oxidation kinetics. The raw material used for the experiments was fir pellets, typical of softwood pellets, having a diameter of around 8 mm, a length of 10–40 mm (Figure 1a) and a bulk density of 585 kg/m^3. The composition of the pellets was 5.87% moisture, 2.22% ash, 73.5% volatile fraction and 18.41% fixed carbon. In order to study the effect of particle size, the pellets were also milled into 0.3–2 mm powder (Figure 1b). the powder has a slightly higher moisture content of 6.3% due to moisture absorption during the processing and a lower bulk density of 370 kg/m^3. Therefore, the basket heating experiments tested the fir pellets and powder.

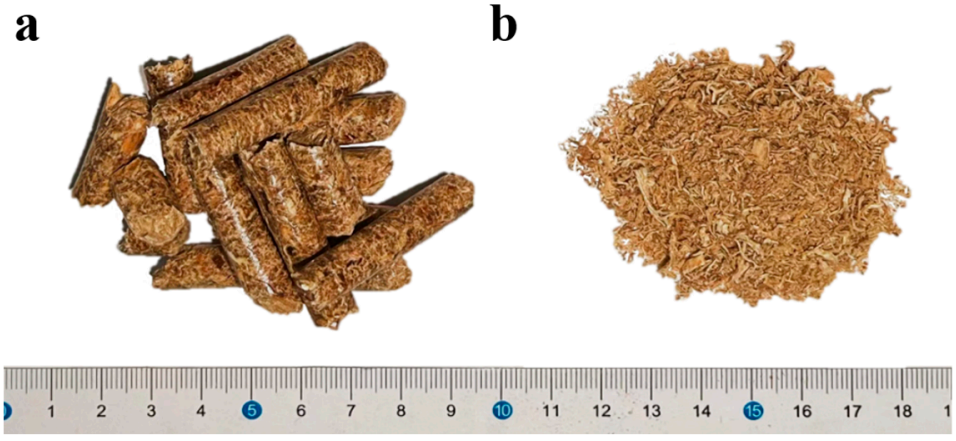


Figure 1. Images of the samples of (**a**) fir particles and (**b**) fir powder.

Figure 2 exhibits the experimental setup. It consists of a well-ventilated isothermal oven, a metal mesh basket container with a cubic side length of 10 cm, thermocouples and corresponding temperature acquisition and display devices. During the experiment, the biomass material was filled into the basket, weighed and recorded, and then three K-type thermocouples were placed at the centre of the basket, the quadrature point (side

point) and outside the basket, respectively. When the oven temperature reached and stabilised at the set value, the basket, together with the thermocouples, was put into the oven. The temperatures were recorded by the data acquisition system every 5 s until the sample temperature soared and exceeded the oven temperature by more than 60 °C or exceeded the oven temperature and then stabilised for a long time. Thereafter, the HR temperature, CPT temperature and corresponding heating rates of the samples were determined based on the temperature records; the apparent kinetic parameters *E* and *QA* were further derived by linear fitting via Equation (8) based on the measurement at several different oven temperatures. According to the characteristics of the samples, the oven temperature was set to 180, 185, 190, 195, and 200 °C for the basket heating experiments of both the pellets and powder, and their low-temperature oxidation kinetic parameters were determined separately.

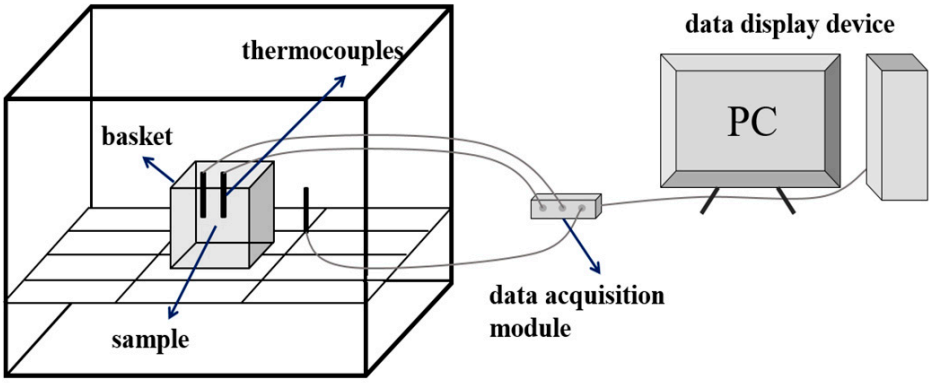


Figure 2. Schematic of the facility for basket heating test.

3. Results and Discussion

3.1. Temperature Evolution from Self-Heating to Spontaneous Combustion Process

Figure 3 illustrates the evolution of the centre temperature of the fir pellets and powder at different oven temperatures in the basket heating tests. As can be seen, both samples went through similar heating stages at different oven temperatures. At first, the temperature of the sample centre increased nearly linearly due to physical heating. Then the heating rate decreased significantly around 60–80 °C because of the endothermic evaporation of the moisture inside the sample. The evaporation stage exhibited a slower rise in temperature. After drying, the sample temperature rose rapidly again, but the increase rate slowed down significantly as approaching the oven temperature and the sample underwent slow oxidation. The heat from the oxidation, together with the oven heating, drove the temperature gradually increase to cross the oven temperature. After that, the centre temperature could be stable and even gradually decrease due to the generated heat offset by the heat loss through conduction, or the temperature increase could accelerate due to the enhanced oxidation to trigger a temperature runaway, i.e., self-ignition occurs. Figure 3 shows that the oven temperature mainly affected the heating rates at the evaporation and slow oxidation stage. The higher the oven temperature, the shorter the evaporation period due to the fast oven heating and rapid water evaporation. The higher the oven temperature, the faster the heating rate of the slow oxidation stage and the shorter the time required for the sample to develop from self-heating to spontaneous combustion.

Figure 3 indicates the main differences in heating characteristics between fir pellets and powder. The heating rates of the pellets were obviously faster than those of the powder in the heating stages before and after the moisture evaporation stage, which was mainly due to the pellets having higher bulk density and lower thermal resistance, resulting in faster heating and interior temperature rise. The pellets sample had a shorter evaporation stage and faster temperature rise at the evaporation stage also because of the fast heating as well as its slightly lower moisture content. In the slow oxidation stage, the temperature rise of the pellets was slower mainly because of the better thermal conductivity and resulting

more rapid heat transfer. Moreover, the larger particle size of the pellets meant slower oxidation, resulting in a slower self-heating rate under the same oven temperature and longer development from self-heating to spontaneous combustion. After heating for 9 h at 180 °C, the central temperature of the fir pellets was stabilised at 173–176 °C without any further rising tendency. However, self-ignition occurred for the pellets when the oven temperature was 185 °C. These indicated the critical self-ignition temperature of the fir pellets sample with the size of 0.001 m^3 to be between 180–185 °C. In contrast, the powder spontaneously ignited after prolonged oxidative heating at the oven temperature of 180 °C, implying its critical self-ignition temperature to be below 180 °C. It is evident in Figure 3 that fir powder was more prone to self-heating and spontaneous combustion than the pellets under the same conditions [33]. The stronger heat transfer performance, as well as lower moisture content of the pellets, resulted in a shorter heating time as compared to the powder, reflecting that the heat transfer and moisture evaporation, to a certain extent, determined the time for the sample to be heated from room temperature to oven temperature. On the other hand, the slower low-temperature oxidation and faster heat transfer of the pellets led to the time from heating to spontaneous combustion longer than that of the powder at the same temperature. These differences were more obvious at lower oven temperatures (Figure 3).

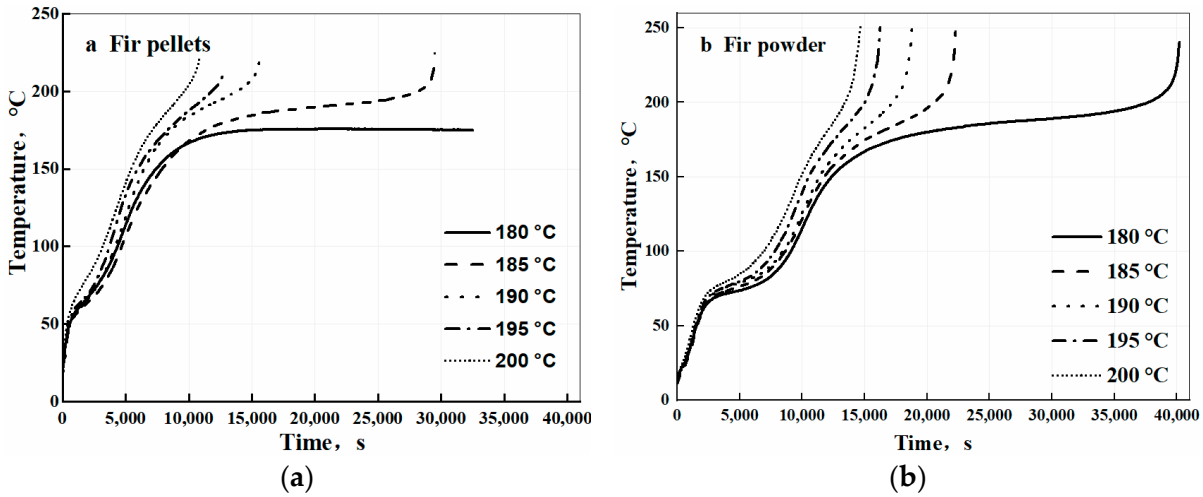


Figure 3. Central temperature evolution of (**a**) fir pellets, (**b**) fir powder under different oven temperatures.

3.2. Determination of Low-Temperature Oxidation Kinetics

Based on the temperature measurements at various oven temperatures, the cross-point temperatures and their corresponding heating rates of the two samples were determined by HR and CPT methods, respectively. The results are summarised in Figure 4. In addition, with the linear fitting of Equation (8), the kinetic parameters of the low-temperature oxidation for fir pellets and powder were obtained and are listed in Table 2.

Table 2. Determined chemical oxidation kinetics of fir pellets and powder.

	CPT	**HR**	**CPT**	**HR**
	***E* kJ/mol**	***QA* J/(kg·s)**	***E* kJ/mol**	***QA* J/(kg·s)**
Fir pellets	62	1.01×10^8	132	7.71×10^{15}
Fir powder	113	7.94×10^{13}	126	2.40×10^{15}

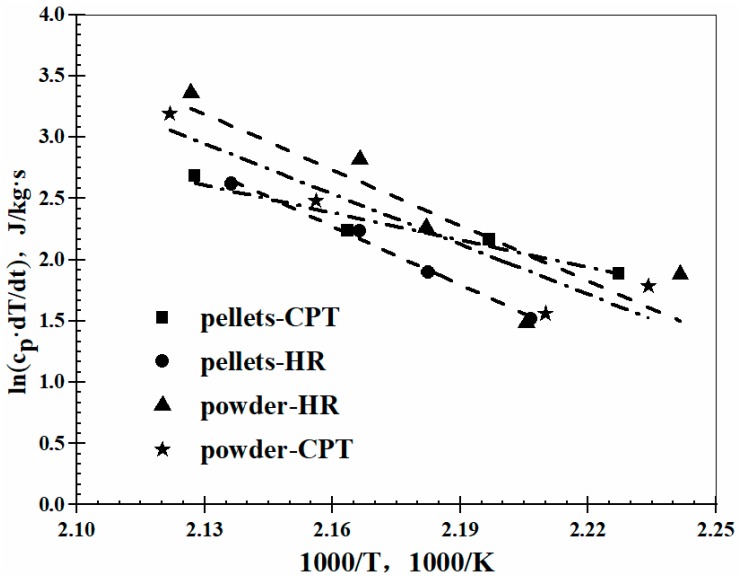


Figure 4. Derivation of chemical oxidation kinetics of fir pellets and powder by CPT and HR methods.

In Figure 4, $c_P \cdot dT/dts$ are the heat release rates of low-temperature oxidation at the cross-point temperatures. As can be seen, the heat release rate of fir powder was, in general, higher than that of fir pellets at the same temperature, exhibiting a stronger oxidative reactivity, i.e., a stronger self-heating capacity of low-temperature oxidation and a higher proneness to self-ignition. It is consistent with the observation on the temperature evolution of low-temperature oxidation driven self-heating to spontaneous combustion in the basket heating tests (Figure 3). Similar observations were reported in a study on wheat biomass pellets and dust [34].

Table 2 indicates that the kinetics of fir powder obtained by the two methods were generally consistent, while those for fir pellets were quite different, although the results of the two methods converged at higher temperatures. The kinetic parameters, E and QA, of the two different forms of fir samples obtained with the HR method were similar and both in the same order of magnitude. However, the activation energies obtained with the HR method are greater than those by the CPT method. Such a difference is attributed to their different assumptions for neglecting thermal conduction. Nevertheless, the kinetic parameters of the two forms of fir samples are all in the range of the kinetics of various biomass materials, including wood pellets [15,19] surveyed in the literature [3].

3.3. Validation of the Self-Heating Model

The self-heating model was validated with the temperature measurements in the basket heating tests on both fir powder and pellets, but only the validation with the tests of the fir powder is presented here. The inputs of chemical oxidation kinetic parameters for the model computation were derived from the basket heating experiments, as shown above. The model inputs for the parameters related to the biomass material properties and reaction conditions are summarised in Table 3.

Table 3. Data input for model calculation.

Parameters	Description	Unit	Data
A	Pre-exponential factor of low-temperature chemical oxidation	s^{-1} or $m^3/kg\ s$	1.0×10^8
$C_{O_{2,0}}$	Ambient oxygen concentration	-	0.21
$C_{v,0}$	Initial vapour concentration	mol/m^3	1.5

Table 3. *Cont.*

Parameters	Description	Unit	Data
$C_{W,0}$	Initial moisture concentration in biomass material	mol/m^3	1300
CD	Pre-exponential factor of water vapour condensation process	s^{-1}	4.7
$c_{p,a}$	Heat capacity of air	J/kg K	1006
$c_{p,b}$	Heat capacity of fir powder	J/kg K	1350
D_o	Diffusivity of oxygen	m^2/s	2.5×10^{-5}
D_v	Diffusivity of vapour	m^2/s	7.5×10^{-6}
E	Apparent activation energy	J/mol	1.26×10^5
EV	Pre-exponential factor of water vapour evaporation process	s^{-1}	3.41×10^4
h	Convective heat transfer coefficient	W/m^2 K	25
l	Half-length of the basket	m	0.05
L_v	Latent heat of water vapour condensation	J/mol	4.2×10^4
Q	Calorific value of the biomass	J/kg	2.4×10^7
R	universal gas constant	J/mol K	8.314
T_0	Initial temperature of the biomass	K	285.9
T_a	Oven temperature	K	453
λ_a	Thermal conductivity of air	W/m K	0.023
λ_b	Thermal conductivity of fir powder	W/m K	0.18
ρ_a	Air density	kg/m^3	1.29
P_b	Fir powder bulk density	kg/m^3	370
ε	Porosity	-	0.3

Taking the heating of the fir powder sample at the oven temperature of 180 °C as an example, Figure 5 compares the model-predicted evolutions of the temperature at the centre and side point with the measurements. It is worth noting that the full model considered in detail the heat effects and associated heat and mass transfer of water exchange associated with physical processes and low-temperature chemical oxidation as well as water-mediated chemical oxidation. As can be seen in Figure 5, the model generally represents experimentally observed trends of the temperature evolutions at the two locations within the sample. During the stages of heating up to the oven temperature, the model-predicted temperature evolution of the side point agreed well with the measurements; the predicted central temperature evolution was also generally consistent with the measurement except for its overestimating the temperature increase rate at the evaporation stage, which may be the result of less accurate kinetics of the evaporation/condensation. When it comes to the oxidation stage prior to spontaneous ignition, despite roughly predicting the time of spontaneous combustion, the model over-predicted the temperatures of the centre and side points as compared to the experimental values. The over-prediction may be attributed mainly to the fact that this stage corresponds to higher temperatures, which enhances heat transfer within the sample as a consequence of, for example, the thermal conductivity increasing with temperature [35,36]. However, the model set with constant thermophysical properties was unable to reflect this variation, leading to an underestimate of the heat dissipation at higher temperatures. Nevertheless, the model predictions of the temperature evolution were generally in agreement with the measurements. The model calculations for the cases at different oven temperatures and for fir pellets (not shown here) also presented similar trends. Therefore, the model developed here can be applied to predicting the process of

self-heating to spontaneous combustion of relatively dry biomass materials provided with experimentally determined kinetics of low-temperature oxidation.

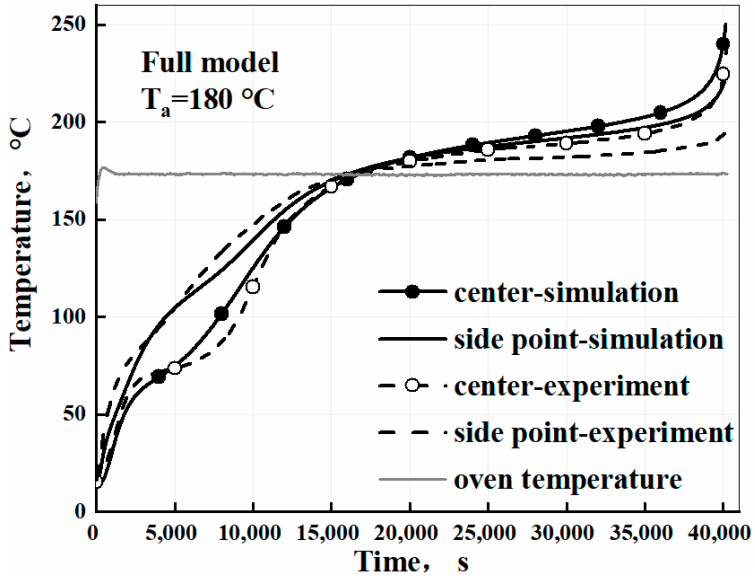


Figure 5. Model-predicted temperature evolutions of the centre and side points are compared with the measurements of fir powder at 180 °C.

Figure 6 displays the predictions of the central temperature evolutions by the full model and its simplified models (Table 1) compared with the measurement from the basket heating test of the fir powder at 180 °C so as to examine the contributions of various mechanistic processes to the self-heating. Without considering the water-mediated oxidation, the simplified model 1 predicted the central temperature evolution profile almost coincident with that from the full model. Therefore, it implies that water-mediated chemical oxidation and its heat effect hardly affect self-heating. However, the comparisons between the calculation results from the two models indicated that, during the evaporation stage, the wet oxidation resulted in a slight decrease in the oxygen concentration in the sample centre, as illustrated in Figure 7. Moreover, the exothermic effect of the wet oxidation also caused slightly higher central temperatures at the evaporation stage, as shown in the zoom-in figure in Figure 6. Nevertheless, these observations revealed a weak contribution of the water-mediated oxidation to the self-heating process of relatively dry material, consistent with the observations in a modelling work [22]. The possible explanation for this phenomenon was the low moisture content (6.3%) of fir powder. For relatively dry biomass materials such as wood pellets, therefore, the effect of the wet oxidation can be neglected when describing the self-heating process.

The comparison in Figure 6 shows that, although the simplified model 2, without considering the water-exchange physical processes, may predict the onset of spontaneous combustion, it significantly overestimates the central temperatures at the evaporation and its subsequent heating stage. The overestimation is attributed to the model omitting the strong heat absorption by moisture evaporation. This demonstrates that describing the water-exchange behaviour and its influence is essential for the prediction of the self-heating process, even for relatively dry materials. As for the simplified model 3, i.e., the traditional F-K model, it predicted neither the time of self-ignition nor the temperature evolution from the self-heating to self-ignition (Figure 6) because the effects of the oxygen diffusion and consumption on the chemical oxidation as well as water behaviour were not considered. It meant that the oxygen consumption and mass transfer process had a significant impact on the self-heating and low-temperature oxidation process, even for such a small volume (0.001 m^3) of biomass materials used in basket heating tests. Therefore, the model and experimental method based on the F-K theory can be applied only for evaluating and

comparing the propensities of biomass materials to spontaneous combustion rather than predicting the self-heating and spontaneous combustion processes of biomass storage in practice.

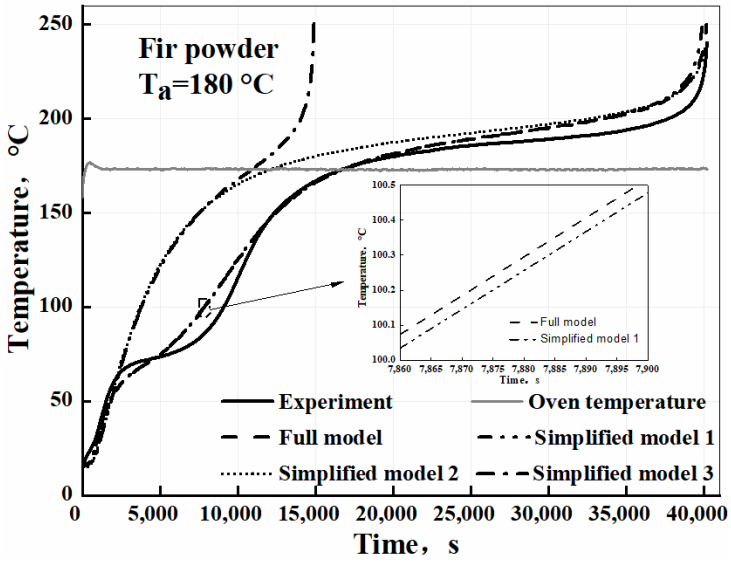


Figure 6. Predicted centre temperature evolution by the self-heating model and its simplifications compared with the measurements of fir powder sample at 180 °C.

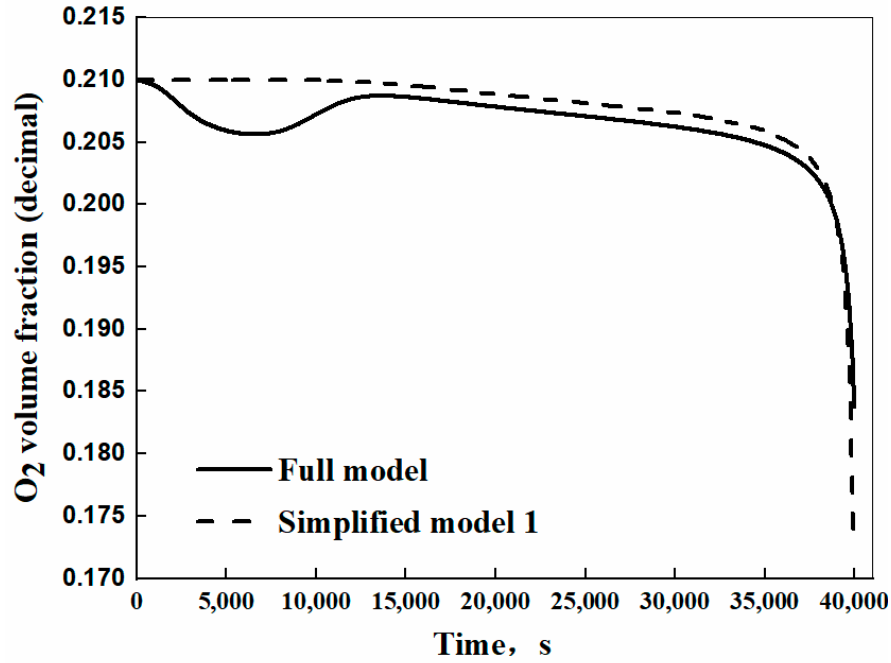


Figure 7. Model predicted evolutions of oxygen concentration at the centre of fir powder sample heated at 180 °C.

3.4. Numerical Study and Sensitive Analysis of the Model

The modelling study above shows that the self-heating process of stored biomass depends on the physical processes of moisture behaviour, low-temperature chemical oxidation, and heat and mass transfer process. Therefore, the model prediction relies on the kinetics, material properties, and process characteristics. Therefore, a sensitivity analysis was performed to investigate the influence of these parameters on the rationality and accuracy of the model to predict the self-heating and self-ignition processes. The main parameters examined and the results of their sensitivity analysis are summarised in Table 4.

It indicates that the storage parameter, ρ_b, material thermophysical properties, λ_b and $c_{p,b}$, and biomass reactivity parameters, QA and E, were critical to predicting the self-heating process reasonably. In particular, a small variation in the reactivity parameters significantly changes the predicted trend of the self-heating process.

Table 4. Sensitivity analysis of the main parameters affecting the self-heating process.

Parameter	Symbol	Increase/ Decrease	Effect on	
			Time to Reach T_a	Autoignition Time
Porosity	ε	−75%	−8.6%	+0.7%
		−25%	−2.7%	−1.5%
		+25%	+2.3%	+1.9%
		+75%	+7.3%	+6.3%
Bulk density	ρ_b	−75%	−48.4%	-
		−25%	−14%	-
		+25%	+13.3%	−9.1%
		+75%	+40.5%	−5.7%
Thermal conductivity	λ_b	−75%	+168.6%	+42.6%
		−25%	+20.3%	−6.6%
		+25%	−12.8%	+44.1%
		+75%	−28.4%	-
Specific heat capacity	$c_{p,b}$	−75%	−50%	−63.8%
		−25%	−14.7%	−20.5%
		+25%	+14.1%	+20.7%
		+75%	+50%	-
Oxygen diffusivity	Do	−75%	0%	+7.7%
		−25%	0%	+0.8%
		+25%	0%	−0.5%
		+75%	0%	−1%
Vapour diffusivity	Dv	−75%	+30.4%	+16%
		−25%	+3.7%	+1.7%
		+25%	−2.6%	−1%
		+75%	−6.1%	−2.3%
Pre-exponential factor of evaporation process	EV	−75%	+12.1%	+5.9%
		−25%	+1.4%	+0.8%
		+25%	−1.7%	−0.6%
		+75%	−3.1%	−1.3%
Pre-exponential factor of condensation process	CD	−75%	−11.1%	−5.1%
		−25%	−3.4%	−1.6%
		+25%	+3.2%	+1.6%
		+75%	+9.6%	+4.6%

Table 4. *Cont.*

Parameter	Symbol	Increase/ Decrease	Effect on	
			Time to Reach T_a	Autoignition Time
Pre-exponential factor of low-temperature chemical oxidation	*QA* or *A*	−25%	+1.1%	-
		−10%	+0.2%	+28.4%
		−5%	+0.06%	+10.9%
		+25%	−1.4%	−24.1%
		+75%	−3.3%	−39.3%
Activation energy	*E*	−5%	−12.2%	−57.3%
		−1%	−2.3%	−29.9%
		+1%	+1.2%	-
		+5%	+4.5%	-
Moisture content	*M*	3%	−17.7%	−7.8%
		10%	+14%	+6.2%
		15%	+32.5%	+13.9%

- No spontaneous combustion occurred; + or − Increase or decrease.

Table 4 indicates that increasing the pre-exponential factor of the chemical oxidation, for example, for a material with stronger oxidation reactivity, led to a significantly reduced self-ignition time but had little effect on the time required for the central temperature to reach oven temperature. The reason is that the heat release of chemical oxidation was very weak before the slow oxidation stage, only in the order of 0.1 W/kg or even smaller. However, reducing *QA* by 10% increased the self-ignition time by 28.4%. No self-heating occurred when *QA* was lowered by 25%, with the central temperature stabilised at around 192 °C. A similar phenomenon was observed for the change in activation energy *E*, but the effect was much more sensitive. Altering *E* by merely 5% resulted in a dramatic difference in the central temperature evolution, increasing rapidly to spontaneous combustion or going stably without ignition, as shown in Figure 8. These reflected the importance of the oxidative reactivity of stored fuels for spontaneous combustion and the necessity of determining the oxidative kinetics for accurate prediction of self-ignition. However, the global kinetics of chemical oxidation vary widely [3], depending on biomass species and properties such as particle size [4,19,34]. Determining the kinetics of specific biomass materials is inconvenient for engineering applications. It implies the necessity and importance of further developing a mechanistic model of the oxidative reaction to replace the global model in the improvement of model prediction and generalisation.

The self-heating and self-ignition processes are the most sensitive to the thermal conductivity and specific heat capacity among the material thermophysical parameters. The thermal conductivity of biomass is generally low. However, it is very varying with biomass species, particle structure and storage structure and increases with increasing particle and bulk density, moisture content and temperature [35–38]. Table 4 indicates that a 75% increase in the thermal conductivity λ_b enhanced the heat transfer (heating or dissipation) and remarkably inhibited the accumulation of heat in the biomass pile, with no spontaneous combustion occurring. On the contrary, a 75% reduction led to a 168.6% and 42.6% increase in the time to reach the oven temperature and spontaneous ignition, respectively (Table 4). Although lowering λ_b slowed down the temperature rise in the biomass pile, it still developed to spontaneous ignition after reaching the oven temperature (Figure 9) because the heat generation was dominated by chemical oxidation reactions during the slow and fast oxidation stages and the lower thermal conductivity were favourable to heat accumulation. Such effects explain the faster heating at the heating stages and slower heating at the oxidation stage of fir pellets than those of fir powder

(Figure 3), mainly because the pellet samples have a higher bulk density and, consequently, higher effective thermal conductivity.

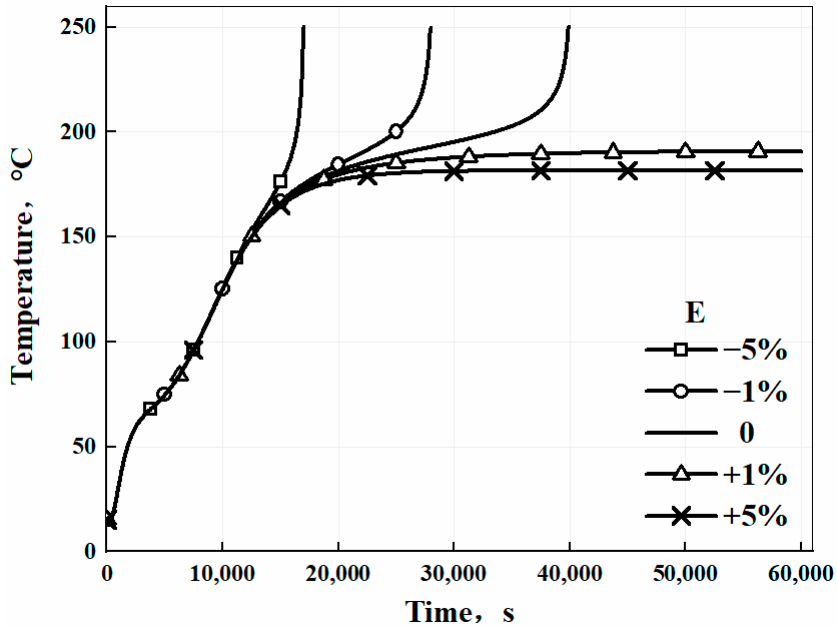


Figure 8. Predicted profiles of the central temperature vary with the activation energy of chemical oxidation E.

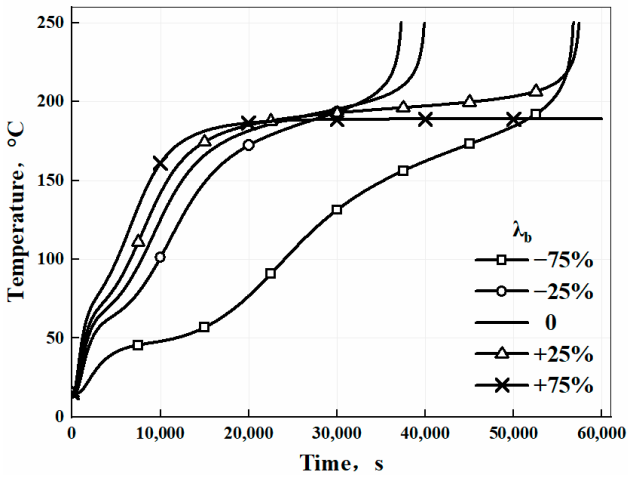


Figure 9. Predicted profiles of the central temperature vary with the thermal conductivity of biomass sample λ_b.

As can be seen from Table 4, the effective specific heat capacity $c_{p,b}$ also plays a significant role in the self-heating and spontaneous combustion processes of biomass. Research has demonstrated that the effective specific heat capacity of biomass increases linearly with density, moisture and temperature [35,37,39]. Therefore, when the biomass undergoes self-heating, the $c_{p,b}$ increases, which in turn results in a delay in all stages of the self-heating process, thus leading to a consequent increase in the time to reach the oven temperature and spontaneous ignition, respectively, even with no ignition occurred.

It is also observed in the sensitivity analysis that changing the evaporation or condensation pre-exponential factors EV and CD did not significantly affect the time to reach the oven temperature and spontaneous combustion (Table 4) and, as expected, changing EV and CD had the opposite effects on the predictions. In contrast, the variation in the moisture content M had positive correlations with the times to reach the oven temperature

and spontaneous ignition (Figure 10a). The time to reach self-ignition increases linearly with increasing the content, as shown in Figure 10b. In particular, increasing the moisture content from 3% to 15% significantly prolongs the time to reach the oven temperature and, subsequently, the thermal runaway state. The main reason is that with the increased moisture content, more heat is required for moisture evaporation, which prolongs the heating of the evaporation stage. In contrast, the model calculations indicated that the effects of the enhanced mass, heat transfer, and wet oxidation are not considered for the moisture content up to 20%. Therefore, even for relatively dry fuels (with M = 3–15%), the description of the moisture exchange behaviour in biomass piles is essential for a reasonable prediction of the self-heating process.

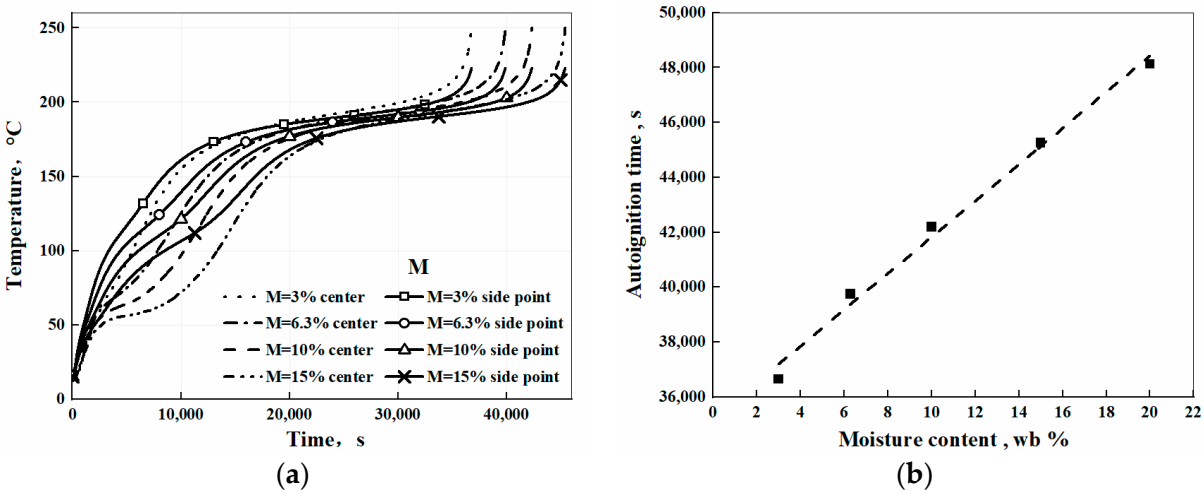


Figure 10. Effect of the moisture content M on the self-heating process of stored biomass: (**a**) model-predicted profiles of the central and side point temperature varying with the moisture content and (**b**) the predicted time to reach the ignition temperature correlated with the moisture content.

4. Conclusions

A mathematical model describing the self-heating and self-ignition process during storage of relatively dry biomass was developed, with the moisture exchange behaviour and low-temperature chemical oxidation and their associated heat and mass transfer processes considered in detail. In order to obtain the model input parameters for model validation and numerical study, the basket heating experiments were carried out to derive the low-temperature oxidation kinetics of fir pellets and powder based on the two transient F-K methods and to observe the temperature evolutions inside the biomass storage. The validation demonstrated that the model could reasonably describe the temperature evolution process and predict the spontaneous ignition within the biomass storage by applying the determined low-temperature oxidation kinetics. The numerical study and sensitivity analysis showed that it is essential to reasonably describe the low-temperature oxidation and its associated oxygen consumption and mass transfer for the prediction of the low-temperature oxidation-driven self-heating process and spontaneous combustion. It implies that developing a mechanistic model to replace the global model of oxidation could improve model prediction and generalisation. Furthermore, it was found that considering the water exchange behaviour is essential to predict the self-heating process even for relatively dry biomass such as pellets with moisture content up to 10–20%, while the role of water-mediated oxidation reaction can be ignored. In addition, the sensitivity analysis revealed that the reactivity parameters, material thermophysical properties and characteristic storage parameters could significantly affect the self-heating and spontaneous combustion process, implying the importance of reliable estimations of the parameters to reasonable predictions.

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