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A heat transfer corrected isothermal model for devolatilization of thermally-thick biomass particles

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Abstract

An isothermal model is commonly used in computational fluid dynamics (CFD) modelling of biomass devolatilization in fluidized beds. However, the particle internal heat transfer, which is neglected by the isothermal model, influences significantly the devolatilization process for large biomass particles. To consider the effect of internal heat transfer, a heat transfer corrected isothermal model is introduced by comparing the differences between an isothermal model and a non-isothermal model. Two correction coefficients for external heat transfer, H_T , and reaction rate, $H_{R,i}$, were defined to correct the conventional isothermal model. The predictions of the heat transfer corrected isothermal model and the non-isothermal model were in good agreement with the experimental data for both thermally-thick (Biot Number, $Bi \geq 1.0$) and thermally-thin ($Bi < 1.0$) biomass particles, while the conventional isothermal model only gave reasonable results for thermally-thin biomass particles. The heat transfer corrected isothermal model was further implemented in a CFD model to simulate biomass devolatilization in a batch bubbling fluidized bed. Compared to the conventional isothermal model, the heat transfer corrected isothermal model had similar computational efficiency, but it predicted a lower heating rate and a lower devolatilization rate, which were in good agreement with the observations from single particle modelling.

Keywords: biomass, devolatilization, internal heat transfer, CFD, fluidized bed

1. Introduction

In CFD modelling of biomass devolatilization in fluidized beds, the biomass particles are usually described by an isothermal model,¹⁻⁶ due to its simplicity and low computational cost. However, the isothermal assumption is only reasonable for small particles with a small Biot number (e.g. $Bi < 1$).^{1,7} A significant internal temperature gradient is observed in a large biomass particle,^{7,8} requiring a non-isothermal model to describe the effects of intra-particle heat transfer on biomass devolatilization.^{1,8-15} Non-isothermal models have been implemented in CFD modelling of biomass devolatilization in fluidized bed reactors.¹⁶⁻²⁵ The individual biomass particles are discretized with a large number of mesh grid points (e.g. 50) to calculate the intra-particle heat transfer and devolatilization rate, resulting in a significant increase of computational demand in CFD.^{17,22,25} To reduce the computational cost, Thunman et al.²⁶ proposed a four-layer model, in which a biomass particle is discretized into four layers (moist wood, dry wood, char, and core layers). This method only needs additional equations to describe the heat transfer between the different layers thereby improves the computational efficiency in CFD modelling, as compared to other non-isothermal models.^{22,23} However, it is still complicated to apply the four-layer model to simulate biomass devolatilization in fluidized beds due to highly diverse particle boundary conditions,²⁷ and the computational cost is still considerably higher than that of the conventional isothermal model.

Considering the easy implementation of an isothermal model in CFD modelling, and the fact that the main difference between an isothermal model and a non-isothermal model is the exclusion and inclusion of the internal heat transfer, a non-isothermal model is possible to be simplified to an isothermal model, by quantitatively evaluating the effects of internal heat transfer on biomass devolatilization. However, such an approach was rarely explored.

In this work, a heat transfer corrected isothermal model is introduced to facilitate CFD modelling of devolatilization of thermally-thick biomass particles in fluidized bed reactors. Correction coefficients of reaction rate ($H_{R,i}$) and external heat transfer (H_T), are introduced to quantitatively evaluate the difference between a conventional isothermal model and the non-isothermal model developed in our

previous work.¹⁵ The model was validated by biomass devolatilization experiments from literature,^{8,28,29} covering both thermally-thin and thermally-thick biomass particles. Finally, the model is implemented in CFD to simulate biomass devolatilization in a batch bubbling fluidized bed.

2. Particle-scale model

The different particle-scale models are discussed in the following section. The correlations used to determine the physical properties (such as gas conductivity (λ_g), pore size (d_{pore}), char thermal capacity (C_{pC}), char conductivity (λ_C), biomass conductivity (λ_B), biomass thermal capacity (C_{pB}) etc.), drying and devolatilization kinetics are available in Luo et al.¹⁵, as well as in Appendix A of Supporting Information.

2.1 Conventional isothermal model

The conventional isothermal model is zero-dimensional. The heat balance equation, the reaction rate (i.e. drying and devolatilization rates), and the heat flux of the conventional isothermal model are given below:

$$C_p m_p \frac{dT_{p,iso}}{dt} = h_c A_p (T_g - T_{p,iso}) + \xi \sigma A_p (T_w^4 - T_{p,iso}^4) - \sum_i R_{iso,i} Q_{R,i} \quad (2)$$

$$R_{iso,i} = \frac{dX_{iso,i}}{dt} \rho_{p0} Y_{i,0} V_p \quad (3)$$

$$q_{iso} = h_c (T_g - T_{p,iso}) + \xi \sigma (T_w^4 - T_{p,iso}^4) \quad (4)$$

Here, i represents different components ($i = 1$ and 2 represents moisture and volatile in biomass particle, respectively); ρ_{p0} is initial particle density, kg/m³, $Y_{i,0}$ is the initial mass fraction of component i in the particle. $T_{p,iso}$ and $X_{iso,i}$ is the time-dependent particle temperature, and conversion of volatile and water. $dX_{iso,i}/dt$ is the rate of moisture evaporation or volatile release, which can be determined by drying and devolatilization kinetics, respectively. V_p is the volume of particle, m³. ξ and σ are the emissivity (0.85) and Stefan-Boltzmann constant (5.6704×10^{-8} J/(m²·K⁴·s)), respectively.

2.2 Non-isothermal model

The non-isothermal model, which was presented in detail in our previous study,¹⁵ includes both intra-particle heat transfer and external heat transfer. The heat balance equation is expressed as Eq. (4).

$$C_p \rho_p \frac{\partial T_{p,non-iso}}{\partial t} = \frac{\partial \left(r^2 \lambda_{eff} \frac{\partial T_{p,non-iso}}{\partial r} \right)}{r^2 \partial r} - \sum_i \frac{dX_{non-iso,i}}{dt} \rho_{p0} Y_{i0} Q_{R,i} \quad (5)$$

Here, C_p , ρ_p , λ_{eff} are the specific heat capacity, J/(kg·K), particle density, kg/m³, effective thermal conductivity, W/(m·K), respectively. ρ_{p0} is the initial particle density, kg/m³, r is the radial position, m, t is time, s. $T_{p,non-iso}$ is the temperature predicted by the non-isothermal model, which depends on both time (t) and radial position (r). $Y_{0,i}$ is the initial mass fraction (dry basis) of species i , $i = 1$ and 2 represent moisture and volatile, respectively. $Q_{R,i}$ is the evaporation heat ($i = 1$) and devolatilization heat ($i = 2$), J/kg, respectively. $dX_{non-iso,i}/dt$ is the evaporation rate of moisture or the release rate of volatile, which can be determined by the drying and devolatilization kinetics, respectively. $X_{non-iso,i}$ is the conversion degree of moisture and volatile, which depends on both time (t) and radial position (r).

The reaction rate at time t is given as:

$$R_{non-iso,i} = \int_0^R 4\pi r^2 \frac{dX_{non-iso,i}}{dt} \rho_{p0} Y_{i,0} dr \quad (6)$$

Here, R is the particle radius, m.

The average particle temperature, conversion of moisture and volatile predicted by the non-isothermal model at time t are calculated as follows,

$$T_{aver} = \frac{\int_0^R 4\pi r^2 T_{p,non-iso} dr}{\int_0^R 4\pi r^2 dr} \quad (7)$$

$$X_{aver,i} = \frac{\int_0^R 4\pi r^2 X_{non-iso,i} dr}{\int_0^R 4\pi r^2 dr} \quad (8)$$

91 The particle boundary conditions are:

$$92 \quad \left. \frac{\partial T}{\partial r} \right|_{r=0} = 0 \quad (9)$$

$$93 \quad q_{non-iso} = \lambda_{eff} \left. \frac{\partial T}{\partial r} \right|_{r=R} = h_c (T_g - T_{surf}) + \xi \sigma (T_w^4 - T_{surf}^4) \quad t \geq 0 \quad (10)$$

94 The particle initial conditions are:

$$95 \quad T_{p,non-iso}(0, r) = T_{p0} \quad (11)$$

96 2.3 Heat transfer corrected isothermal model

97 The general assumptions of the heat transfer corrected isothermal model are the same as the non-
 98 isothermal model,¹⁵ expect the model is zero-dimensional. It is assumed that an isothermal particle has
 99 the same average particle temperature ($T_{p,aver}$) history, average conversion history of moisture and
 100 volatile ($X_{aver,i}$) predicted by the non-isothermal model, namely $T_{p,iso} = T_{p,aver}$ and $X_{iso,i} = X_{aver,i}$. To
 101 simplify the non-isothermal model to an isothermal model, two correction coefficients, H_T and $H_{R,i}$, are
 102 introduced to equalize external heat transfer and reaction rate predicted by those models. The H_T and
 103 $H_{R,i}$ are expressed as Eq.(11) and Eq.(12), respectively, according to the definition.

$$104 \quad H_T = \frac{q_{non-iso}}{q_{iso}} = \frac{h_c (T_g - T_{surf}) + \xi \sigma (T_w^4 - T_{surf}^4)}{h_c (T_g - T_{aver}) + \xi \sigma (T_w^4 - T_{aver}^4)} \quad (12)$$

$$105 \quad H_{R,i} = \frac{R_{non-iso,i}}{R_{iso,i}} = \frac{\int_0^R \frac{dX_{non-iso,i}}{dt} \rho_{p0} Y_{i,0} 4\pi r^2 dr}{\frac{dX_{aver,i}}{dt} \rho_{p0} Y_{i,0} V_p} \quad (13)$$

106 Therefore, the heat balance equation of the conventional isothermal model corrected by H_T is introduced
 107 as:

$$108 \quad C_p m_p \frac{dT_{p,cor}}{dt} = H_T \left(h_c A_p (T_g - T_{p,cor}) + \xi \sigma A_p (T_w^4 - T_{p,cor}^4) \right) - \sum_{i=1}^n R_{cor,i} Q_{R,i} \quad (14)$$

109 Here, $T_{p,cor}$ is the particle temperature calculated by the heat transfer corrected isothermal model.

110 The reaction rate of the model corrected by $H_{R,i}$ is expressed as:

$$R_{cor,i} = H_{R,i} R_{iso,i} \quad (15)$$

According to Eq. (11), with predefined T_w , and T_g , H_T is a function of $(T_{aver}, h_c, T_{surf})$. The unknowns, including the particle temperature distribution ($T_{p,non-iso}$), conversion distribution of moisture ($X_{non-iso,1}$) and volatile ($X_{non-iso,2}$), and particle surface temperature (T_{surf}), are determined by the non-isothermal model with known values of h_c at time t . The average particle temperature, T_{aver} , and average conversion degree of moisture and volatiles, $X_{aver,i}$ are further calculated by Eq. (6) and Eq. (7), which means that each T_{aver} , and $X_{aver,i}$ is corresponding to a value of T_{surf} and h_c at time t . Therefore, H_T is simplified as a binary function of (T_{aver}, h_c) at time t . $H_{R,i}$ is also correlated as a binary function of (T_{aver}, h_c) with the defined $X_{iso,i} = X_{aver,i}$. A dimensionless temperature is defined as Eq. (15) based on the maximum of T_g and T_w (ensure θ is in a range of 0-1) for the ease of implementation in CFD modelling. The correction coefficients, H_T and $H_{R,i}$, are expressed as a binary function of (θ, h_c) after the arrangement.

$$\theta = \frac{T_p - T_{p0}}{T_e - T_{p0}} \quad (16)$$

Here, T_e is the environmental temperature, K . It is default equal to bulk gas temperature (T_g), but it is equal to T_w when the wall temperature is higher than bulk gas temperature.

With given input parameters of gas temperature, T_g , wall temperature, T_w (when radiative heat transfer is included in the model), initial particle density (ρ_{p0}), diameter (d_p), particle initial temperature (T_{p0}), and proximate analysis of biomass. The solution steps to obtain H_T and $H_{R,i}$ are shown in Fig. 1, more details are given below:

Step 1: Defining a trial range of h_c . The h_c starts with a minimum h_{cmin} and ends with a maximum h_{cmax} value. The range of h_c should cover the possible values of convective heat transfer coefficient under a specified operating condition, m is the total number of h_c values used to calculate H_T and $H_{R,i}$, j is the current iteration number. The h_{cmin} is estimated by a value smaller than $2.0\lambda_g/d_p$, which is the smallest convective heat transfer coefficient calculated by Ranz and Marshall Equation.³⁰ The h_{cmax} should be chosen sufficiently large (e.g. 1000 W/(m²K) for a 10 mm particle).

Step 2: With a given h_c from Step 1, the temperature history ($T_{p,non-iso}$), conversion history of moisture

and volatile ($X_{non-iso,i}$) inside the particle, and particle surface temperature history of biomass devolatilization, are calculated by solving the non-isothermal model. Then, the average particle temperature history ($T_{p,aver}$), and average conversion history of moisture and volatile ($X_{aver,i}$), and dimensionless temperature (θ) history are calculated by Eq. (6), Eq. (7), and Eq. (15), respectively. The heat flux history ($q_{non-iso}$), and reaction rate history ($R_{non-iso,i}$) of the non-isothermal model are calculated by Eq. (9) and (5), respectively. Based on the results, a series of data (θ , $q_{non-iso}$, $R_{non-iso,i}$) are obtained for the given h_c .

Step 3: The heat flux history (q_{iso}) and reaction rates history ($R_{iso,i}$) of the conventional isothermal particle model are calculated by Eq. (2) and Eq. (3), respectively. Based on the results, a series of data (θ , q_{iso} , $R_{iso,i}$) are obtained.

Step 4: Based on the non-isothermal data (θ , $q_{non-iso}$, $R_{non-iso,i}$) and the conventional isothermal data (θ , q_{iso} , $R_{iso,i}$), H_T and $H_{R,i}$ are calculated by Eq. (11) and Eq. (12), respectively. To avoid a numerical problem, H_T is specified as 1 when the dimensionless temperature is larger than 0.999, and $H_{R,i}$ is specified as 1 when the conversion of component i is larger than 0.999.

Step 5: Repeating Step 1 to Step 4 with a new h_c until $h_c > h_{cmax}$, namely $j > m$. A matrix with (θ , h_c , H_T , $H_{R,i}$) is obtained when all h_c value is covered in the calculation.

Step 6: The saved matrix is applicable in either CFD simulation or single particle modelling. A two-dimensional linear interpolation method³¹ is used to fit H_T and $H_{R,i}$ as a binary function of (θ , h_c).

Figure 1. The calculation steps to obtain H_T and $H_{R,i}$ of the heat transfer corrected isothermal model (An example is shown in Appendix B of Supporting Information to demonstrate the procedure for H_T and $H_{R,i}$).

Following the solving scheme of Fig. 1, the two corrected coefficients, H_T and $H_{R,i}$, of a 10 mm spherical wood particle with convective heat transfer coefficient of 10-1000 W/(m²·K) (corresponding Biot number in a range of 3.71-57.26) are shown in Fig. 2. The correction degrees of both external heat transfer, and drying and devolatilization rate increase with the increase of h_c . H_T decreases firstly with an increase of θ and then increase to 1, the trends are caused by the history of the temperature difference between the particle surface temperature and particle average temperature. $H_{R,i}$ increases firstly with the increase of θ and then decreases to lower than 1. $H_{R,i}$ finally reaches 1 when the drying and devolatilization are completed. Because the drying process finished at a much lower temperature than the devolatilization, $H_{R,i}$ reaches 1 with a smaller θ . At $\theta = 0$, both H_T and $H_{R,i}$ is 1, due to uniform temperature and volatile moisture conversion in the biomass particle. At $\theta = 1$, H_T and $H_{R,i}$ is also 1, because of uniform temperature distribution and the completed drying and devolatilization process, respectively.

Figure 2. The heat transfer corrected coefficients (H_T and $H_{R,i}$) for isothermal model (Gas: N₂, spherical particle, $d_p = 10$ mm, $\rho_{p0} = 580$ kg/m³, Vol = 90.0 db%, MC = 6.38 db%, $T_g = T_w = 1173$ K, $h_c = 10$ -1000 W/(m²·K), Bi = 3.71-57.26).

Fig. 3 compares H_T and $H_{R,i}$ for a small wood particle ($d_p = 0.1$ mm) and a large wood particle ($d_p = 10$ mm) with $h_c = 10, 100$, and 1000 W/(m²·K). Because of the negligible internal heat transfer, both H_T and $H_{R,i}$ are close to 1 with $h_c = 10, 100$, and 1000 W/(m²·K) for the small particle. However, the correction coefficients for external heat transfer, drying rate, and devolatilization rate, are in a range of 0-1, 10⁻⁴-10⁵, 10⁻⁴-10¹⁰ for the 10 mm particle under the investigated conditions. This implies a significant difference between the isothermal model and the non-isothermal model for large particles, supported by the previous studies.^{1,7,28,32} For a 10 mm biomass particle with different h_c values

(10/100/1000 W/(m²·K)), the correction factor of heat transfer increases with the increase of h_c , because the difference between $(T_g - T_{surf})$ and $(T_g - T_{aver})$ is larger for a larger h_c . However, the correction factor of reaction rate increases with an increase of h_c at the beginning, but later decreases with an increase of temperature.

Figure 3. A comparison of the heat transfer corrected coefficients (H_T and $H_{R,i}$) between particle size $d_p = 0.1$ mm ($Bi = 0.03$ - 0.14 , 0.06 - 0.18 and 0.32 - 0.57 for $h_c = 10$, 100 , and 1000 W/(m²·K), respectively.) and $d_p = 10$ mm ($Bi = 3.25$ - 14.02 , 5.83 - 18.01 , and 31.57 - 57.29 for $h_c = 10$, 100 , and 1000 W/(m²·K), respectively.). (Gas: N_2 , spherical particle, $\rho_{p0} = 580$ kg/m³, Vol = 90.0 db%, MC = 6 ar%, $T_g = T_w = 1173$ K).

3. Particle-scale model validation and analysis

The conventional isothermal model, the non-isothermal model, and the heat transfer corrected isothermal model are compared by modelling a series of experiments. A sensitivity analysis of the non-isothermal model is carried out to investigate the uncertainty of modelling parameters and particle boundary conditions.

3.1 Experimental data for model validation

The experiments are categorized according to biomass particle size as shown in Table 1. For the small particles (0.06-0.09 mm, mean particle diameter is 0.079 mm), the bulk gas flow velocity is ~ 5 m/s, and the reactor temperature was 1405 and 1667 K, respectively.⁴ For the medium particles (1-5 mm), biomass devolatilization experiments were conducted in a single particle combustor with a bulk gas

velocity 2.76 m/s.²⁹ For the large particle (> 5 mm), the experimental data of Lu et al.⁸ is used to evaluate the model. In their experiments, a 9.5 mm biomass particle was put in a single particle combustor with gas and wall temperatures of 1050 K and 1276 K, respectively. The proximate analysis of the above-mentioned fuel particles is given in Appendix C in Supporting Information.

Table 1. An overview of the experimental setup and operating conditions used for model validation.

Cases	Fuel type	Diameter (mm)	Moisture (ar%)	Density (kg/m ³) (dry basis)	Shapes	T_{p0} (K)	Ref.
Small	Pine wood	0.079	0.0	1180	Sphere	298	⁴
Medium	Schima wood	3-5	1.0-4.0	520-720	Sphere	298	²⁹
Large	Poplar wood	9.5	6.0	580	Sphere	298	⁸

3.2 Results and discussion

3.2.1 Small particles

Fig. 4 shows a comparison of the measured and computed particle conversion history of small pine wood particles (0.079 mm) at 1405 K and 1667 K. The conversion is calculated as $(m_0-m)/(m_0-m_\infty)$ (m_0 is the initial wood particle mass, m is the particle mass at time t , m_∞ is the particle mass after devolatilization). The three models give reasonable results but slightly underestimate the devolatilization rate before $t=0.02$ s. The reason is that the kinetics used in this study was derived by Wagenaar et al.³³ at a temperature range of 573-873K. For small particles (0.079 mm), the heating rate is in an order of 10000 K/s, and the devolatilization would primarily take place at temperatures higher than 873 K in the reactor. Therefore, high-temperature kinetics is needed to accurately simulate the experimental data.²⁸ Although Fig. 4 is based on small particles (0.079 mm), the internal heat transfer still plays a small role, resulting in a slight increase of the devolatilization time in the non-isothermal model and the corrected isothermal model compared to that of the conventional isothermal model.

Figure 4. A comparison between measured and computed particle conversion history by using different models. (Con-iso: conventional isothermal model, Non-iso: non-isothermal model, Cor-iso: corrected isothermal model. The abbreviations used in here are also used in other figures)

3.2.2 Medium particles

A comparison of the devolatilization time predicted by using different models and the experimental data of Lu et al.²⁹ based on 3-5 mm raw and torrefied spherical wood particles is shown in Fig. 5 (a). Both the non-isothermal and corrected isothermal models predict reasonably the devolatilization time (99% of particle conversion) compared to the experimental data. However, the devolatilization time is under-predicted by the conventional isothermal model, especially for the larger particles. Fig.5 (b) shows the particle temperature history of the 4mm raw wood predicted by using the different models. The temperature predicted by the isothermal model raises much faster than that of the other two models which predict similar temperature profiles with changes of time, indicating that the heat flux predicted by the isothermal model is much faster than that of the non-isothermal model.

Figure 5. (a): The devolatilization time predicted by different models and its comparison with experimental data²⁹, (b): The particle temperature history of raw wood with $d_p = 4$ mm predicted by using different models. (Raw represents wood without torrefaction, 230C1h, 260C1h, and 290C1h represents the wood was torrefied at 230, 260, and 290 °C with 1 hour, respectively. 290C4h represents the wood was torrefied at 290 °C with 4 hours, Gas: 3% O₂ and 97% N₂, 1504 K).

3.2.3 Large particles

Fig. 6 (a) shows the particle conversion history predicted by different models and their comparison with experimental data of a 9.5 mm particle.⁸ The results predicted by the heat transfer corrected isothermal and non-isothermal model are in good agreement with experimental data, while the conventional isothermal model underestimates the conversion at the beginning and overestimates the conversion at a later time. Similar to the results in Fig. 5(b), the corrected isothermal model predicts similar particle average temperature profiles as the non-isothermal model, while the conventional isothermal model overestimates the heating rate as shown in Fig.6 (a). A similar trend was also reported by Lu et al.⁸

Figure 6. The particle conversion history (a) and temperature history (b) of spherical wood particles during devolatilization. (Conditions: $d_p = 9.5$ mm, MC = 6 ar%, Vol = 90.0 db%, FC = 9.5 db%, Ash = 0.5 db%, $T_g = 1050$ K, $T_w = 1276$ K). Exp. # represents #th experiments did under the same operating conditions.

3.2.4 Influence of modelling parameters on non-isothermal model

According to the Table S1 given in Supporting Information, several parameters used in the non-isothermal model may influence the modelling results, such as shrinkage coefficient (ϕ), fixed carbon content (FC), moisture content (MC), gas conductivity (λ_g), pore size (d_{pore}), char thermal capacity (C_{pC}), char conductivity (λ_C), biomass conductivity (λ_B), heat of devolatilization ($Q_{R,2}$), biomass thermal capacity (C_{pB}), particle dry density (ρ_{p0}), drying and devolatilization rates (dX_1/dt and dX_2/dt). The radiative heat transfer is neglected in the sensitivity analysis, because biomass devolatilization in fluidized bed reactor is dominated by convective heat transfer. The devolatilization time is selected as the indicator to show the influence of the above-mentioned parameters. Fig. 7 shows the results of a sensitivity analysis done by decreasing and increasing each parameter by 50% for a 5 mm and 10 mm biomass particle devolatilized in 100% N₂ at $T_g = 1173$ K. The particle pore size and gas conductivity have limited influence on the devolatilization time, due to its small contribution (<20%) to the effective particle conductivity. The fixed carbon content is found to have no significant influence on devolatilization time. The shrinkage coefficient also shows an insignificant impact on devolatilization time for both 5 and 10 mm wood particle. The drying and devolatilization rates also show a limited effect on the modelling results, because the devolatilization process is heat transfer dominated for both

5 and 10 mm particles.¹ The effect of char conductivity on the predicted devolatilization is smaller than 15%, implying that it is reasonable to use a constant value in the modelling. The predicted devolatilization time is most sensitive to the particle dry density, indicating the importance of measuring/obtaining the density by experiments. The biomass thermal conductivity, biomass thermal capacity and the heat of devolatilization also show significant influences on the modelling results, indicating that such physical properties may need to be selected carefully according to the biomass types. The parameters listed in Table S1 is proved to suitable for woody biomass as discussed in our previous study.¹⁵

Figure. 7. Sensitivity analysis of the model with respect its physical properties, gas temperature and drying and devolatilization kinetics for a 5 mm and 10 mm particle (Base case: $T_g = 1173$ K, MC = 6 ar%, Vol = 90 db%, FC = 9.5 db%, Ash = 0.5 db%, $\rho_{p0} = 580$ kg/m³, $h_c = 100$ W/(m²·K), physical properties used in the calculation are listed in Table S1 of Supporting Information).

3.2.5 Effect of convective heat transfer coefficient

The corrected coefficients are pre-calculated by quantitatively evaluating the differences between the conventional isothermal model and the non-isothermal model. However, the particle boundary conditions (e.g. slip velocity, gas composition, gas temperature, solid concentration etc.) of the biomass particles are dynamically changed in the fluidized bed reactor, It means that the convective heat transfer coefficient (h_c) changes dynamically during drying and devolatilization process. To test whether the pre-calculated H_T and $H_{R,i}$ are applicable in dynamically changed boundary conditions, two scenarios are designed. In Scenario I, we assume that the convective heat transfer coefficient has step changes

according to Fig. 8 (a). Fig. 8 (b) and (c) show the predicted results of the three models. The non-isothermal model and the corrected isothermal model predict similar conversion and particle temperature profiles. However, the conventional isothermal model predicts much faster devolatilization and particle heating rates. In Scenario II, a random convective heat transfer coefficient is used as shown in Fig. 8 (d). The conclusion is the same as Scenario I according to Fig. 8 (e) and (f). Therefore, the pre-calculated corrected coefficients are applicable to model biomass devolatilization in a fluidized bed where the convective heat transfer coefficient is dynamically changed.

Figure 8. The effect of convective heat transfer coefficient on particle conversion and temperature profiles. Scenario I: constant h_c of different sections times: (a) Step changed convective heat transfer coefficient, (b) Particle conversion profiles, (c) Particle temperature profiles. Scenario II: random time varied h_c : (d) Random convective heat transfer coefficient, (e) Particle conversion profiles, (f) Particle temperature profiles. (Conditions: $d_p = 5.0$ mm, spherical particle, MC = 6 ar%, Vol = 90 db%, FC = 9.5 db%, Ash = 0.5 db%, $T_g = 1173$ K, gas conditions: 100% N₂). Radiation is neglected in the modelling.

4 Implementation of heat transfer corrected isothermal model into CFD modelling biomass devolatilization

A CFD model coupled with the heat transfer corrected isothermal model is presented to simulate devolatilization of thermally thick biomass particles in a batch bubbling fluidized bed. The purposes are to demonstrate the feasibility of implementing the heat transfer corrected isothermal model in CFD and to compare its performance with the conventional isothermal model, rather than to validate the CFD

modelling results. Compared to three dimensional (3D) CFD simulations, a two dimensional (2D) CFD simulations can give similar qualitative results as those of 3D simulation and reduce computational time^{34–36}. Therefore, the 2D CFD modelling is selected in this study.

4.1 Model description

Besides the assumptions of the heat transfer corrected isothermal model, the following additional assumptions are applied to simplify CFD simulation: (1) constant particle diameter during devolatilization, the biomass particle considered as a mixture of raw wood species and char species, the particle density is calculated by volume weighed raw wood and char density; (2) dry biomass particle, therefore the correction coefficient of drying is not included; (3) since the devolatilization biomass particle is either floating on the bed’s surface or immersed in the particle surface with occasionally contact with bubble, and a fluidized bed reactor for biomass gasification and combustion is usually operated at a low-temperature range (773-1273 K), the radiative heat transfer between the walls of reactor and particle is insignificant. Therefore, following the approach of literature,^{37,38} the radiative heat transfer is neglected in our CFD simulations; (4) the heat transfer between sand and biomass contacting is neglected,^{34,38,39} due to the convective heat transfer dominated the heating process of the large particle in fluidized bed⁴⁰ and the limitation of the Eulerian multi-fluid model.

The Eulerian multi-fluid model in ANSYS Fluent® 18.0 is used to simulate biomass devolatilization behavior in the batch fluidized bed.³⁷ The gas phase, biomass, and sand particles are treated as inter-penetrating continuums. The gas mixture has 2 species: N₂ and volatile, the solid phase is considered as a mixture of char and raw wood. The kinetic theory of granular flow (KTGF) is applied to calculate solids stress.⁴¹ More details can be found in the user guide of ANSYS Fluent® 18.0.⁴² The momentum exchange between gas and solid phase was described by Gidaspow drag model,⁴¹ which has been applied to model biomass devolatilization in bubbling fluidized bed reactors.^{16,18,43} The interaction forces between the different solid phases are expressed in terms of the drag force and the enduring contact force in the plastic regime as described in Syamlal et al.⁴⁴ The heat exchange between the fluid and solid phase is determined by the model derived by Gunn,⁴⁵ which applies to a porosity range of

0.35–1.0 and Reynolds number of up to 10^5 ,⁴⁶ and has been widely used in previous studies to describe the heat transfer between gas and solid phase for biomass gasification.^{34,38,39}

Following the previous studies,^{34,38,39} the Nusselt Number (Nu_{gsm}) is calculated as:

$$Nu_{gsm} = (7 - 10\varepsilon_g + 5\varepsilon_g^2)(1 + 0.7 Re_{sm}^{0.2} Pr^{1/3}) + (1.33 - 2.4\varepsilon_g + 1.2\varepsilon_g^2) Re_{sm}^{0.7} Pr^{1/3} \quad (17)$$

Here, m represents different solid phases, $m = 1$, biomass phase, $m = 2$, sand phase.

For the conventional isothermal model, the convective heat transfer coefficient for biomass particles is given as^{47,48}

$$h_{gs1} = \frac{6k_g \varepsilon_g \varepsilon_{s1} Nu_{gs1}}{d_{s1}^2} \quad (18)$$

For the heat transfer corrected isothermal model, the convective heat transfer coefficient is calculated by multiplying H_T :

$$h_{gs1} = \frac{6\varepsilon_g \varepsilon_{s1}}{d_{s1}} \left(H_T \frac{k_g Nu_{gs1}}{d_{s1}} \right) \quad (19)$$

The devolatilization model is defined as source terms by using User Defined Functions (UDFs) in ANSYS Fluent® 18.0, which is given in Appendix D in Supporting Information.

4.2 Geometry and operating conditions

Fig. 9 shows the 2D domain of the batch fluidized bed. The diameter and height are 1 and 4 m, respectively. Nitrogen stream flows to the bed from a distributor of the bottom with a uniform velocity of 0.65 m/s, and flows out of the bed. The reactor is operated at atmospheric pressure, and the temperatures of the inlet stream and reactor wall are 1173 K. More details of operating conditions and biomass properties are shown in Table 2 and Table 3, respectively.

Figure 9. 2D domain and initial conditions of CFD modeling the batch fluidized bed.

Table 2 Operating conditions of the batch fluidized bed.

N_2 inlet, m/s	0.65
Initial sand patched height, m	1.0
Sand patch volume fraction	0.5
Sand diameter, mm	0.5
Sand density, kg/m^3	2600
Biomass diameter, mm	1/3/6/10
Operating pressure, Pa	101325
Bed temperature, K	1173
Wall temperature, K	1173

Table 3 Properties of the biomass particles used in CFD simulation.

Raw wood density, kg/m^3	580
Volatile, wt%	90
Fixed carbon, wt%	9.5
Ash, wt%	0.5
Moisture, wt%	0.0
Char density, wt%	58

4.3 Simulation procedure and settings

The CFD simulations are performed in two stages. At the first stage, only the sand particles are loaded in the bed with a height of 1 m, and the simulation starts with a temperature of 1173 K without biomass particle. The solid flux and bed expansion at different heights are monitored to determine when the simulation reaches a quasi-steady state. The simulations show that the reactor reaches a quasi-steady state after 10 seconds of fluidization. The results at the moments of 10s are used as the initial conditions of the second stage. In the second stage, the biomass particles are fed into the reactor by patching biomass particle in a region ($0.5 \text{ m} \times 1 \text{ m}$ with a center coordinate (2.5, 2.5)) with a volume fraction of 0.02 and initial temperature of 298 K. The devolatilization rate may be affected by the amount of biomass particle patched. However, it does not influence the results of a qualitative comparison between the heat transfer corrected model and the conventional isothermal model.

The algebraic form of the granular temperature model is chosen for both sand and biomass particle instead of the full granular energy balance model^{49–51} to obtain better computational efficiency and numerical convergence. The no-slip and the partial-slip boundary condition of gas phase and solid phase are used in the modelling, respectively. The specular coefficient is set to 0.001, as suggested by Vashisth et al.⁵² The physical properties of biomass particle are calculated based on the correlations given in Table S1 in Supporting Information, but with particle shrinkage coefficient of 0.

To compare the results of the conventional and corrected isothermal model, both models are implemented in ANSYS Fluent® 18.0 by using UDFs. The raw data of H_T and $H_{R,2}$ are obtained from the heat transfer corrected isothermal model and then stored by using “Execute on Demand” UDFs in ANSYS Fluent® 18.0. A two-dimensional linear interpolation method³¹ is used to interpolate the pre-calculated H_T and $H_{R,2}$ in each cell by using UDFs. A plot of raw data of H_T and $H_{R,2}$ for different particle size are given in Appendix E in Supporting Information. The grid size is $15 \text{ mm} \times 30 \text{ mm}$ and the total number of meshes is about 9000, which is fine enough for coarse grid simulation of Group B particle as discussed in Li et al.⁵³ The particle conversion and particle temperature are monitored. All simulations are carried out by using 16 cores in HPC system of Technical University of Denmark. The

simulation settings are summarized in Table 4.

Table 4. Simulation settings of the batch fluidized bed.

Unsteady formulation	Unsteady, 2nd-order Implicit ⁴²
Granular viscosity	Gidaspow ⁴²
Granular bulk viscosity	Lun et al. ⁴²
Frictional viscosity	Schaeffer ⁴²
Granular temperature	Algebraic ⁴⁹
Frictional pressure	Based KTGF ⁴¹
Solid pressure	Lun et al. ⁴²
Radial distribution	Lun et al. ⁴²
Angle of internal friction	30
Drag model	Gidaspow ⁴¹
Time step	0.0005 s

4.4. Results and discussions

4.4.1 Devolatilization rate

Fig. 10 compares the devolatilization rate predicted by using the heat transfer corrected isothermal model and the conventional isothermal model. For the heat transfer corrected isothermal model, the devolatilization starts at ~500 K and reaches a maximum rate at ~650 K, while the corresponding temperature for the isothermal model is ~600 K and ~750 K, respectively. Compared to the conventional isothermal model, the devolatilization rate predicted by the corrected isothermal model starts at a lower temperature and ends at higher particle temperature. It is consistent with the results obtained in section 3 and previous studies.^{9,54} Due to the significantly different devolatilization history predicted by the two models, the volatile concentration in the gas phase also differs significantly.

Figure 10. Comparisons of biomass conversion rates versus particle temperature predicted by the conventional isothermal and the heat transfer corrected isothermal models. The contour plots of the volatile mass fraction with the particle temperature 600 K and 800 K are also shown in the figure. The case is $d_p = 10$ mm.

4.4.2 Conversion

Fig. 11 shows the predicted conversion of devolatilization by using the conventional and corrected isothermal models. The conversion time predicted by the corrected isothermal model is shorter than that of the conventional isothermal model for all particle size. The deviation degree between those two models increases from 10% to 30% with an increase of particle size from 1 mm to 10 mm.

Figure 11. Biomass devolatilization conversion history of different particle sizes (1/3/6/10 mm) predicted by using the conventional and corrected isothermal models in CFD simulations.

4.4.3 Temperature

Fig. 12 shows the predicted biomass temperature history by using the two models. For all particle size, the conventional isothermal model predicts a higher particle temperature than the corrected isothermal model, until the particles reach the environmental temperature. Additionally, the deviation between the conventional and corrected isothermal model becomes large with the increase of particle size, because the effect of the intra-particle heat transfer becomes more significant on devolatilization of thermally-thick biomass.

Figure 12. The temperature history of different particle sizes (1/3/6/10 mm) predicted by using the conventional and corrected isothermal models in CFD simulations.

4.4.4 Computational time

The simulations have been carried out by using 16 CPU cores in HPC system at Technical University of Denmark. All simulation cases finished within 1 week for both the conventional and heat transfer corrected isothermal model. No significant computational time difference is observed between the two models. Therefore, the corrected isothermal model, which can give similar biomass devolatilization behavior as a non-isothermal model, has similar computational efficiency of the conventional isothermal model. For a 2D case with 100000 meshes and a time-step size of 0.0005 s, 2 min of real biomass devolatilization process in a fluidized bed can be finished within 1 month with 32 CPU cores. Such a number of meshes can be used to 2D coarse grid simulation of a pilot- or large-scale fluidized bed. As compared to the non-isothermal models of Papadikis et al.,^{16,18} and Ström and Thunman,²² and Lattice Boltzmann method,²⁰ which requires additional computational cost for internal grid points, the biomass particles do not require to be discretized radially by using the heat transfer corrected isothermal model.

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Therefore, we expect that the corrected isothermal model has a better performance on computational efficiency, compared to the above-mentioned models.

5 Conclusions

In this paper, a heat transfer corrected isothermal model for CFD simulation of devolatilization of thermal-thick biomass in fluidized beds is presented. The correction coefficients of heat transfer, H_T , and reaction rates, $H_{R,i}$, are introduced. Compare to the conventional isothermal model, the corrected isothermal model exhibited a higher accuracy in simulating a series of devolatilization experiments with thermally-thick biomass particles. The corrected isothermal model was further implemented in the CFD simulation of biomass devolatilization in a batch bubbling fluidized bed. The computational efficiency of the corrected isothermal model is comparable to that of the conventional isothermal model. Consistent with the trend seen in particle-scale modelling, the corrected isothermal model predicts a lower heating rate and devolatilization rate. This demonstrates the applicability and improved performance of using the corrected isothermal model to simulate thermally-thick biomass devolatilization in fluidized bed reactors.

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450 **Supporting Information**

451 Appendix A: Physical properties, drying, and devolatilization model

452 Appendix B: A demonstration of how to calculate H_T and $H_{R,i}$

453 Appendix C: Particle proximate analysis of the experiments for particle-scale modelling

454 Appendix D: The implementation of devolatilization model in CFD modelling

455 Appendix E: Heat transfer corrected coefficients (H_T and $H_{R,i}$) used in CFD modelling

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460 Engineering.

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4 461 **Nomenclature**

5	A_p	Particle surface area	m^2
6	Bi	Biot Number	-
7	C_p	Heat capacity of particle	$J/(kg \cdot K)$
8	d_p	Diameter of particle	m
9	h_c	Convective heat transfer coefficient	$W/(m^2 \cdot s)$
10	$H_{R,i}$	Heat-transfer corrected coefficient for reaction i	-
11	H_T	Heat-transfer corrected coefficient for heat convection	-
12	Nu	Nusselt Number	-
13	m_p	Mass of particle	kg
14	q_{iso}	Heat flux predicted by isothermal model	$J/(m^2 \cdot s)$
15	$q_{non-iso}$	Heat flux predicted by non-isothermal model	$J/(m^2 \cdot s)$
16	$Q_{R,i}$	Heat of reaction i	J/kg
17	r	Radius position	m
18	R	Radius of biomass particle	m
19	Re	Reynolds number	-
20	R_{iso}	Reaction rate predicted by the conventional isothermal model	kg/s
21	$R_{non-iso}$	Reaction rate predicted by the non-isothermal model	kg/s
22	R_{cor}	Reaction rate predicted by the corrected isothermal model	kg/s
23	t	Time	s
24	T_g	Gas temperature	K
25	$T_{p,cor}$	Particle temperature calculated by the heat transfer corrected isothermal model	K
26	$T_{p,non-iso}$	Particle temperature calculated by the non-isothermal model	K
27	$T_{p,iso}$	Particle temperature calculated by the conventional isothermal model	K
28	T_{aver}	Average particle temperature	K
29	T_{surf}	Particle surface temperature	
30	T_w	Wall temperature	K
31	u	Velocity	m/s
32	V_p	Particle volume	m^3
33	X	Total conversion	-
34	$X_{non-iso,i}$	Conversion of species i calculated by the non-isothermal model	-
35	$X_{iso,i}$	Conversion of species i calculated by the conventional isothermal model	-
36	$X_{aver,i}$	Average conversion of species i	

462	Y	Mass fraction	-
463	Greek symbols		
	λ	Conductivity	W/(m·K)
	ε	Particle voidage or bed voidage	-
	ρ	Density	kg/m ³
	ξ	Emissivity	-
	σ	Stefan-Boltzmann constant	J/(m ² ·K ⁴ ·s)
464	Subscripts		
	0	Initial conditions	
	p	Particle	
	B	Raw biomass	
	C	Char	
	g	Gas phase	
	i	i^{th} species in biomass ($i = 1$: moisture, $i = 2$: volatile)	
	p	Particle	
	sm	m^{th} solid phase ($m = 1$, biomass, $m = 2$, sand)	
	w	Wall	
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Figure 2. The heat transfer corrected coefficients (H_T and $H_{R,i}$) for isothermal model (Gas: N_2 , spherical particle, $d_p = 10$ mm, $\rho_{p0} = 580$ kg/m³, Vol = 90.0 db%, MC = 6.38 db%, $T_g = T_w = 1173$ K, $h_c = 10$ -1000 W/(m²·K), Bi = 3.71-57.26).

176x50mm (300 x 300 DPI)

Figure 3. A comparison of the heat transfer corrected coefficients (H_T and $H_{R,i}$) between particle size $d_p = 0.1$ mm ($Bi = 0.03$ - 0.14 , 0.06 - 0.18 and 0.32 - 0.57 for $h_c = 10$, 100 , and 1000 W/(m²·K), respectively.) and $d_p = 10$ mm ($Bi = 3.25$ - 14.02 , 5.83 - 18.01 , and 31.57 - 57.29 for $h_c = 10$, 100 , and 1000 W/(m²·K), respectively.). (Gas: N_2 , spherical particle, $\rho_{p0} = 580$ kg/m³, Vol = 90.0 db%, MC = 6 ar%, $T_g = T_w = 1173$ K).

178x80mm (300 x 300 DPI)

Figure 4. A comparison between measured and computed particle conversion history by using different models. (Con-iso: conventional isothermal model, Non-iso: non-isothermal model, Cor-iso: corrected isothermal model. The abbreviations used in here are also used in other figures)

272x208mm (300 x 300 DPI)

Figure 5. (a): The devolatilization time predicted by different models and its comparison with experimental data²⁹, (b): The particle temperature history of raw wood with $d_p = 4$ mm predicted by using different models. (Raw represents wood without torrefaction, 230C1h, 260C1h, and 290C1h represents the wood was torrefied at 230, 260, and 290 °C with 1 hour, respectively. 290C4h represents the wood was torrefied at 290 °C with 4 hours, Gas: 3% O_2 and 97% N_2 , 1504 K).

175x71mm (300 x 300 DPI)

Figure 6. The particle conversion history (a) and temperature history (b) of spherical wood particles during devolatilization. (Conditions: $d_p = 9.5$ mm, MC = 6 ar%, Vol = 90.0 db%, FC = 9.5 db%, Ash = 0.5 db%, $T_g = 1050$ K, $T_w = 1276$ K). Exp. # represents #th experiments did under the same operating conditions.

176x73mm (96 x 96 DPI)

Figure. 7. Sensitivity analysis of the model with respect its physical properties, gas temperature and drying and devolatilization kinetics for a 5 mm and 10 mm particle (Base case: $T_g = 1173$ K, MC = 6 ar%, Vol = 90 db%, FC = 9.5 db%, Ash = 0.5 db%, $\rho_{p0} = 580$ kg/m³, $h_c = 100$ W/(m²·K), physical properties used in the calculation are listed in Table S1 of Supporting Information).

177x72mm (300 x 300 DPI)

Figure 8. The effect of convective heat transfer coefficient on particle conversion and temperature profiles. Scenario I: constant h_c of different sections times: (a) Step changed convective heat transfer coefficient, (b) Particle conversion profiles, (c) Particle temperature profiles. Scenario II: random time varied h_c : (d) Random convective heat transfer coefficient, (e) Particle conversion profiles, (f) Particle temperature profiles. (Conditions: $d_p = 5.0$, spherical particle, MC = 6 ar%, Vol = 90 db%, FC = 9.5 db%, Ash = 0.5 db%, $T_g = 1173$ K, gas conditions: 100% N_2). Radiation is neglected in the modelling.

177x92mm (300 x 300 DPI)

Figure 9. 2D domain and initial conditions of CFD modeling the batch fluidized bed.
59x135mm (300 x 300 DPI)

Figure 10. Comparisons of biomass conversion rates versus particle temperature predicted by the conventional isothermal and the heat transfer corrected isothermal models. The contour plots of the volatile mass fraction with the particle temperature 600 K and 800 K are also shown in the figure. The case is $d_p = 10$ mm.

83x54mm (300 x 300 DPI)

Figure 11. Biomass devolatilization conversion history of different particle sizes (1/3/6/10 mm) predicted by using the conventional and corrected isothermal models in CFD simulations.

176x133mm (300 x 300 DPI)

Figure 12. The temperature history of different particle sizes (1/3/6/10 mm) predicted by using the conventional and corrected isothermal models in CFD simulations.

177x133mm (300 x 300 DPI)