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Identify dominant parameters of comprehensive pyrolysis model - Part I: Variance-based sensitivity analysis of wooden materials

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Abstract: Comprehensive pyrolysis models can involve numerous parameters, making it difficult to identify the dominant physics and often requiring computational optimization. This study applies variance-based sensitivity analysis to identify the key parameters governing pyrolysis, using birch wood and medium-density fibreboard as fuels. First, the effects of kinetics properties were investigated by varying the activation energy and reaction order according to changes in the peak temperature and conversion rate of the DTG curve. The results show that the sensitivity of activation energy is generally more than ten times that of reaction order, indicating that the pyrolysis reaction temperature range is much more important than the detailed reaction path. Second, moisture kinetics were found to have a relatively small effect on mass loss, although they influence the center temperature. Finally, the competition between chemical reaction and physical heat transfer was analyzed. Under low moisture content (10%), chemical reactions are more important for mass loss, while heat transfer is more influential on center temperature. At 50% moisture content, the effects of wood and char thermal properties are significantly reduced. Nevertheless, both chemical reaction and physical heat transfer should be considered in pyrolysis modeling.

Keywords: Chemical kinetics; pyrolysis; kinetics property; thermogravimetry; modelling.

NOMENCLATURE

A pre-exponential factor (s^{-1})

c specific heat capacity ($J \cdot kg^{-1} \cdot K^{-1}$)

cp component

D variances of functions

d maximum number of inputs

E activation energy ($kJ \cdot mol^{-1}$)

f function

i i-th input

j j-th input

k thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$) or superscript of Ω

N number of data points

N_s number for supplied argument

N_m number of materials of the mixture

N_α number of sub-reactions (components) of certain material

n reaction order

q'''_s source of heat ($J \cdot m^{-3}$)

R ideal gas constant ($J \cdot mol^{-1} \cdot K^{-1}$)

r reaction rate (s^{-1})

s solid

S sensitivity index

T sample temperature (K)

V model outputs

x inputs for variance-based sensitivity analysis

X input variables such as the activation energy

Z sample depth (m)

Greek symbols

α material

ρ density ($kg \cdot m^{-3}$)

φ component or sub-reaction

Φ error coefficient

Ω Input domain of variance-based sensitivity analysis

1 INTRODUCTION

Pyrolysis modelling, which predicts the generation of heat and gaseous species during combustion of materials, is of concern for decades in various research communities [1-4] . So far, the state-of-the-art modelling techniques of pyrolysis usually involve two major mechanisms: the chemical reaction and physical heat transfer. The heat transfer process is determined by the material thermophysical properties while the chemical reaction is determined by the kinetics properties. However, a typical pyrolysis process could involve tens of parameters leading to the complexity of model, uncertainty of output and more importantly the synergy effect [4] resulting in the difficulties of highlighting key factors for model improvement. For engineering use, computational optimization methods such as genetic algorithms (GA) [5][6] have been widely used to compromise the challenge of pyrolysis modelling. However, the use of these methods may conceal some of the physics therefore further efforts are worthwhile devoting to reveal the controlling mechanism of material pyrolysis. In this sense, Richter et al. [1] performed a set of pyrolysis modelling for charring softwood and hardwood and indicated that the variation of chemical kinetics induced by different chemical compositions between wood species is insignificant to pyrolysis modelling compared to the heat transfer in solid phase. “Modellers should, therefore, focus on the difference in the physical properties instead of the kinetics between wood species”, as stated by the authors [1], pinpoints the control mechanism. The conclusion can simplify the pyrolysis model for improvements, i.e. the model developer can now focus more on improving the heat transfer prediction and save the energy of developing highly “accurate models” for thermogravimetry (TG) curves. In fact, the same effect has also been implied in [4] that the discrepancy of pyrolysis kinetics does not propagate from mircoscale to mesoscale in pyrolysis modelling. However, the findings were based on the results of trial modelling while a detail sensitivity analysis could be more convincing in this regard given totally opposite opinions on the effect of chemical kinetics have been reported in the literature for polymers [7][8].

Sensitivity analysis is the study of how the uncertainty in the output of a mathematical model or system (numerical or otherwise) can be divided and allocated to different sources of uncertainty in its inputs [9][10]. Sensitivity analysis can be used to understand the relationships between input and output variables in a system or model and further simplify the model by fixing model inputs that have no effect on the output, or identifying and removing redundant parts of the model structure [11]. A comprehensive pyrolysis model can easily involve tens of parameters [12], for instance, a typical pyrolysis model of charring wood would have the kinetics properties of hemicellulose, cellulose and lignin [13] plus the thermophysical properties of raw wood and char [14]. As a result, there are at least 15 parameters with unknown effects in the model. The parameters can be determined using various experimental methods such as thermogravimetry [15] and transient plane source method [16]. However, the limitations of these experimental methods reproducing actual pyrolysis process, such as the different heating rate and temperature range, have reduced the reliability of the measurements. The difference of measured parameters and their real values may cause the discrepancy between model prediction and experimental result. Therefore, by adjusting or improving the measurements of key parameters the model predictions can be significantly improved. Sensitivity analysis can help us identify the key parameters of a pyrolysis model and thus focus on the adjustment or improvement of the key parameters which have really noticeable impacts on the model predictions. The current paper develops a computer model using

variance-based sensitivity analysis combined with a general pyrolysis model to perform sensitivity analysis for typical charring wooded materials. The significances of kinetics and thermophysical properties to the model predictions are investigated and the outcomes will be used to develop a simplified method for kinetics triplets in the following paper.

2 Sensitivity analysis model

2.1 Variance-based sensitivity analysis

Variance-based sensitivity analysis is a form of global sensitivity analysis [10][17]. It studies the global impact of inputs on the model (not only at a certain point, but at different locations). The variance of inputs can be extended to the entire input domain and the inputs can vary at the same time. Therefore, the analyzed model can be nonlinear, non-superimposed and non-monotonic. It is a variance-based Monte Carlo method while working within a probabilistic framework, it decomposes the variance of output of model or system into fractions which can be attributed to inputs or sets of inputs. The sensitivity of each input is often represented by a numeric value, called the sensitivity index. Sensitivity indices come in several forms [18]:

First-order indices: measures the contribution to the output variance by a single model input alone.

Second-order indices: measures the contribution to the output variance caused by the interaction of two model inputs.

Total-order index: measures the contribution to the output variance caused by a model input, including both its first-order effects (the input varying alone) and all higher-order interaction.

In variance-based sensitivity analysis, the input domain can be expressed as

$$\Omega^k = \{x|0 \le x_i \le 1 \; for \; i = 1,2,\dots,d\} \tag{1}$$

The input variables, X_i, in the pyrolysis model that are evaluated in the sensitivity analysis are rewritten from the bound of $[X_{i(min)}, X_{i(max)}]$ to [0,1] as

$$x_i = \frac{\left|X_i - X_{i(min)}\right|}{\left|X_{i(max)} - X_{i(min)}\right|} \tag{2}$$

The mass loss rate and temperature determined by the pyrolysis model, expressed as $f(x_1, x_2 \dots, x_d)$, can be decomposed in the following matter

$$f(x_1, x_2 \dots, x_d) = f_0 + \sum_{i-1}^{d} f_i(x_i) + \sum_{i<j}^{d} f_{ij}(x_i, x_j) + \cdots + f_{1,2,\dots,d}(x_1, x_2 \dots, x_d) \tag{3}$$

where f_0 is a constant and f_i is a function of x_i, f_{ij} a function of x_i and x_j, etc. A condition of the decomposition is that

$$\int_0^1 f_{i_1,i_2,\dots,i_s}(x_{i_1}, x_{i_2}, \dots, x_{i_s})\, dx_{i_j} = 0, \qquad for \quad 1 \le j \le s \tag{4}$$

All the terms in the functional decomposition are orthogonal. In other words, if

$$(i_1, i_2, \dots, i_s) \ne (j_1, j_2, \dots, j_s) \tag{5}$$

then,

$$\int_{\Omega^k} f_{i_1,i_2,\ldots,i_s} \cdot f_{j_1,j_2,\ldots,j_s} dx = 0 \tag{6}$$

The terms in Equation (3) can be expressed as

$$f_0 = \int_{\Omega^k} f(x)\, dx \tag{7}$$

$$f_i(x_i) = -f_0 + \int_0^1 \ldots \int_0^1 f(x)\, dx_{-i} \quad for \quad 1 \le i \le d \tag{8}$$

$$f_{ij}(x_i, x_j) = -\left(f_0 + f_i(x_i) + f_j(x_j)\right) + \int_0^1 \ldots \int_0^1 f(x)\, dx_{-ij} \quad for \quad 1 \le i < j \le d \tag{9}$$

In Equations (8) and (9), x_{-i} and x_{-ij} denote the inputs other than x_i and x_i and x_j. Similar method leads to the other terms in Equation (3). Further assuming that the $f(x)$ is square-integrable, the total variance of $f(x_1, x_2 \ldots, x_d)$ can be given as

$$D = \int_{\Omega^k} f^2(x)\, dx - f_0^2 = \sum_{i-1}^{d} D_i + \sum_{i<j}^{d} D_{ij} + \cdots + D_{1,2,\ldots,d} \tag{10}$$

where the terms at the right-hand side are the variances of terms at the right-hand side of Equation (3), which can be expressed as

$$D_{i_1,i_2,\ldots,i_s} = \int_0^1 \ldots \int_0^1 f^2_{i_1,i_2,\ldots,i_s}(x_{i_1}, x_{i_2}, \ldots, x_{i_s})\, dx_{i_1} dx_{i_2} \ldots dx_{i_s} \quad (1 \le i_1 < \cdots i_s \le d) \tag{11}$$

The First-order sensitivity index is then derived as

$$S_i = \frac{D_i}{D} \tag{12}$$

This is the contribution to the output variance of the main effect of x_i, therefore it measures the effect of varying x_i alone, but averaged over variations in other input parameters. It is standardised by the total variance to provide a fractional contribution. Higher-order interaction indices S_{ij}, S_{ijk} and so on can be formed by dividing other terms in the variance decomposition by D. According to Equation (10), it has

$$\sum_{i-1}^{d} S_i + \sum_{i<j}^{d} S_{ij} + \cdots + S_{1,2,\ldots,d} = 1 \tag{13}$$

Using the S_i, S_{ij} and higher-order indices given above, one can build a picture of the importance of each variable in determining the output variance. However, when the number of variables is large, this requires the evaluation of $2d - 1$ indices, which can be too computationally demanding. For this reason, a measure known as the "Total-effect index" or "Total-order index", S_{Ti}, is used. This measures the contribution to the output variance of x_i, including all variance caused by its interactions, of any order,

with any other input variables. It is given as,

$$S_{Ti} = \sum S_{(i)} \tag{14}$$

For a typical pyrolysis model, the impacts of variables on the outcomes are usually non-linear therefore we mainly focus on the Total-order index to represent the effect of variables.

2.2 The determination of material property variances

One of the important applications of variance-based sensitivity analysis is so called "model simplification", which can be used to identify and fix the model inputs that have less significant or no effect on the output, or identify and remove the redundant parts of the model structure. The current research intends to use this feature on pyrolysis model so that the modelers may reveal the dominant effects and even enhance the confidence on the modelling results. However, it is always a difficulty, as implied in the previous works by Bal [19] and Marcos [20], to determine the variance of material properties. In the literature, the range of certain properties could be relatively huge due to the gradual understanding the problem, such as the activation energies of PMMA [19] and cellulose [21]. As known, the sensitivity of input increases with increasing variance of input and thus unrealistic variance will fail the judgement of property effects on pyrolysis model. Therefore, we have to come up with a reliable strategy of determining the property variance.

In the current study, firstly the variances of kinetics properties were determined using derivative thermogravimetry (DTG) curves based on the combined analysis of literature knowledge and potential engineering use. As shown in Fig.1 where cellulose is used as a representative, the peak temperature of DTG curve varies in the 80% and 120% range of the base case by changing the activation energy while the peak conversion rate varies in the same range by adjusting the reaction order. The variances come approximately from the ranges of ±10% activation energy and ±50% reaction order. Fig.1 has also shown the variance of water which has been set relatively larger as 65 ˚C– 200 ˚C without overlapping the lowest peak temperature of hemicellulose to evaluate the sensitivity of water compared to other pyrolyzing components. It should be aware that the kinetics properties have different effects on the DTG curves [22], which leads to the possibility of applying DTG curve on sensitivity analysis. The sensitivities of kinetics properties were then analyzed without taking into account the thermophysical properties. The purpose of analyzing the kinetics properties solely is to address to the concern of "whether the detail reaction path is critical to the pyrolysis model". The second part of current research involves the thermophysical properties to determine if the chemical reaction or heat transfer dominates the pyrolysis model. The variances of thermophysical properties are determined as 80% and 120% of those in the base case. It should be noted that the range also apply to temperature-dependent properties.

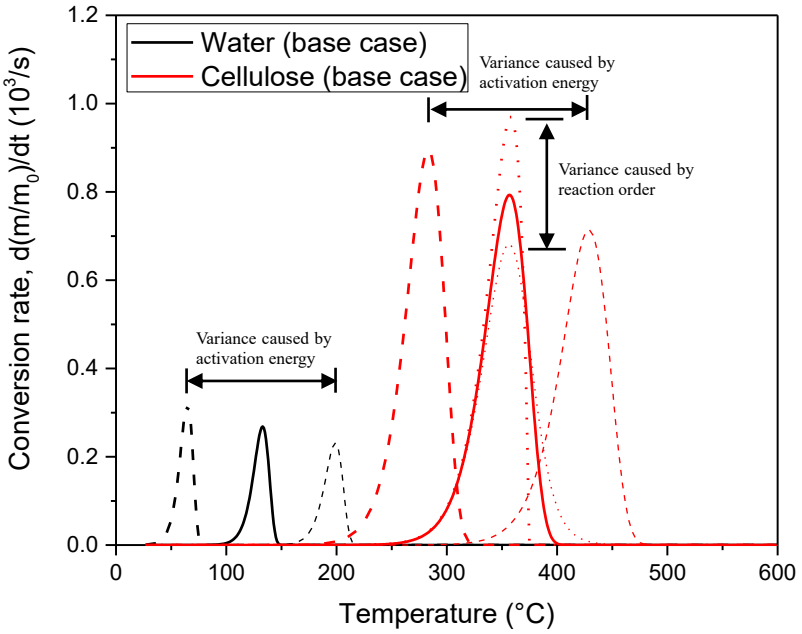


Fig.1 Comparison of experimental and modelled DTG curves

2.3 Building sensitivity matrix

The current paper mainly focuses on overall mass loss and temperature histories induced by different material properties, although it should be aware that the sensitivity analysis can be conducted to single data point [20]. In order to quantify the difference of modelled curves and thus determine the errors between models, an error coefficient has to be involved. It is found that the Pearson correlation coefficient [23] would reflect the relative change between two curves instead of the absolute error at each data point, which is not suitable for the current application. Therefore, in this case a new error coefficient adopting the concept of curves fitness [24] is used, which is expressed as

$$\Phi(\%) = \left(1 - \frac{1}{N_V}\sum \frac{V_{base}}{|V_m - V_{base}| + V_{base}}\right) \times 100 \tag{15}$$

where Φ is the error coefficient, N_V is the number of data points, V denotes the model outputs and in this case it is either mass loss rate or temperature of respective the evaluated and base models. According to Equation (15), Φ increases as the error of two curves increases and its maximum value is 100% whereas Φ equal to 0% indicates that the two curves are identical.

In the meantime, an input matrix with in total $N_s(2d+2)$ samples is built expressed as

$$[X] = \begin{bmatrix} X_{11} & X_{12} & \cdots & X_{1d} \\ X_{21} & X_{22} & \cdots & X_{2d} \\ \vdots & \vdots & \cdots & \vdots \\ X_{N_s(2d+2)1} & X_{N_s(2d+2)2} & \cdots & X_{N_s(2d+2)d} \end{bmatrix} \Bigg\} N_s(2d+2) \tag{16}$$

where Ns is the supplied argument and d is the number of model inputs. The accuracy of the estimators is dependent on Ns. The value of Ns can be chosen by sequentially adding point and calculating the indices until the estimated values reach some acceptable convergence. For this reason, when using low-discrepancy sequences, it can be advantageous to use those that allow sequential addition

of points (such as the Sobol sequence), as compared to those that do not (such as Latin hypercube sequences). The trial calculations show that the sensitivity value usually converge when Ns ≥ 100 (8 inputs) and as the number of model input increases the Ns of convergence increases. Therefore, conservatively a Ns of 1000 was used, which leads to a computation time of approximately 300 hours when using a i7-7500U CPU with a main frequency of 2.90 GHz for a case with 8 model inputs. At the end, a matrix is built with $[X]$ and its corresponding output list of $[\Phi_1 \quad \cdots \quad \Phi_{N_s(2d+2)}]$ for further sensitivity analysis.

2.4 Pyrolysis model

In this work, a pyrolysis model dealing with complex kinetics and multiple reactions is used for pyrolysis modelling. The model solves the pyrolysis process for materials using a set of 1D mesh taking into account the heat transfer and chemical kinetics simultaneously. The transport process of pyrolysis gas within the solid was neglected. A general pyrolysis gas was generated at the same temperature as the local solid, and was assumed to leave the solid phase instantaneously. The model is developed using Python v3.7 [25] and Kivy v1.10 [26]. The basic logics and algorithms of the model are similar to those in widely used pyrolysis models [14]. In the model, the governing equations in the solid include:

Pyrolysis rate:

$$r_{\alpha\varphi} = \left(\frac{\rho_{s,\alpha}-\rho_{char,\alpha}}{\rho_{s0,\alpha}-\rho_{char,\alpha}}\right)^{n_{s,\alpha\varphi}} A_{s,\alpha\varphi}\, exp\left(-\frac{E_{s,\alpha\varphi}}{RT_s}\right) \tag{17}$$

Energy conservation:

$$\rho_s c_s \frac{\partial T_s}{\partial t} = \frac{1}{Z}\frac{\partial}{\partial Z}\left(k_s \frac{\partial T_s}{\partial t}\right) + \dot{q}_s''' \tag{18}$$

Heat of pyrolysis:

$$\dot{q}_s''' = -\rho_{s0,\alpha} \sum_{\alpha=1}^{N_m} \sum_{\varphi=1}^{N_\alpha} r_{\alpha\varphi} H_{r,\alpha\varphi} \tag{19}$$

where A is the pre-exponential factor, E the activation energy and n the reaction order. c is the specific heat, k is the thermal conductivity and H is the heat of reaction of each pyrolysis reaction. Subscript α and φ refer to the α'th material of the mixture and its φ'th reaction, respectively. Subscript s refers to "solid phase". It should be noted that the current model of pyrolysis kinetics is different from the one used in Fire Dynamics Simulator [27], which is

Pyrolysis rate:

$$r_{\alpha\varphi} = \left(\frac{\rho_{s,\alpha}}{\rho_{s0}}\right)^{n_{s,\alpha\varphi}} A_{s,\alpha\varphi}\, exp\left(-\frac{E_{s,\alpha\varphi}}{RT_s}\right) \tag{20}$$

The effects caused by the difference can by find in [28], while, the behaviors of DTG curve are better interpreted for the current model [22][29].

The average heat capacity in the solid phase was estimated in the mass basis as

$$c_s = \sum_{i=1}^{N_m} Z_i c_i \tag{21}$$

while the average thermal conductivity in the solid phase was estimated in the volumetric basis as

$$k_s = \bar{\rho} \sum_{i=1}^{N_m} \left(\frac{Z_i}{\rho_i} k_i \right) \tag{22}$$

which changes with the local density.

For charring materials, the cell size of *Z*-discretization is set as a constant whereas for non-charring materials without residue the grids are removed from calculation once the substance is fully consumed.

3 EVALUATED WOODEN MATERIALS

3.1 Birch wood

In the previous study a set of cone calorimeter (ISO 5660-1) experiments were made using the samples of birch wood [30]. The dry density of the samples was 585 ± 20 kg/m^3. When conditioned at +21 °C and 50 % relative humidity, the moisture content of the material was 10 ± 1 % (wet basis). The cone experiments were carried out in air at 35, 50 and 75 kW/m^2 heat fluxes and using the spark ignition. In two of the experiments at 50 kW/m^2, the sample size was 100 mm×100 mm×20 mm, which was the main focus of the current paper.

To construct the reaction scheme, commercially extracted powders of the primary wood components, cellulose, hemicellulose and lignin, were separately degraded to obtain the respective DTG curves. As a result, a non-first-order (n≠1) kinetic model with 4 parallel reactions(water, hemicellulose, cellulose, and lignin) was proposed for birch wood. The final thermo-chemical properties were determined based on existing experimental data optimized by GA to fit the experimental DTG and cone results. The validations of the pyrolysis model using the experimental DTG, mass loss rate and heat release rate curves have been presented in the previous work [30]. It is noting that the flame heat flux in the 1D model was found to be 10-15 kW/m^2 [31] which leads to a total incident heat flux of 60-75 kW/m^2 to the sample surface.

3.2 Medium density fibreboard

The 15 mm thick, dehydrated MDF samples were charred experimentally in pure nitrogen atmosphere under different external heat fluxes. The detailed introductions to the experimental facility, pyrolysis process and comprehensive pyrolysis modelling have been presented in our previous work [32] where the thermophysical properties of MDF and char can be found in [4]. Four external heat fluxes, 20, 30, 40 and 50 kW/m^2, were used in the experiments while the current work focuses on the heat flux range from 20 to 80 kW/m^2, which covers the experimental heat flux range.

Based on a set of TG experiments under multiple heating rates, a non-first-order (n≠1) kinetic model with 4 parallel reactions(resin, hemicellulose, cellulose, and lignin) was proposed for MDF [12]. Using genetic algorithm, the kinetic parameters, initial mass fractions, and char yields were found previously [12] and also listed in our previous work [4]. The experimental DTG, mass loss rate and center temperatures were compared to the model results to validate the pyrolysis model previously, therefore, it is not repeated in the current paper. More detail information can be referred to [12][32].

3.3 External heat flux and duration of pyrolysis modelling

The sensitivity analysis was done under 4 incident heat fluxes of 20, 40, 60 and 80 kW/m^2 to cover most of the cone heat fluxes plus the flame feedback during the experiments. The modelling results of base cases show that the durations of fully pyrolyzing the materials are approximately 1800, 1200, 950, 800 s for birch wood and 1600, 1000, 730, 600 s for MDF under respective 20, 40, 60 and 80 kW/m^2. Therefore, the modelling cases of sensitivity analysis have been run at the same durations corresponding to the external heat fluxes.

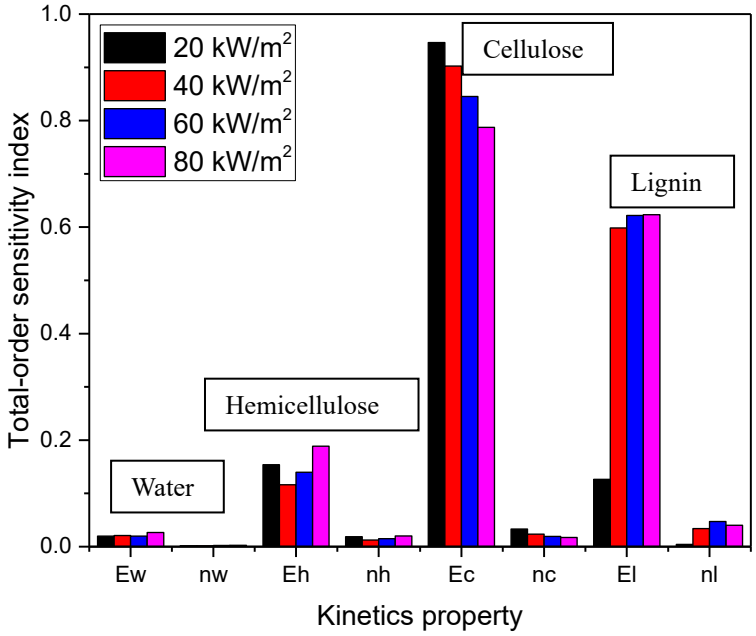
4 RESULTS AND DISCUSSIONS

4.1 The sensitivity of pyrolysis kinetics

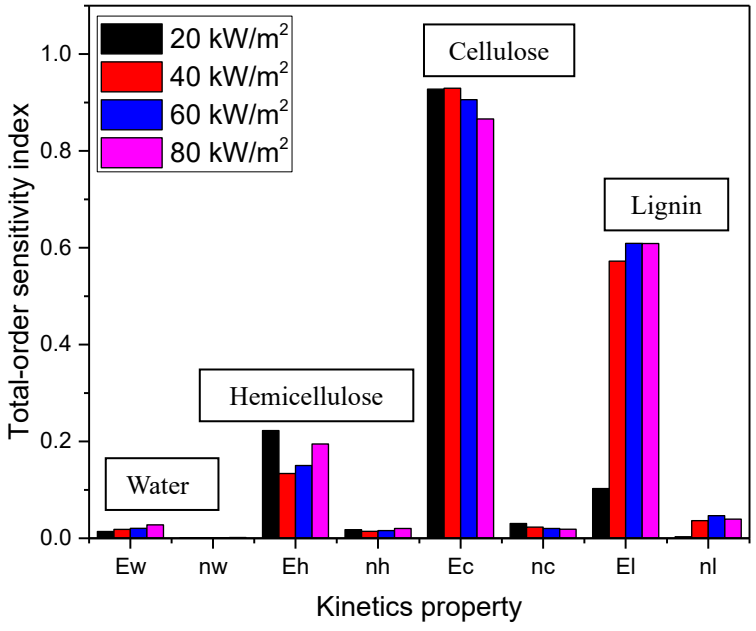
Fig.2 and Fig.3 shows the Total-order sensitivity indexes of kinetics property of difference components. It can be seen from Fig.2 and Fig.3 that the sensitivity indexes of activation energy are in general over 10 times higher than those of reaction order, which indicates that the reaction order has little effect on the pyrolysis modelling results. The literature [22][29] has shown the reaction order mainly dominates the shape of DTG curve representing the detail reaction path while the activation energy determines the temperature range of reaction, as also presented in Fig.1 Therefore, it can be concluded that compared to the temperature range of reaction the detail reaction path is significantly less important to pyrolysis modelling. This finding will possibly allow us to approximate the reaction order with simplified method rather than chasing the exact values with time consuming methodologies such as GA.

It should be noted that for birch wood 3 different modelling outputs including total mass loss, fuel mass loss and center temperature are evaluated as there is moisture inside the samples while for MDF there are only fuel (total) mass loss and center temperature. From Fig.2, it can be seen that the kinetics properties of water have noticeably stronger effects to the center temperature than to total and fuel mass losses. Fig.4 shows the model results with different kinetics properties of water under 80 kW/m^2, while the moisture content is 10%. From Fig.4(a), the kinetics properties have very little effect on the total and fuel mass losses up to approximately 400 s after which the differences become more noticeable at the second peaks of MLR curves caused by the heat accumulation at the sample bottom. For the center temperature, Fig.4(b) shows the differences in the center temperatures of varying the kinetics property, which is worthwhile for more discussion. From Fig.4(b), low activation energy leads to low inside wall temperatures which however increases faster than those of high activation energies as time progresses. This behavior leads to temperatures overlapping at some time instants, which can be clearly seen in the 2.5 mm and 5.0 mm depths as shown in Fig.4(a). The temperature overlapping takes place at the temperature ranges within which the material decomposes. The overlapping temperatures could be the driving force of similar total and fuel mass losses and the temperature difference after the overlapping can be caused by the heat accumulation at the sample bottom. Given the temperature differences at the later stage may be led by the sample boundary, the near surface zone of the sample might not be affected and the temperature curves should be similar. To justify this assumption, the sample thickness was increased to 50 mm and the model results are presented in Fig.5. From Fig.5, it is seen that up to 1/3 of the sample thickness fairly strong temperature overlapping is identified, which also indicates similar mass losses at the early pyrolysis stage. This finding will potentially benefit the engineering calculation

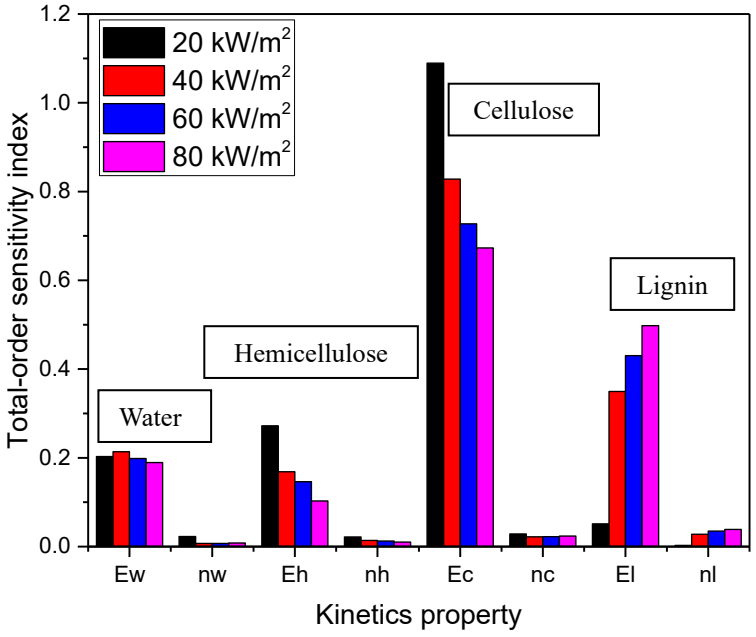
of fire resistance of timber structure. For such calculations, the effects of moisture kinetics can be less focused up to 1/3 of sample thickness regardless of whether mass loss or temperature (300 °C) has been used as the criterion for the charring rate.



(a) Total mass loss (fuel + water)



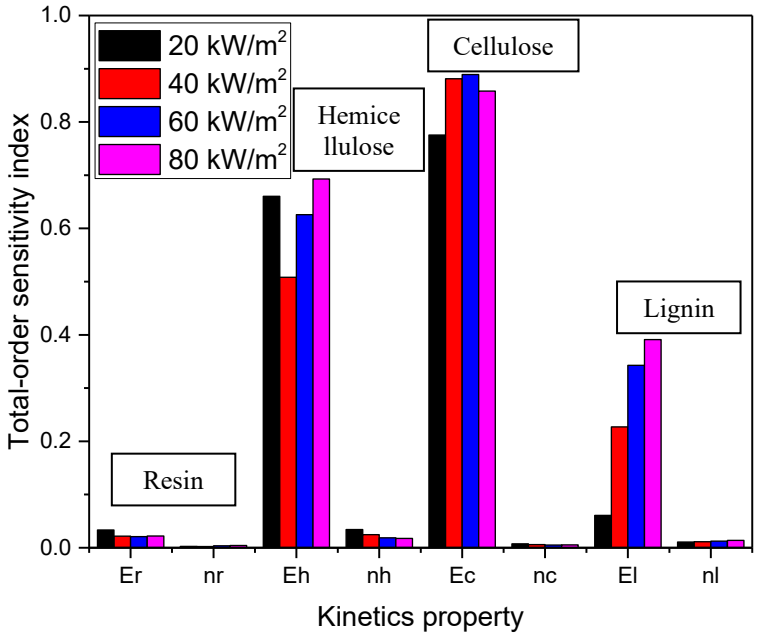
(b) Fuel mass loss



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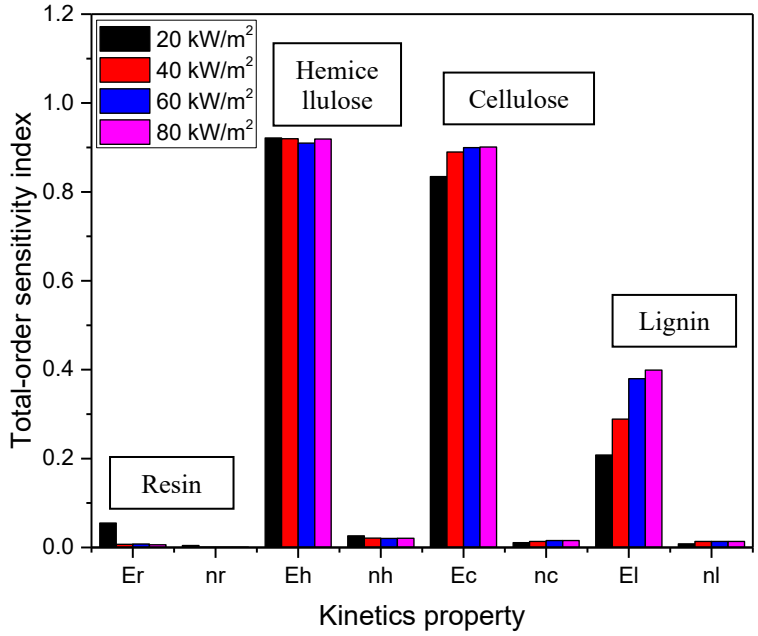
317 (c) Center temperature

318 **Fig.2 Sensitivity analysis of kinetics properties on birch wood**

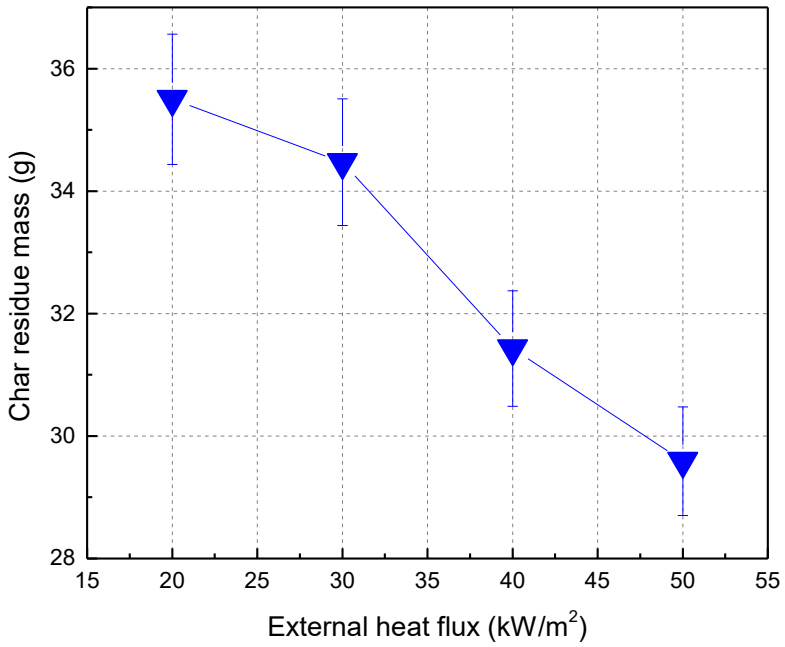


319

320 (a) Fuel mass loss

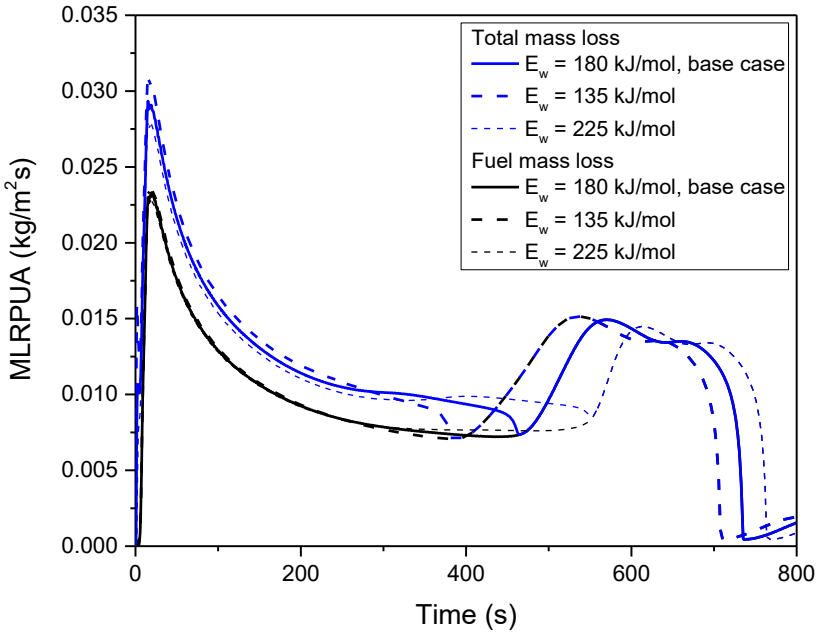


(b) Center temperature

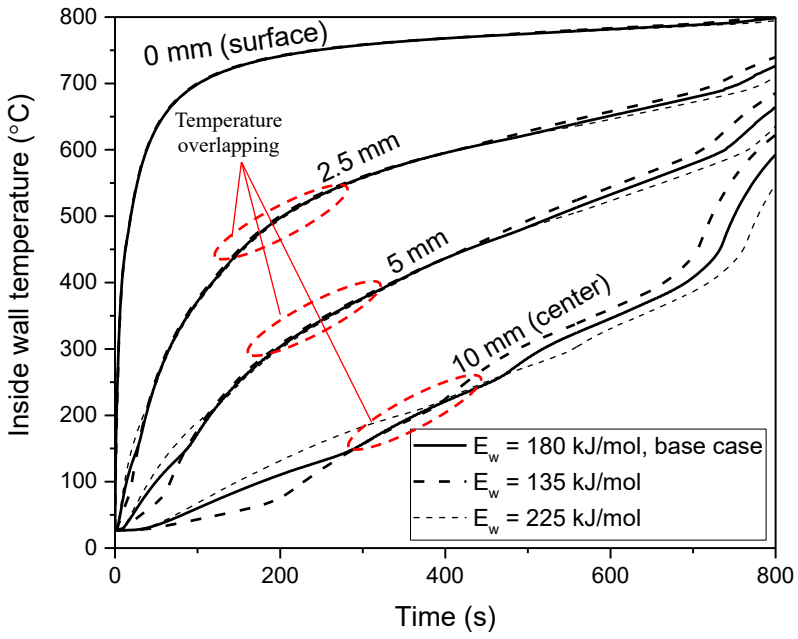


(c) Experimental char residue mass

Fig.3 Sensitivity analysis of kinetics properties on MDF and char residue mass of MDF

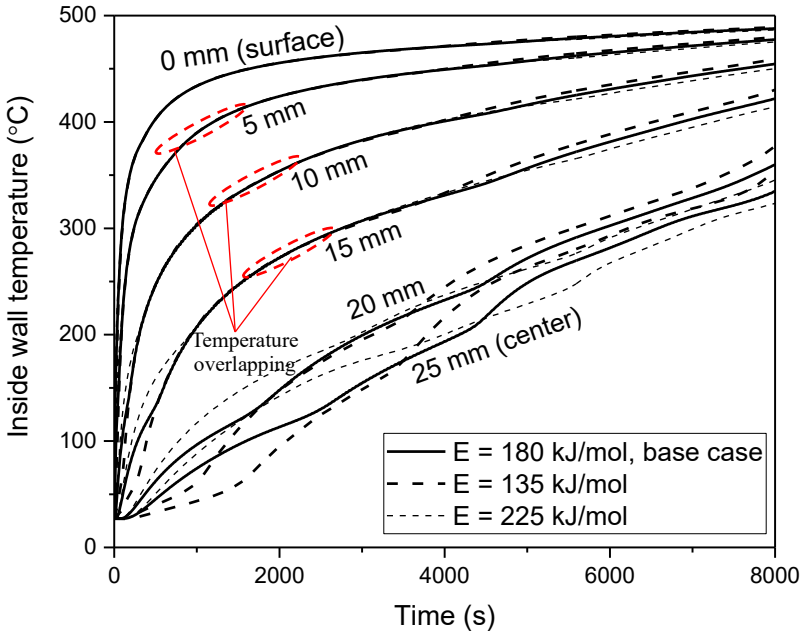


(a) Mass loss rate

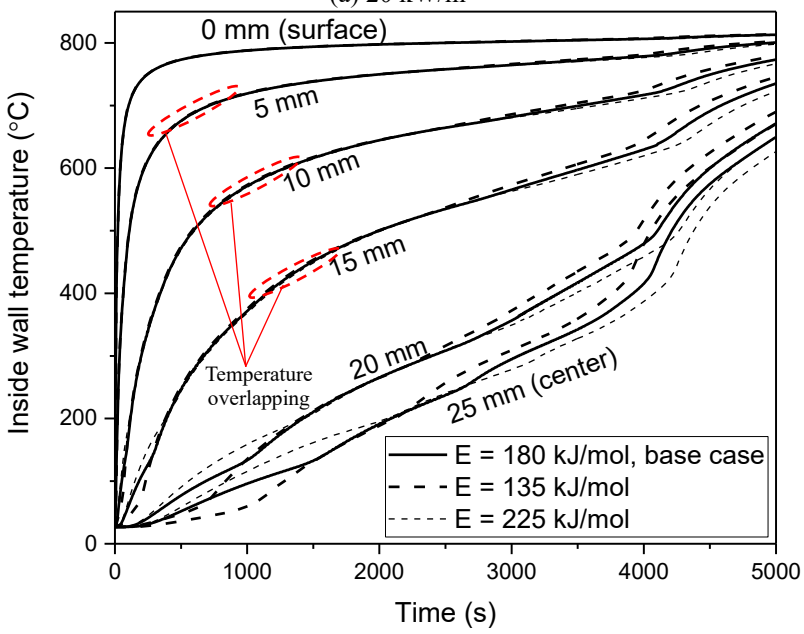


(b) Inside wall temperature

Fig.4 Modelled mass loss rates and inside wall temperatures with different kinetics properties of water under 80 kW/m²



(a) 20 kW/m^2



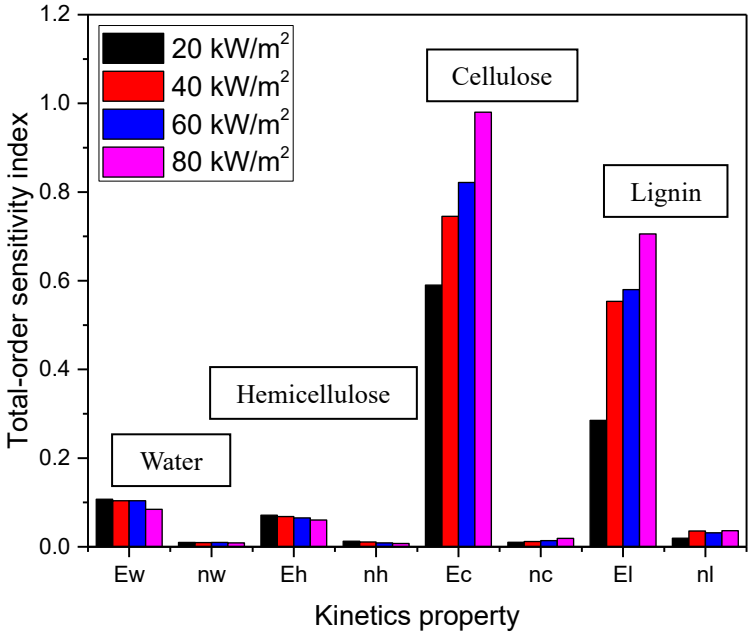
(b) 80 kW/m^2

Fig.5 Inside wall temperatures of 50 mm birch sample under 20 kW/m^2 and 80 kW/m^2

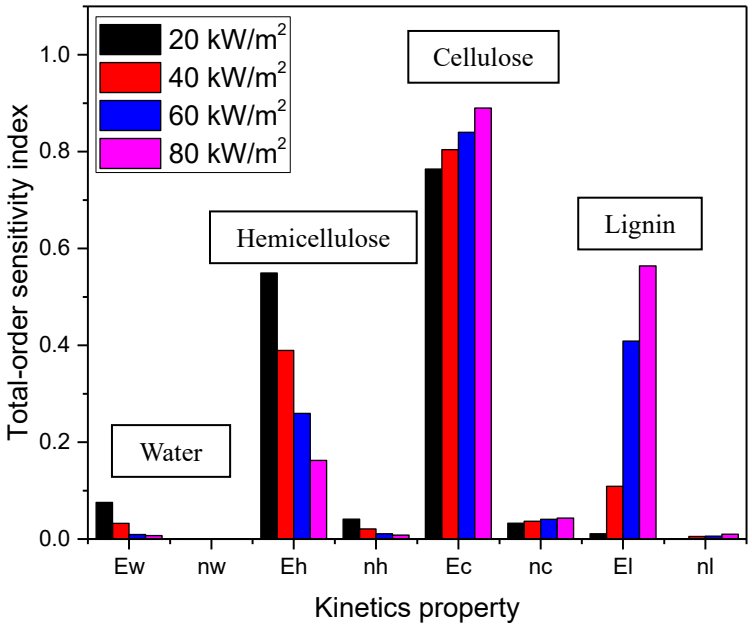
For MDF, the mass fraction of resin is similar as the moisture content of 10% while its variation range on the DTG curve is not as large as the one of moisture for birch. Moreover, the heat of reaction of resin is significant less than that of water. As a result, the effects of resin can be ignored compared to the other 3 components, regardless of the evaluated modelling output, as shown in Fig.3. It can also be seen from Fig.2 and Fig.3 that the effects of lignin kinetics properties increase with increasing heat flux, for both birch and MDF. This is mainly attributed by the relatively high pyrolysis temperature of lignin, which leads to less lignin decomposition under low external heat fluxes with low temperatures of the sample as shown in Fig.4 and Fig.5. This finding can also be confirmed by the experimental results shown in Fig.3(c) where it is clearly seen that the mass of char residue decreases with increasing external heat flux as a result of more lignin decomposition.

4.2 The effect of moisture content

The moisture content of wood can be as high as 60% [33] and increasing the moisture content might affect the sensitivity of water pyrolysis kinetics. To investigate the effect of moisture content, the moisture mass fraction of birch wood was increased from 10% to 50% in the model. Fig.6 presents the sensitivities with respect to different model outputs. From Fig.6, the sensitivity of water pyrolysis kinetics to the total mass loss increases compared to the one of 10% moisture while to the fuel mass loss the water pyrolysis kinetics has also negligible effect as the 10% case. However, for the center temperature the sensitivity of water pyrolysis kinetics is sharply higher than the other three components, which indicates the center temperature is strongly sensitive to the variation of activation energy of water. Fig.6(d) presents the inside wall temperatures under 80 kW/m^2 where the temperature variations is found higher than those of 10% moisture content however noticeable temperature overlapping can still be identified at the near surface zone (< 5 mm), which leads to the mass losses being less sensitive to the kinetics of water. Therefore, for cases with high moisture contents the center temperature might be more appropriate for the validation of kinetics of moisture compared to the mass loss.

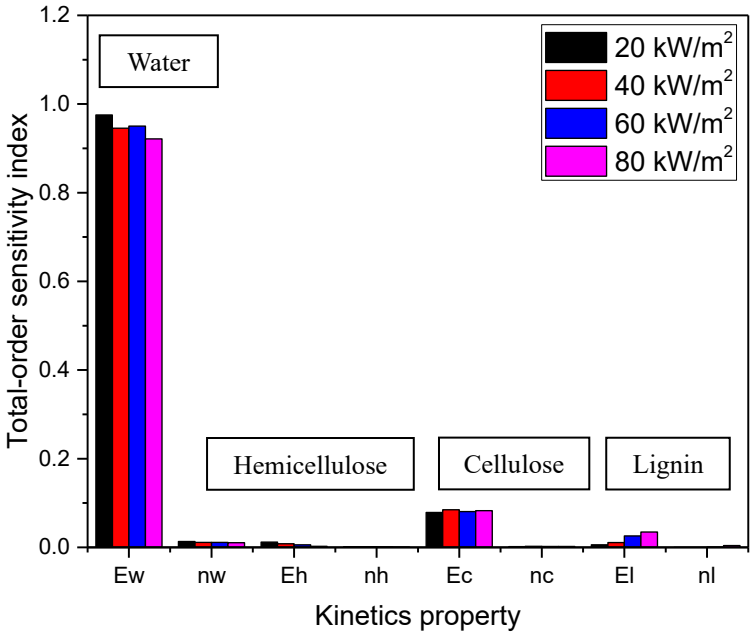


(a) Total mass loss (fuel + water)



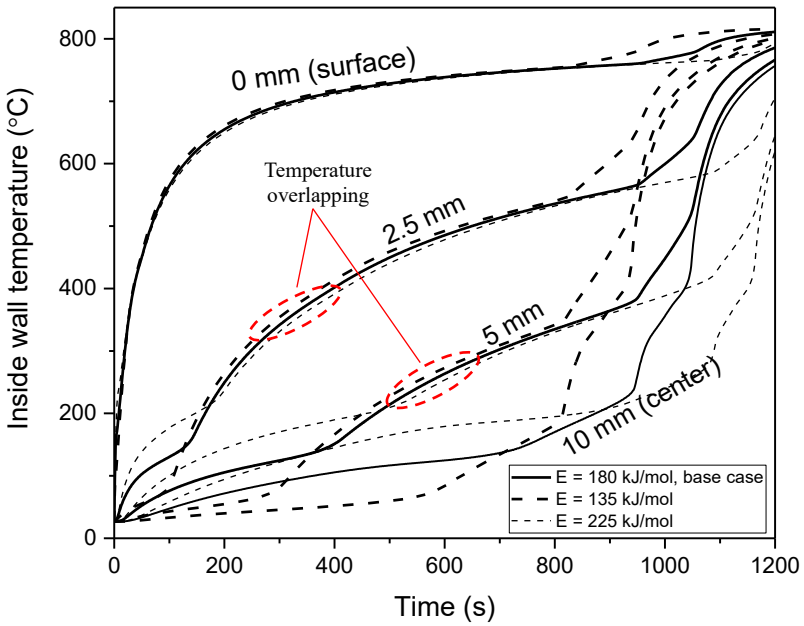
363

364 (b) Fuel mass loss



365

366 (c) Center temperature

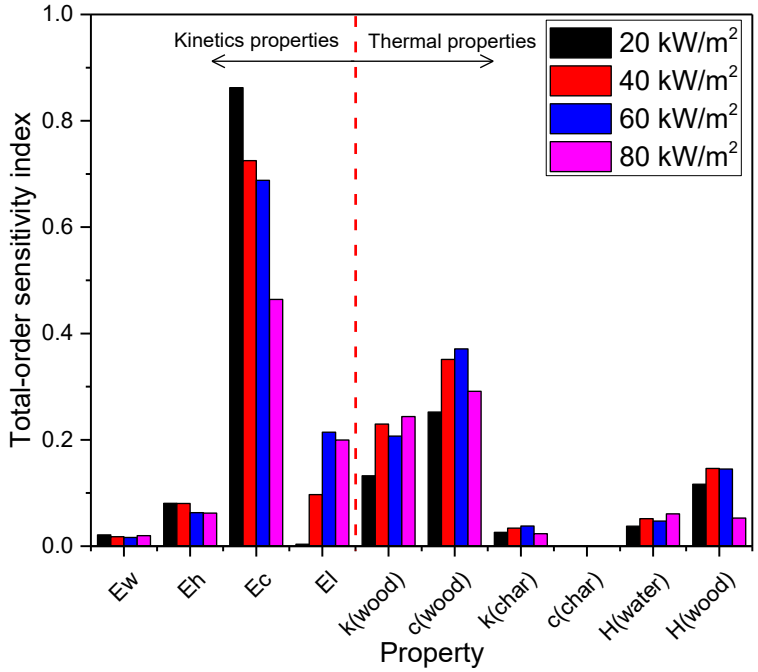


(d) Inside wall temperature under 80 kW/m^2

Fig.6 Sensitivity analysis of kinetics properties on birch wood with a moisture content of 50%

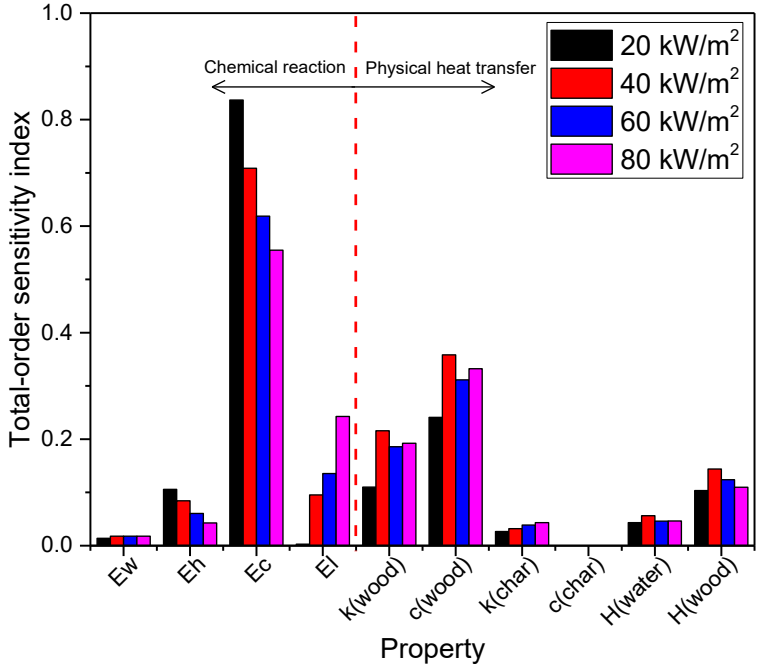
4.3 Competition of chemical reaction and physical heat transfer

Fig.7 compares the two dominating mechanisms in the pyrolysis process, for birch wood and MDF. It is clearly seen in Fig.7 that both mechanisms can not be neglected for pyrolysis modelling. For the mass losses, the sensitivity of cellulose kinetics is much higher than those of thermal properties while the hemicellulose and lignin have comparably sensitivities to the ones of thermal conductivity and specific heat of raw birch. However, for center temperature the sensitivities of thermal conductivity and specific heat of raw birch become comparable to that of cellulose and noticeably higher than those of other kinetics properties. This is understandable as the mass loss is mainly affected by the chemical reactions while the center temperature has strong connection to the heat transfer process determined by the thermal properties. In this case, Fig.7(a) – Fig.7(c) also implies that the heat transfer process of birch is mainly governed by the thermal properties of raw birch. The MDF has similar behaviors. Nevertheless, it can be seen in Fig.7(d) and Fig.7(e) that the heat transfer process of MDF is governed by the specific heat of raw MDF and the thermal conductivity of char, which are different from those of birch. At the stage, it is difficult to tell which heat transfer model is correct although the properties of birch were mainly from GA [30] while those of MDF were validated experimentally [16]. However, it is clearly shown that the sensitivity analysis can reveal the effects of properties, which might assist the model verification, meanwhile, Fig.7 still exposes the competitions of chemical and physical processes in pyrolysis modelling.



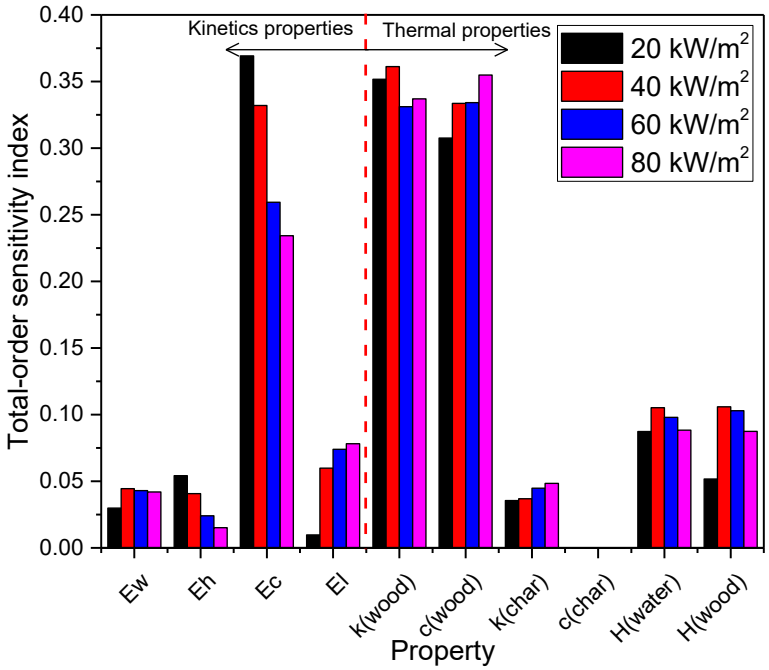
388

389 (a) Total mass loss (fuel + water) of birch



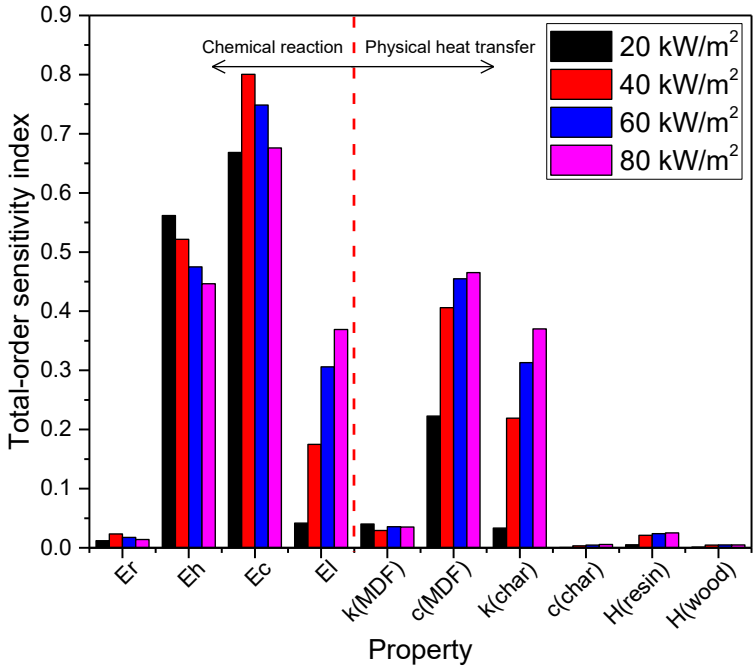
390

391 (b) Fuel mass loss of birch



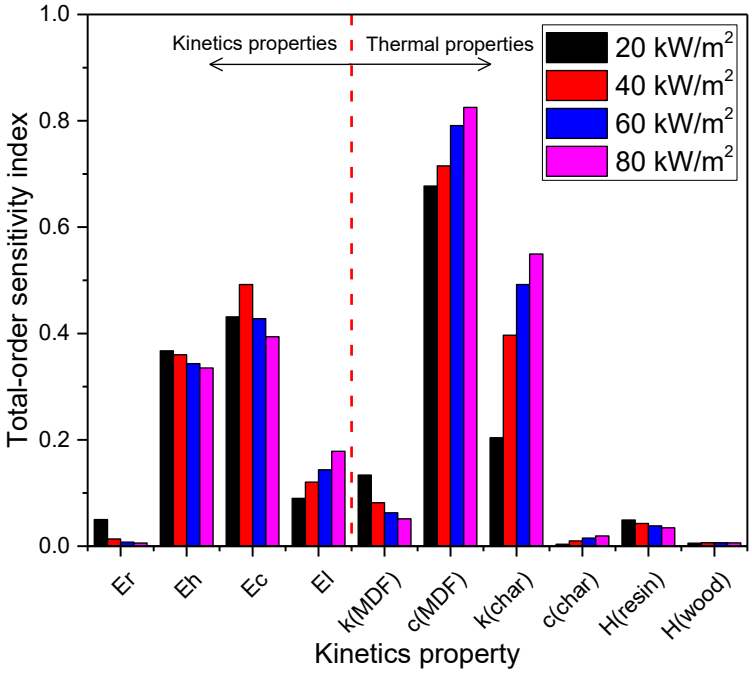
392

393 (c) Center temperature of birch



394

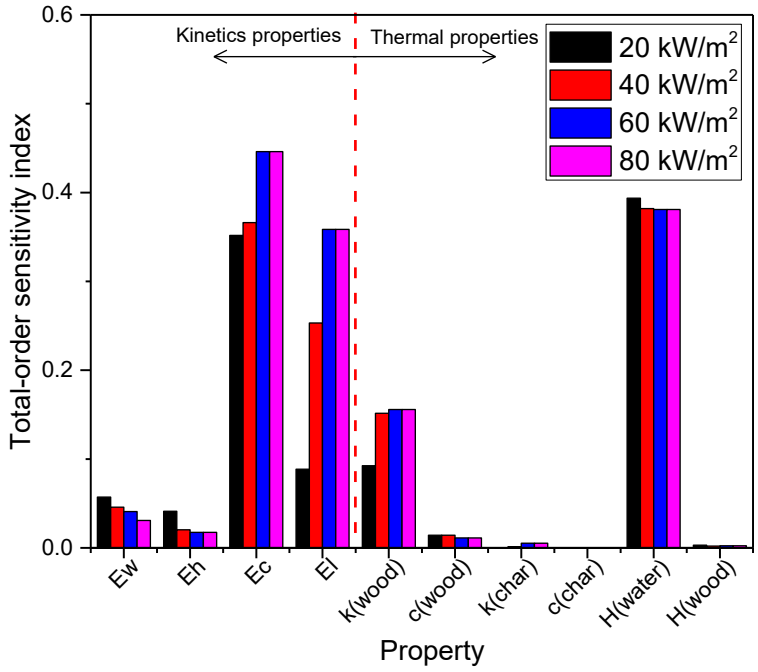
395 (d) Fuel mass loss of MDF



(e) Center temperature of MDF

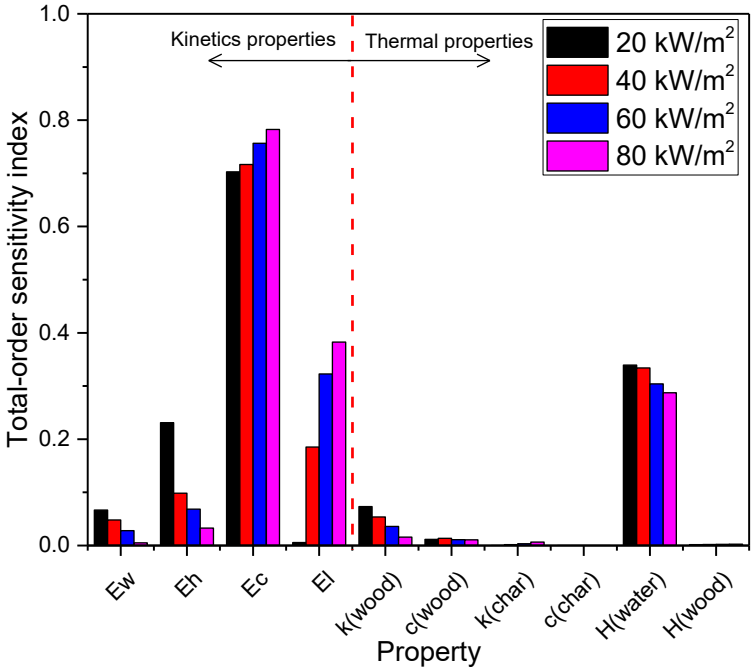
Fig.7 Competition of chemical reaction and physical heat transfer based on sensitivity analysis

Fig.8 compares the two mechanisms with the moisture content of 50%. As shown in Fig.8(a) to 8(c), the effects of moisture, denoted by the activation energy of water and heat of vaporization, have strongly increased. Moreover, the sensitivities of thermal properties of raw birch and its char have been significantly reduced. Compared to the those of 10% moisture content, the sensitivities of specific heat of raw birch and thermal conductivity of char have become neglectable while the thermal conductivity of birch has only noticeable effect to the total mass loss. For the total and fuel mass losses, the activation energy of water is much less sensitive compared to the heat of vaporization whereas for the center temperature the activation energy of water dominates the pyrolysis model with a sensitivity index being at least 4 times higher than the rest of the properties.



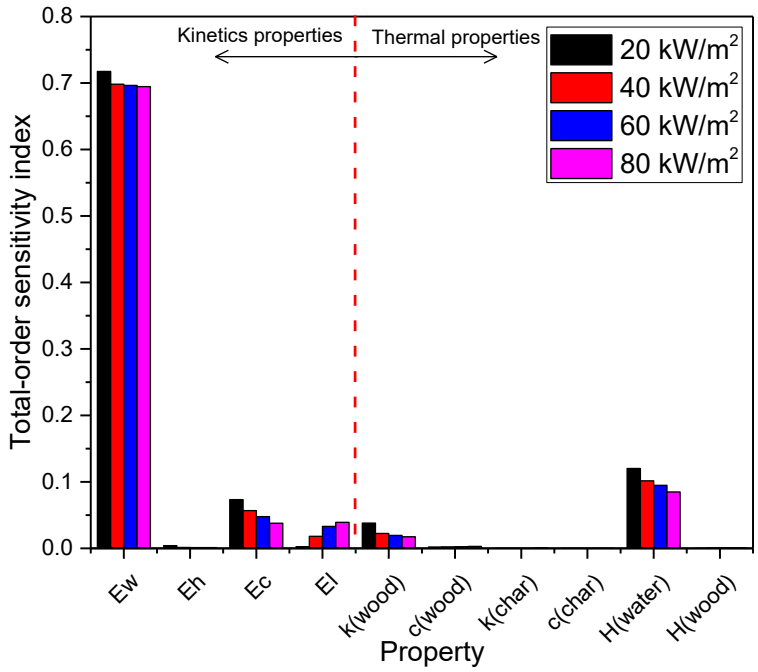
408

409 (a) Total mass loss (fuel + water) of birch



410

411 (b) Fuel mass loss of birch



(c) Center temperature of birch

Fig.8 Competition of chemical reaction and physical heat transfer of birch wood with a moisture content of 50%

5 CONCLUSIONS

In the current study, the sensitivities of chemical kinetics and thermal parameters of comprehensive pyrolysis model are evaluated using variance-based sensitivity analysis, to identify the dominating physics out of complex thermo-kinetics model. The major findings include:

1. The sensitivity of activation energy is found generally over 10 times higher than the sensitivity of reaction order, although the variance of activation energy is much narrower than the one of reaction order. This result indicates that compared to the temperature range of pyrolysis reaction the detail reaction path is significantly less important to pyrolysis modelling.

2. The temperatures difference caused by different kinetics properties of moisture would finally approach similar, especially at the near surface zone, leading to similar mass losses. As a result, the pyrolysis kinetics of moisture is much less significant to the total and fuel mass losses compared to pyrolysis kinetics of other components, even for moisture content as high as 50%. For low external heat flux, the pyrolysis of lignin may be ignored as the relatively low sample temperature can not fully pyrolyze the component.

3. The combined analysis of chemical reaction and physical heat transfer shows that the chemical reaction is more important to the mass losses whereas the physical heat transfer is more sensitive to the center temperature for the moisture content of 10%. For the 50% moisture content, the heat transfer process is mainly dominated by the heat of vaporization therefore the effects of thermal properties of wood and char have been significantly reduced. At the end, the research has confirmed that both chemical reaction and physical heat transfer should not be neglected in pyrolysis modelling.

CRediT authorship contribution statement

Yan Yang: Conceptualization, Methodology, Investigation, Visualization, Writing - original draft. **Junhao Yu:** Investigation, Data curation, Validation. **Ranran Fan:** Formal analysis, Validation, Visualization. **Xi Deng:** Investigation, Data curation. **Linlin Yi:** Formal analysis, Validation. **Dan Liao:** Resources, Writing - review & editing. **Kaiyuan Li:** Conceptualization, Methodology, Supervision, Project administration, Funding acquisition, Writing - review & editing. **Pan Li:** Supervision, Writing - review and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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520 Technology. 1991; 37: 161-168.