Modelling of Biomass Combustion and Gasification: from Particle-scale to Reactor-scale

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Hao Luo
PhD Thesis

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Hao Luo
September 2019
Preface

The present thesis is the results of three years PhD project, from 2016 to 2019. The project has been carried out at the Combustion and Harmful Emission Control (CHEC) research centre, at the Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), under the supervision of Professor Kim Dam-Johansen, Associate Professor Weigang Lin, and Associate Professor Hao Wu.

I would like to thank my supervisors for their guidance and support during the last three years. I would like to thank Weigang and Hao for their inspirations, valuable discussions, critical reading of my status report, and encouragement during my projects. I am very sincerely grateful to Kim Dam-Johansen for his support and encouragement during this project.

I would also like to thank Peter Arendt Jensen and Peter Glarborg for their useful comments regarding single particle model for biomass devolatilization and char conversion. I would also like to thank Zhimin Lu for providing single particle combustion experiments, Wenli Song and Songgeng Li for providing experimental data of the dual fluidized bed system for biomass gasification and the useful suggestions.

I was also fortunate to be a part of CHEC group surrounded by motivated PhD students and researches. I would also like to thank the technical support from DTU Computing Center.

I would like to thank my girlfriend Xinyan Liu, my parents, as well as all my friends for their support and encouragement.

Hao Luo
Lyngby, Denmark
September 2019
Summary

The PhD project is aimed to develop modelling tools to simulate biomass combustion and gasification both in a particle-scale and in a reactor-scale. The work includes the development of comprehensive particle-scale models for biomass devolatilization and char conversion, simplified models for CFD modelling of biomass devolatilization and char conversion, and a meso-scale drag model for CFD modelling of biomass combustion and gasification in fluidized bed reactors.

A comprehensive biomass devolatilization model including both external and internal heat transfer has been developed based on the model proposed by Johansen et al. [1]. The model was validated by single wood particle devolatilization experiments under different gas temperatures (1473-1723 K), particle sizes (3-4 mm), particle moisture content (5-52 ar%), and particle dry density (180-1100 kg/m³). Both the modelling and experimental results indicated that the devolatilization time increases linearly with an increase of particle dry density. The gas temperature, particle size, and the particle moisture content influenced significantly on the devolatilization time, while volatile content and the slip velocity have small effects. The kinetics of devolatilization did not influence significantly on the devolatilization time of large wood particles (> 1 mm). Based on the results from the comprehensive devolatilization model, a simple correlation was derived to predict the devolatilization time of wood particles.

A comprehensive char conversion model including both external and internal mass and heat transfer, particle shrinkage, the heterogeneous reactions of the char oxidation and gasification, and the homogeneous reactions occurring in the particle boundary layer, has been developed. The model was validated by single particle combustion experiments of pine and beech wood char at high temperatures (1473-1723 K) with different oxygen concentrations (0.0-10.5 vol%) and steam content (25-42 vol%). The modelling results indicated that the CO oxidation in the particle boundary layer has a significant effect on the char conversion process. Both char oxidation and gasification reactions contributed to char conversion, with the latter becoming important at high temperature (e.g. > 1273 K) and large particle size (e.g. > 1 mm) conditions.

Based on the comprehensive biomass devolatilization model, a heat transfer corrected isothermal model for biomass devolatilization model has been developed to facilitate CFD modelling of the devolatilization of thermally-thick biomass particles. In the model, two heat transfer corrected coefficients ($H_T$, correction of heat transfer, and $H_{K_c}$, correction of reaction rates) were introduced based on the difference of external heat transfer and devolatilization rate between the comprehensive biomass devolatilization model and a conventional isothermal model. Compared to the comprehensive devolatilization model, the heat transfer corrected isothermal model predicted a similar devolatilization behaviour with a much lower computational cost. The model was implemented in a Eulerian multiphase flow model to
simulate the biomass devolatilization in a batch bubbling fluidized bed reactor. Compared to a conventional isothermal model, the heat transfer corrected isothermal model had similar computational efficiency, but provided more reasonable results for thermally-thick biomass particles.

Based on the comprehensive char conversion model, a mass transfer corrected uniform char conversion model was developed to reduce the computational cost of CFD modelling char conversion process. Three coefficients, \( H_T \), correction of heat transfer, and \( H_{R,i} \), correction of reaction rates, and \( H_{m,i} \), correction of external mass transfer rate) were introduced by comparing a uniform char conversion model and the comprehensive char conversion model. Compared to the uniform char conversion model, the mass transfer corrected uniform char conversion model gave more reasonable results, and expected to have comparable computation efficiency.

A hybrid EMMS drag model has been developed to simulate the hydrodynamics of three dimensional full-loop CFD modelling biomass gasification in a dual fluidized bed system. Compared to the Gidaspow drag model, the pressure distributions predicted by the hybrid EMMS drag model were in a better agreement with the measurement. The effects of solid inventory on the hydrodynamics of the dual fluidized bed system have been evaluated by the hybrid EMMS drag model. It was found that the solid circulation rate increased with an increase of solid inventory. When the solid inventory was larger than 160 kg, an unstable regime was identified for the dual fluidized bed system.
**Resumé**

Dette Ph.d.-projekt mål er at udvikle modelleringssværkøjer til simulering af forbrænding og forgasning af biomasse både i både partikelskala og reaktorskala. Arbejdet inkluderer udvikling af detaljerede partikelskala modeller til biomasse devolatisering og koks omdannelse, forenkled modeller til CFD modellering af biomasse devolatisering og koks omdannelse og en mesoskala drag model til CFD modellering af forbrænding og forgasning af biomasse i fluidbed reaktorer.

En detaljerede biomasse-devolatiseringssmodel der inkluderer både ekstern og intern varmeoverførsel er udviklet på baggrund af modellen foreslået af Johansen et al. [1]. Modellen blev valideret ved hjælp af en enkelt partikel devolatiseringseksperimenter under forskellige gastemperaturer (1473-1723 K), partikelstørrelser (3-4 mm), partikelfugtighedsindhold (5-52 ar%) og tør partikel densiteter (180-1100 kg/m3). Både modellerings og eksperimentelle resultater indikerede, at devolatiseringstiden øges lineært med en forøgelse af tør partikel densiteten. Gasstemperaturen, partikelstørrelsen og partikels fugtighedsindhold påvirkede devolatiseringstiden væsentligt, mens effekten af flygtindhold og sliphastigheden var lille. Devolatiseringens kinetik påvirkede ikke træpartiklernes devolatiseringstid betydeligt (> 1 mm). Baseret på resultaterne fra den detaljerede devolatiseringssmodel blev der aflæst en simpel korrelation for at forudsige devolatiseringstiden for træpartikler i størrelsesområdet 1-10 mm.

En omfattende koks-konverteringsmodel, der inkluderer både ekstern og intern masse- og varmeoverførsel, partikelkrympning, de heterogene reaktioner af koks-oxidation og forgasning og de homogene reaktioner, der forekommer i partikelgrænselaget, er blevet udviklet. Modellen blev valideret ved forbrændingsforsøg med partikler af fyrretræ og birketræ ved høje temperaturer (1473-1723 K) med forskellige iltkoncentrationer (0.0-10.5 vol%). Modelresultaterne indikerede, at CO-oxidationen i partikelgrænselaget har en signifikant effekt på koks-omdannelsesprocessen. Både koksoxidations- og forgasningsreaktioner bidrog til koksomdannelse, hvor sidstnævnte blev vigtigere ved høje temperaturer (f.eks. > 1273 K) og store partikelstørrelser (f.eks. > 1 mm).

model en lignende devolatiliseringstid med en langt lavere beregningsomkostning. Modellen blev implementeret i en eulerisk metode til at simulere biomasse-devolatilisering i en batch boblende fluidbed reaktor. Sammenlignet med en konventionel isotermisk model havde den varmeoverførselskorrigerede isotermiske model lignende beregningseffektivitet, men tilvejebragte mere retvisende resultater for termisk tykke biomassepartikler.

Baseret på den detaljerede koks-konverteringsmodel blev der udviklet en masseoverførsel-korrigerede uniform char-konverteringsmodel for at reducere beregningsomkostningerne ved CFD-modellering af koks-omdannelsen. Tre koefficienter ($H_T$, korrektion af varmeoverførsel og $H_{R,i}$, korrektion af reaktionshastigheder, og $H_{m,i}$, korrektion af ekstern masseoverførsel) blev introduceret ved sammenligning af en uniform koks-omdannelsesmodel og den detaljerede koks-konverteringsmodel. Sammenlignet med en standard uniform koks-konverteringsmodel gav den masseoverførsel-korrigerede uniforme char-konverteringsmodel mere retvisende resultater og forventedes at have sammenlignelig beregningseffektivitet.

En hybrid EMMS-trækmodel er udviklet til at simulere hydrodynamikken i tredimensionel CFD-modellering af biomasse i fuld loop-modellering i et dobbelt fluidbed system. Sammenlignet med Gidaspow-dragmodellen var de trykkfordelinger, der blev forudsagt af hybrid EMMS-trækmodellen, i bedre overensstemmelse med målingen. Påvirkningerne fra det totale partikel indhold på hydrodynamikken i det dobbelte fluidbed system blev evalueret ved hjælp af hybrid EMMS-dragmodellen. Det blev konstateret, at partikel cirkulationshastighed steg med en stigning i det totale partikel indhold af systemet. Når det totale partikel indhold var større end 160 kg, blev der identificeret et ustabilt regime i systemet med dobbelt fluidbed.
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<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
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<tr>
<td>$A_p$</td>
<td>Particle surface area</td>
<td>$m^2$</td>
</tr>
<tr>
<td>Bi</td>
<td>Biot number</td>
<td>-</td>
</tr>
<tr>
<td>$C_D$</td>
<td>Drag coefficient</td>
<td>-</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Molar concentration of species $i$</td>
<td>$mol/m^3$</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Heat capacity of particle</td>
<td>J/(kg·K)</td>
</tr>
<tr>
<td>$C_{pa}$</td>
<td>Heat capacity of particle’s ash</td>
<td>J/(kg·K)</td>
</tr>
<tr>
<td>$C_{pb}$</td>
<td>Heat capacity of biomass</td>
<td>J/(kg·K)</td>
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<tr>
<td>$C_{pc}$</td>
<td>Heat capacity of particle’s char</td>
<td>J/(kg·K)</td>
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<tr>
<td>$C_{pg}$</td>
<td>Heat capacity of gas</td>
<td>J/(kg·K)</td>
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<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
<td>$m^2/s$</td>
</tr>
<tr>
<td>$D_{eff}$</td>
<td>Effective mass diffusion coefficients</td>
<td>$m^2/s$</td>
</tr>
<tr>
<td>$D_{Kn}$</td>
<td>Knudsen diffusion coefficient</td>
<td>$m^2/s$</td>
</tr>
<tr>
<td>$D_{m,i}$</td>
<td>Mass diffusion coefficient of component $i$ in gas mixtures</td>
<td>$m^2/s$</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Particle size</td>
<td>m</td>
</tr>
<tr>
<td>$F_c$</td>
<td>Collision force</td>
<td>N</td>
</tr>
<tr>
<td>$F_d$</td>
<td>Drag force</td>
<td>N</td>
</tr>
<tr>
<td>$g$</td>
<td>Gravity acceleration</td>
<td>$m/s^2$</td>
</tr>
<tr>
<td>$h_c$</td>
<td>Convective heat transfer coefficient</td>
<td>W/(m²·K)</td>
</tr>
<tr>
<td>$H_D$</td>
<td>Heterogeneous coefficients</td>
<td>-</td>
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<tr>
<td>$h_m$</td>
<td>Mass transfer coefficient</td>
<td>m/s</td>
</tr>
<tr>
<td>$H_m$</td>
<td>Correction coefficients of diffusion rate</td>
<td>-</td>
</tr>
<tr>
<td>$H_R$</td>
<td>Correction coefficients of reaction rate</td>
<td>-</td>
</tr>
<tr>
<td>$H_T$</td>
<td>Correction coefficients of heat transfer</td>
<td>-</td>
</tr>
<tr>
<td>$I$</td>
<td>Moments of inertia</td>
<td>kg·m²</td>
</tr>
<tr>
<td>$m$</td>
<td>mass</td>
<td>kg</td>
</tr>
<tr>
<td>$M$</td>
<td>Molecular weight</td>
<td>mol/kg</td>
</tr>
<tr>
<td>$M_c$</td>
<td>Moisture content</td>
<td>-</td>
</tr>
<tr>
<td>$n$</td>
<td>Reaction order</td>
<td>-</td>
</tr>
<tr>
<td>Nu</td>
<td>Nusselt number</td>
<td>-</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>Pr</td>
<td>Prandtl number</td>
<td>-</td>
</tr>
<tr>
<td>$Q$</td>
<td>Heat transfer rate</td>
<td>J/s or J/(m³·s)</td>
</tr>
<tr>
<td>$q$</td>
<td>Heat flux</td>
<td>J/(m²·s)</td>
</tr>
<tr>
<td>$Q_{pyro}$</td>
<td>Heat of devolatilization</td>
<td>J/kg</td>
</tr>
<tr>
<td>$R$</td>
<td>Reaction rate</td>
<td>kg/s or kg/(m³·s)</td>
</tr>
<tr>
<td>$r$</td>
<td>Radial positions</td>
<td>m</td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds number</td>
<td>-</td>
</tr>
<tr>
<td>$R_g$</td>
<td>Ideal gas constant</td>
<td>J/(mol·K)</td>
</tr>
<tr>
<td>$r_i$</td>
<td>Reaction rate of reaction $i$</td>
<td>mol/s</td>
</tr>
<tr>
<td>$S$</td>
<td>Source term of mass balance equation</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Sc</td>
<td>Schmidt number</td>
<td>-</td>
</tr>
<tr>
<td>Sh</td>
<td>Sherwood number</td>
<td>-</td>
</tr>
<tr>
<td>$S_m$</td>
<td>Source term of momentum equation</td>
<td>-</td>
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</tbody>
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XI
$T$ Temperature $K$
$t$ time $s$
$u$ Velocity $m/s$
$v$ The yield of products -
$V$ Volume fraction of volatile -
$V_p$ Volume of particle $m^3$
$X$ Conversion -
$Y$ Mass fraction -

Greek symbols

$\rho$ density $kg/m^3$
$\mu$ Viscosity $Pa.s$
$\beta$ Momentum exchange coefficient $kg/(m^3.s)$
$\delta$ Boundary layer thickness $m$
$\Delta H_{\text{evap}}$ Enthalpy of evaporation $kJ/kg$
$\varepsilon$ Voidage -
$\Gamma$ Torque arising from tangential components of contact force of particle $kg\cdot m^2/s^2$
$\eta$ The production ratio of CO/CO$_2$ -
$\phi$ Particle shrinkage -
$\lambda$ Thermal conductivity $W/(m\cdot K)$
$\theta$ Dimensionless temperature -
$\sigma$ Stefan-Boltzmann constant $J/(m^2\cdot K^4\cdot s)$
$\tau$ Viscous stress tensor -
$\tau_{dev}$ Devolatilization time $s$
$\omega$ Angular velocity $1/s$
$\xi$ Emissivity (0.85) -

Subscripts

$0$ Initial time
$a$ Ash
$\text{aver}$ Averaged parameter
$\text{bulk}$ Bulk gas
$B$ Biomass
$c$ Char
$DB$ Dry biomass
$\text{eff}$ Effective
$f$ Fluid/gas phase
$i$ Reaction or species $i$
$iso$ Isothermal model
$\text{Non-iso}$ Non-isothermal model
$p$ Particle phase
$pore$ Pore in the particle
$s$ Particle surface
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$w$</td>
<td>Wall</td>
</tr>
<tr>
<td>$Cor$</td>
<td>Corrected model</td>
</tr>
<tr>
<td>$UCM$</td>
<td>Uniform char conversion model</td>
</tr>
<tr>
<td>$PCM$</td>
<td>Progressive char conversion model</td>
</tr>
</tbody>
</table>
1 Introduction

In Denmark, the renewable energy share is over 40% of the total energy consumption, and 70% of renewable energy contributed by bioenergy in 2017 [2]. As a CO$_2$ neutral energy source [3–5], biomass can be utilized through thermochemical processes such as gasification, and combustion. Gasification is aimed to produce syngas gas, that can be further combusted or produce chemicals/liquid fuels, while combustion is aimed to produce heat and power. Biomass gasification and combustion can take place at fixed-bed reactors [6], fluidized bed reactors [7–9], and entrained flow reactors [10,11] (i.e. entrained flow gasifiers and pulverized combustors).

To support the optimization of these processes, Computation Fluid Dynamics (CFD) has been developed to describe biomass combustion and gasification. However, the following challenges are still faced in both particle-scale and reactor-scale:

- **Particle-scale model**: A number of comprehensive single particle biomass devolatilization models [12–20] and char conversion models [21–29] have been developed. However, most of the models were only validated under low temperature conditions (e.g. < 1273 K) that are relevant for fixed-bed and fluidized-bed reactors. Development and validation of single particle models that are applicable for a wide range of conditions, especially high-temperature conditions that are relevant for entrained flow gasification and pulverized biomass combustions, are limited. In addition, in the existing comprehensive char combustion models, the heterogeneous gasification reactions and the homogeneous reactions in the boundary layer are often ignored, due to the insignificant contribution of these reactions at low temperatures [30]. However, under high temperature conditions, it is expected that both the heterogeneous gasification reactions and the homogeneous reactions will become important during char conversion. Thus, it is needed to evaluate the impacts of those reactions at high temperature conditions relevant for entrained flow gasification and pulverized biomass combustions.

- **Reactor-scale**: CFD has been applied to simulate biomass combustion and gasification in fixed-bed [31], fluidized bed [9,32–34] and entrained flow reactors [35]. Due to a large number of particles in fluidized-bed and entrained flow reactors, the internal heat and mass transfer of biomass particles are neglected in current CFD modellings [7,35–46] to reduce computational cost. Since the biomass used in fluidized-bed and entrained-flow reactors are usually in millimetre-size range, the internal heat and mass transfer are therefore important for particle combustion and gasification. Therefore, a reliable and efficient approach to consider the effect of internal heat and mass transfer in CFD modelling of biomass combustion and gasification is required. In additional, biomass gasification is usually carried out in a dual-bed system (i.e. bubbling fluidized
bed (BFB) for gasification and fast fluidized bed (FFB) for char combustion), and one of the challenges of CFD modelling of a loop-system is to describe the hydrodynamics in the dual-bed with different flow regimes. Currently, a single drag model is used to simulate both a BFB and a FFB in most cases [9,32,33,47–49]. However, different flow regimes are required different drag models to achieve accurate simulation in the dual bed system. Therefore, it is essential to developing a hybrid drag model to simulate such a system.

1.1 Project objectives and content

The main objective of this project is to develop efficient and reliable models to simulate biomass combustion and gasification both in a particle-scale and a reactor-scale. The following topics are addressed:

- Developing and validating particle-scale models for biomass combustion and gasification. The particle-scale models focus on the heterogeneous processes, including the biomass devolatilization and char conversion. For the devolatilization model, it focuses on developing and validating a model that is applicable in a wide range of conditions, especially for high temperature conditions, and identifying the key factors that control the devolatilization process. For the char conversion, it focuses on developing a model describe the competing of heterogeneous relations (char oxidation and char gasification) and the effects of the homogeneous reactions in the particle boundary layer.
- Proposing a strategy to simplify the developed comprehensive particle model for biomass devolatilization and char conversion. With this strategy, the internal and external mass and heat transfer can be included in the simple particle models used in current CFD modelling.
- Developing a drag model to simulate a dual fluidized bed system for biomass gasification.

1.2 Thesis structure

There are eight chapters in this thesis, including the introduction as Chapter 1.

Chapter 2: a literature review for modelling biomass combustion and gasification

A comprehensive review of particle-scale modelling and CFD modelling of biomass combustion and gasification was presented. In the particle-scale modelling part, the drying model, devolatilization model, char conversion model as well as the kinetics of char conversions, and homogeneous reactions were discussed. In the CFD modelling part, CFD modelling of biomass gasification and combustion in fluidized bed reactors were focused.
Chapter 3: Comprehensive devolatilization model
This chapter focused on developing a comprehensive model for biomass devolatilization. The model was validated by single particle combustion experiment under high temperature conditions (1473-1723 K). The effects of gas temperature, particle size, particle density, and moisture content on biomass devolatilization were studied. The content of this chapter was accepted by the peer-reviewed journal of FUEL.

Chapter 4: Comprehensive char conversion model
This chapter focused on developing and validating a comprehensive char conversion model. Homogeneous reactions in the particle boundary layer, heterogeneous char oxidation and gasification reactions, particle shrinkage, internal and external mass and heat transfer are considered in the model. The model was validated by single particle combustion experiments under high temperature conditions (1473-1723 K) with different oxygen concentrations (0.0-10.5 vol%) and steam concentrations (25-42 vol%). The effects of gas temperature, oxygen and steam concentration on char conversion were studied. This chapter was written in manuscript form and the slightly revised version will be submitted to a peer-review journal.

Chapter 5: A heat transfer corrected isothermal model for biomass devolatilization
In this chapter, a heat transfer corrected isothermal model was developed to simulate the devolatilization of thermally-thick biomass particles. The model was developed by comparing the difference between the comprehensive biomass devolatilization model developed in Chapter 3 and a conventional isothermal model. The model was validated at particle-scale and implemented in a Eulerian multiphase flow model to simulate biomass devolatilization in a batch fluidized bed reactor. This chapter was written in manuscript form and the slightly revised version will be submitted to a peer-review journal.

Chapter 6: A mass transfer corrected uniform char conversion model
This chapter presented a mass transfer corrected uniform char conversion model developed by comparing the differences between a uniform char conversion and a progressive char conversion model. The mass transfer corrected uniform char conversion model was expected to be easily implemented in CFD modelling.

Chapter 7: CFD modelling a dual fluidized bed system for biomass combustion and gasification
A meso-scale drag model to simulate hydrodynamic behaviours in a dual fluidized bed system for biomass gasification was proposed in this chapter. The modelling results were validated by experimental data from a dual fluidized bed for biomass gasification. The effects of solid inventory on hydrodynamics behaviours were studied. The content of this chapter was published in the peer-reviewed journal of FUEL PROCESSING TECHNOLOGY as:

Chapter 8: conclusions and future work

The main conclusions and suggestions for future work were presented in this chapter.
2 Literature review

2.1 Particle scale model

As shown in Fig. 2.1, the biomass combustion and gasification process is divided into four stages: heating and drying, biomass devolatilization, char conversion, and homogeneous reactions (e.g. volatile combustion, etc.). Evaporation of moisture takes place usually at low temperatures (~373 K) during the heating and drying stages. Afterwards, the biomass devolatilization occurs typically in a temperature range of 600-800 K, producing volatile, tar, and char [7], and the tar is further converted to volatile and char by secondary pyrolysis. The char is consumed by heterogeneous reactions of char oxidation and gasification. The stage four is homogeneous reactions occurring from the stages of biomass devolatilization to the end of char conversion. The mathematical models for describing the four stages are discussed in the following sections.

![Fig. 2.1 Different stages of biomass combustion and gasification [42]](image)

2.1.1 Drying process

The drying process is endothermic, and the drying rate is mainly dependent on the heat transfer between particle and the surrounding gas and partially dependent on the mass transfer rate of H₂O from particle to the surrounding gas. The drying process can be described by different models, including the heat flux model [50], the equilibrium model [51], and the chemical kinetics model [52–54], which are introduced as below.

2.1.1.1 Heat flux model

The heat flux model assumes that the drying process is dominated by the heat transfer between the bulk gas and the particle, and the heat transfer from the bulk gas is equal to the evaporation enthalpy of the released moisture. Therefore, the model is introduced as Eq. (2.1) [50]. This model is independent of the physical properties of biomass particles, which has been employed in many references [50,52,55]. The limitation of the heat flux model is that it cannot predict the drying rate below the boiling point.
\[ R_{H_2O} = \begin{cases} \frac{Q}{\Delta H_{evap} V_p} & (T \geq T_{evap}) \\ 0 & (T < T_{evap}) \end{cases} \] (2.1)

Where \( Q \) denotes the heat transfer rate, J/s, \( \Delta H_{evap} \) is the evaporation enthalpy of moisture, J/kg, \( R_{H_2O} \) is the evaporation rate, kg/(m\(^3\)·s), \( V_p \) is particle volume, m\(^3\).

### 2.1.1.2 Equilibrium model

To determine the drying rate below the boiling point of water, an equilibrium model is introduced as shown in Eq. (2.2) [51]. In the model, the drying rate below the boiling point is determined by the mass transfer rate, while the rate above the boiling point is described by the heat balance. Therefore, the model can describe the drying process at any temperatures. Lu et al. [12] used this model to simulate the evaporation of free water from a biomass particle. Fatehi and Bai [52] also tested this model in biomass combustion, and compared it with the heat flux model and chemical kinetics model. They found that this model showed a better agreement with the experimental data [52].

\[ R_{H_2O} = \begin{cases} h_m A_p (\rho_{w, sat} - \rho_{g, w}) & (T_p < 373 \text{ K}) \\ \frac{Q}{\Delta H_{evap} V_p} & (T_p \geq 373 \text{ K}) \end{cases} \] (2.2)

Where \( A_p \) is the external particle surface area, m\(^2\), \( \rho_{w, sat} \) denotes the saturation vapour density calculated by Clausius–Clapeyron relation [52], and \( \rho_{g, w} \) is the density of H\(_2\)O in the bulk gas, \( h_m \) is the mass transfer coefficients, m/s.

### 2.1.1.3 Chemical kinetics model

Compared to the heat transfer model and the equilibrium model, the chemical reaction model describes the drying process as a first-order chemical reaction using an Arrhenius expression as shown in Eq. (2.3) [52–54]. This model is easy to implement in modelling and numerically stable, commonly adopted in single particle modelling [1,12,52,56]. However, the pre-exponential factor and activation energy are dependent on physical properties and operating conditions (e.g. heating rate) [52,57].

\[ R_{H_2O} = k_0 \rho_w \exp \left( -\frac{Ea}{R T_p} \right) \] (2.3)

Where \( k_0 \) and \( Ea \) are the pre-exponential factor and the activation energy, respectively, and \( T_p \) is particle temperature, K. According to Bryden et al.[58,59], \( k \) and \( Ea \) are $5.13 \times 10^{10}$ s\(^{-1}\) and 88 kJ/mol, respectively.
2.1.2 Devolatilization

Devolatilization is the primary decomposition of solid fuel into char, tar (has a high content of organic compounds), volatile (e.g. CO, CO₂, H₂, and CH₄, etc.), and water [7]. The volatile is a mixture of different gas species (e.g. CO, CO₂, CH₄, H₂O, C₂H₆, etc.). It is usually expressed globally as below:

\[
\text{Biomass} \rightarrow v_c \text{Char} + v_r \text{Tar} + v_g \text{Volatile}
\] (2.4)

To predict the rates and yields of the released species, the following kinetic models were developed [60]:

- Step-wise mechanism model
- The distributed activation energy model
- Chemical structure-based model

2.1.2.1 Step-wise mechanism model

The step-wise mechanism model is the most commonly used to describe the devolatilization of biomass. The model can be classified into three main groups [61]:

- One-step global model
- One-step multi-reactions model
- Two-stage semi-global model

One step global model

The one-step global model assumes that biomass directly converts to char and volatile as shown in Eq. (2.5).

\[
\text{Biomass} \xrightarrow{k} v_c \text{Char} + (1-v_c) \text{Volatile}
\] (2.5)

The devolatilization rate can be expressed as below:

\[
\frac{dX}{dt} = kf(X)
\] (2.6)

Where \( X \) is the conversion of biomass and \( f(X) \) is a function of \( X \), a typical expression is \( f(X) = (1-X) \). \( k \) is the rate constant, expressed as Arrhenius formula:

\[
k = k_0 \exp \left( -\frac{E_a}{R \cdot T_p} \right)
\] (2.7)

Where \( k_0 \) and \( E_a \) are the pre-exponential factor (1/s) and the activation energy (kJ/mol), respectively. These two parameters are fitted from experimental data, most of them obtained by TGA or DTG measurements [62–64]. The heating rate of TGA and DTG measurements is relatively low, compared to the operating conditions of fluidized bed reactors and pulverized fuel boilers (High heating rate, > 100 K/s). Table 2.1 shows the kinetics parameters of different biomass with different heating rates and particle sizes in the literature. The kinetic parameters
vary significantly since the biomass devolatilization is affected by chemical structures and physical properties of biomass particles as well as the operating conditions (e.g. heating rate, temperature, etc.), and particle properties (e.g. particle size, wood type, etc.). The one-step global model is simple and easy to implement in single particle model or CFD model. However, the yield of char and tar cannot be given [7]. Moreover, the experimental data at high temperatures (> 1273 K) conditions are rarely reported [35].

Table 2. A summary of kinetic parameters for one step global model

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Heating rate (K/s)a</th>
<th>Particle size (mm)</th>
<th>T(K)b</th>
<th>k0 (s⁻¹)</th>
<th>Ea (kJ/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine seed shells</td>
<td>5-20</td>
<td>&lt;0.3</td>
<td>&lt;1073</td>
<td>1.2×10¹¹</td>
<td>142.2</td>
<td>[62]</td>
</tr>
<tr>
<td>Wood chips</td>
<td>5-20</td>
<td>&lt;0.3</td>
<td>&lt;1073</td>
<td>1.2×10⁹</td>
<td>121.2</td>
<td>[62]</td>
</tr>
<tr>
<td>Olive husk</td>
<td>5-20</td>
<td>&lt;0.3</td>
<td>&lt;1073</td>
<td>1.4×10¹⁴</td>
<td>167.4</td>
<td>[62]</td>
</tr>
<tr>
<td>Almond Shell</td>
<td>0.08-1.67</td>
<td>0.91</td>
<td>573-1123</td>
<td>4.9×10⁹</td>
<td>92.8</td>
<td>[63]</td>
</tr>
<tr>
<td>Hazelnut shell</td>
<td>0.08-1.67</td>
<td>0.91</td>
<td>573-1123</td>
<td>4.8×10⁹</td>
<td>92.4</td>
<td>[63]</td>
</tr>
<tr>
<td>Beech Wood</td>
<td>0.08-1.67</td>
<td>0.91</td>
<td>573-1123</td>
<td>4.8×10¹²</td>
<td>123.0</td>
<td>[63]</td>
</tr>
<tr>
<td>Almond Shell</td>
<td>-</td>
<td>NA</td>
<td>733-833</td>
<td>5.8×10⁵</td>
<td>99.7</td>
<td>[65]</td>
</tr>
<tr>
<td>Wood</td>
<td>-</td>
<td>NA</td>
<td>321-720</td>
<td>1.0×10⁸</td>
<td>125.4</td>
<td>[61]</td>
</tr>
<tr>
<td>Corn cob</td>
<td>0.167-0.333</td>
<td>&lt;1</td>
<td>463-553</td>
<td>1.9×10⁶</td>
<td>75.0</td>
<td>[64]</td>
</tr>
<tr>
<td>Corn stalk</td>
<td>0.167-0.333</td>
<td>&lt;1</td>
<td>462-553</td>
<td>3.0×10⁹</td>
<td>107</td>
<td>[64]</td>
</tr>
<tr>
<td>Olive prunings</td>
<td>0.167-0.333</td>
<td>&lt;1</td>
<td>463-591</td>
<td>4.7×10⁸</td>
<td>101</td>
<td>[64]</td>
</tr>
<tr>
<td>Sunflower</td>
<td>0.167-0.333</td>
<td>&lt;1</td>
<td>477-648</td>
<td>2.4×10⁴</td>
<td>26.3</td>
<td>[64]</td>
</tr>
<tr>
<td>Sunflower</td>
<td>0.167-0.333</td>
<td>&lt;1</td>
<td>639-675</td>
<td>2.8×10²</td>
<td>25.7</td>
<td>[64]</td>
</tr>
<tr>
<td>Corn cob</td>
<td>High</td>
<td>&lt;1</td>
<td>563-1023</td>
<td>1.2×10¹¹</td>
<td>20.12</td>
<td>[64]</td>
</tr>
<tr>
<td>Corn stalk</td>
<td>High</td>
<td>&lt;1</td>
<td>533-1023</td>
<td>1.1×10⁵</td>
<td>62.0</td>
<td>[64]</td>
</tr>
<tr>
<td>Olive prunings</td>
<td>High</td>
<td>&lt;1</td>
<td>573-873</td>
<td>8.32</td>
<td>10.97</td>
<td>[64]</td>
</tr>
<tr>
<td>Sunflower</td>
<td>High</td>
<td>&lt;1</td>
<td>633-983</td>
<td>1.03×10³</td>
<td>73.81</td>
<td>[64]</td>
</tr>
<tr>
<td>Wood</td>
<td>-</td>
<td>&lt;1.5</td>
<td>500-673</td>
<td>7.0×10⁷</td>
<td>125.5</td>
<td>[66]</td>
</tr>
<tr>
<td>Wood</td>
<td>-</td>
<td>&lt;1.5</td>
<td>548-633</td>
<td>4.0×10¹⁷</td>
<td>234.4</td>
<td>[66]</td>
</tr>
<tr>
<td>Wood</td>
<td>-</td>
<td>&gt;10</td>
<td>500-558</td>
<td>1.2×10⁸</td>
<td>108.8</td>
<td>[66]</td>
</tr>
<tr>
<td>Wood</td>
<td>-</td>
<td>&gt;10</td>
<td>500-714</td>
<td>6.0-7.5×10⁸</td>
<td>125.5</td>
<td>[66]</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>High</td>
<td>&lt;0.1</td>
<td>290-900</td>
<td>1.05×10¹</td>
<td>31.65</td>
<td>[67]</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>High</td>
<td>&lt;0.1</td>
<td>290-900</td>
<td>6.8×10³</td>
<td>48.73</td>
<td>[67]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>High</td>
<td>&lt;0.1</td>
<td>290-900</td>
<td>1.19×10³</td>
<td>39.30</td>
<td>[67]</td>
</tr>
<tr>
<td>Cotton Stalk</td>
<td>High</td>
<td>&lt;0.1</td>
<td>290-900</td>
<td>2.44×10³</td>
<td>40.84</td>
<td>[67]</td>
</tr>
<tr>
<td>Wood</td>
<td>High</td>
<td>&lt;0.1</td>
<td>&lt;1667</td>
<td>1.89×10⁴</td>
<td>21.31</td>
<td>[35]</td>
</tr>
</tbody>
</table>

*a*The “High” heat rate means that the heating rate of biomass particle over 100 K/s

*b*The temperatures range measured in the experiments

One-step multi-reactions model

To describe the formation rate of tar and char, a one-step multi-reactions model has been developed [60]. In this model, biomass devolatilization is lumped to several parallel reactions as shown in Fig. 2. 2. The rate of biomass devolatilization can be described as Eq. (2.8).
Fig. 2. Kinetic schemes for the primary pyrolysis of biomass [60].

\[
\frac{dX}{dt} = (k_v + k_i + k_c) f(X)
\]  

(2.8)

Table 2.2 shows the kinetic parameters for one step multi-reaction models. Similar to the one-step global model, the kinetic parameters are affected by the biomass properties and experimental conditions. However, this model includes the release of tar, volatile, and char with their own rate during devolatilization, it can be used to describe the yield of tar and char. The model is still oversimplified when the secondary devolatilization of tar is important at high temperature conditions with long particle residence time [61].

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Particle size (mm)</th>
<th>Experimental system</th>
<th>Temperature (K)</th>
<th>Kinetic constants: ( k_0 ) (s(^{-1})), ( E_a ) (kJ/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>0.65</td>
<td>Tube furnace</td>
<td>573-673</td>
<td>( k_v = 1.43 \times 10^6 \exp(-88.6/RT) ) ( k_i = 4.12 \times 10^6 \exp(-112.7/RT) ) ( k_c = 7.4 \times 10^5 \exp(-106.5/RT) )</td>
<td>[68]</td>
</tr>
<tr>
<td>Almond Shells</td>
<td>0.3-0.5</td>
<td>Pyroprobe</td>
<td>733-878</td>
<td>( k_v = 1.521 \times 10^7 \exp(-139/RT) ) ( k_i = 5.851 \times 10^6 \exp(-119/RT) ) ( k_c = 2.981 \times 10^3 \exp(-73/RT) )</td>
<td>[69]</td>
</tr>
<tr>
<td>Almond Shells</td>
<td>0.3-0.5</td>
<td>Fluidized bed reactor</td>
<td>673-733</td>
<td>( k_v = 6.803 \times 10^8 \exp(-156/RT) ) ( k_i = 8.229 \times 10^6 \exp(-148/RT) ) ( k_c = 2.91 \times 10^2 \exp(-61/RT) )</td>
<td>[69]</td>
</tr>
<tr>
<td>Beech</td>
<td>&lt;0.08</td>
<td>Tube furnace</td>
<td>573-708</td>
<td>( k_v = 4.4 \times 10^8 \exp(-153/RT) ) ( k_i = 1.1 \times 10^10 \exp(-148/RT) ) ( k_c = 3.3 \times 10^6 \exp(-112/RT) )</td>
<td>[70]</td>
</tr>
</tbody>
</table>

Two-stage semi-global models

A two-stage semi-global model was proposed by Shafizadeh and Chin [71] to describe the secondary devolatilization of tar as shown in Fig. 2.3. As compared to the one-step global and one-step multi-reactions models, the secondary devolatilization of tar has been included in the model. The kinetics derived by Wagenaar et al. [72] with a modification of kinetics of secondary devolatilization of tar [73,74] was commonly used in single particle modelling [12,52]. The kinetic parameters are shown in Table 2.3.
Fig. 2.3 The two-stage semi-global kinetics scheme for the pyrolysis of biomass [71].

Table 2.3 The kinetics parameters of two-stage semi-global kinetics scheme for biomass devolatilization

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pre-exponential factor (s⁻¹)</th>
<th>Activation energy (kJ/kg)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_v$</td>
<td>$1.11 \times 10^{11}$</td>
<td>177</td>
<td>[72]</td>
</tr>
<tr>
<td>$k_i$</td>
<td>$9.29 \times 10^9$</td>
<td>149</td>
<td>[72]</td>
</tr>
<tr>
<td>$k_c$</td>
<td>$3.05 \times 10^7$</td>
<td>125</td>
<td>[72]</td>
</tr>
<tr>
<td>$k_{tv}$</td>
<td>$4.28 \times 10^6$</td>
<td>107.5</td>
<td>[74]</td>
</tr>
<tr>
<td>$k_{tc}$</td>
<td>$1.00 \times 10^5$</td>
<td>107.5</td>
<td>[73]</td>
</tr>
</tbody>
</table>

2.1.2.2 Distributed activation energy model

The distributed activation energy model (DAEM) was first proposed by Pitt [75] to describe the coal devolatilization. The model assumes that a series of parallel first-order reactions occurring during devolatilization, and the number of these reactions is large enough to describe the activation energy by a continuous distribution function [7]. For species $j$, the reaction rate is described as below:

$$\frac{dV_j}{dt} = \sum_i k_i (V_j^* - V_j)$$  \hspace{1cm} (2.9)

Where $V_j$ is the released mass fraction at time $t$ for species $j$ and $V_j^*$ is the total released mass fraction for species $j$. $k_i$ is the rate coefficient of reaction $i$ which is expressed as Eq. (2.10).

$$k_i = k_{i0} \exp\left(-\frac{Ea_i}{R_g T_p}\right)$$  \hspace{1cm} (2.10)

For a first-order reaction, the reaction rates coefficients of species $j$ are described by

$$k_j = \sum_i k_{i0} \exp\left(-\frac{Ea_i}{R_g T_p}\right)$$  \hspace{1cm} (2.11)

By integration of Eq.(2.11),

$$V_j = V_j^* \left(1 - \exp\left(\int \sum_i k_{i0} \exp\left(-\frac{Ea_i}{R_g T_p}\right) dt\right)\right)$$  \hspace{1cm} (2.12)
Eq. (2.12) is employed to describe the devolatilization rate of biomass. All pre-exponential factors, $k_{i0}$, and activation energies, $E_a$, are based on experimental data. Thus, too many parameters are required to fit from the experiment. To solve this issue, a continuous distribution function of the activation energy $f(E_a)$ with $f(E_a)dE_a$ representing the fraction of potential volatile loss with active energy should satisfy Eq. (2.13) and (2.14):

$$dV^* = V^* f(E_a)dE_a$$  \hspace{1cm} (2.13)

$$\int_{0}^{\infty} f(E_a)dE_a = 1$$  \hspace{1cm} (2.14)

Combining Eq. (2.12) and Eq. (2.13), the global conversion of biomass can be described by

$$V = V^* \left(1 - \int_{0}^{\infty} \exp\left(\sum_{i} k_{i0} \exp\left(-\frac{E_{ai}}{RT}\right) dt\right) f(E_a)dE_a\right)$$  \hspace{1cm} (2.15)

With the assumption of $k_{i0} = k_0$, which means all pre-exponential coefficients are equal, finally, the DAEM is written by

$$V = V^* \left(1 - \int_{0}^{\infty} \exp\left(\int_{0}^{t} k_{0} \exp\left(-\frac{E_{a}}{RT}\right) dt\right) f(E_a)dE_a\right)$$  \hspace{1cm} (2.16)

In this way, only $V^*$, $k_0$, and distribution function of $f(E_a)$ need to be fitted from the experimental data. The most often used distribution function $f(E_a)$ is Gaussian [76–80], as shown in Eq. (2.17). A number of studies have been done to improve the performance of the DAEM model [81–83]. These models showed good comparisons with experimental data of references [81–83]. Xiong et al. [84] also proposed a method to couple CFD and DAEM model.

$$f(E) = \frac{1}{\sigma \sqrt{2\pi}} \exp\left[-\frac{(E_a - \bar{E_a})^2}{2\sigma^2}\right]$$  \hspace{1cm} (2.17)

As compared to the step-wise mechanism model, the DAEM model is applicable to a wider range of operating conditions. The DAEM model can also be coupled with the chemical structure-based model, which is introduced in section 2.1.2.3. However, the DAEM model was rarely employed in single particle modelling, since it is more complicated. Moreover, the model is still semi-empirical with kinetic parameters highly influenced by the biomass chemical compositions [79].

2.1.2.3 Chemical structure-based model

The chemical composition of biomass is complex, and different chemical compounds have significant different devolatilization behaviours. As summarized in Johansen [85], there is a large variation in the macromolecular composition, i.e. the content of cellulose, hemicellulose, and lignin. This is one of the reasons which cause large variations of kinetic parameters when
using the step-wise mechanism model and the DAEM model for different biomass. To overcome the limitations, the chemical structure-based model was developed to predict the devolatilization process on the basis of the macromolecular composition [61,86–89]. As a lignocellulosic material, biomass is generally regarded as a mixture of cellulose, hemicellulose, and lignin, as shown in Eq. (2.18). The devolatilization rate is the sum of cellulose, hemicellulose, and lignin pyrolysis rates, the kinetic models of cellulose, hemicellulose, and lignin are described separately.

\[ \text{Biomass} \rightarrow \alpha \text{Cellulose} + \beta \text{Hemicellulose} + \gamma \text{lignin} \quad (2.18) \]

Where \( \alpha, \beta, \gamma \) represent the composition of each component in the lignocellulosic material, which can be determined by experiments.

The devolatilization rate of cellulose, hemicellulose, and lignin is described by the kinetics scheme shown in Fig. 2.4 [88]. It is assumed that the material components are firstly converted to active material and then decomposed to tar, char, and volatile. And finally, the tar is further decomposed to gas by second pyrolysis [90–93]. A commonly used kinetics model in the modelling are shown in Table 2.4 [88]. There are also have other kinetics models for the pyrolysis of those material components [94–97].

![Material components](image)

**Fig. 2.4 Global kinetic scheme for cellulose, hemicellulose, and lignin [88]**

**Table 2.4 A commonly used kinetics parameters of chemical-structure based model [88]**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( v ) for ( k_3 )</th>
<th>Pre-exponential factor (s(^{-1}))</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>2.80×10(^{19})</td>
<td>242.4</td>
<td></td>
</tr>
<tr>
<td>( k_2 )</td>
<td>3.28×10(^{14})</td>
<td>196.5</td>
<td></td>
</tr>
<tr>
<td>( k_3 )</td>
<td>0.35</td>
<td>1.30×10(^{10})</td>
<td>150.5</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>2.10×10(^{16})</td>
<td>186.7</td>
<td></td>
</tr>
<tr>
<td>( k_2 )</td>
<td>8.75×10(^{15})</td>
<td>202.4</td>
<td></td>
</tr>
<tr>
<td>( k_3 )</td>
<td>0.6</td>
<td>2.60×10(^{11})</td>
<td>145.7</td>
</tr>
<tr>
<td>Lignin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>9.60×10(^{8})</td>
<td>107.6</td>
<td></td>
</tr>
<tr>
<td>( k_2 )</td>
<td>1.50×10(^{9})</td>
<td>143.8</td>
<td></td>
</tr>
<tr>
<td>( k_3 )</td>
<td>0.75</td>
<td>7.70×10(^{6})</td>
<td>111.4</td>
</tr>
<tr>
<td>Tar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_4 )</td>
<td>4.28×10(^{6})</td>
<td>108.0</td>
<td></td>
</tr>
</tbody>
</table>
2.1.3 Char conversion

According to Fig. 2.1, char conversion process, mainly char oxidation, and char gasification with H₂O and CO₂, subsequently or meanwhile occurs with the biomass devolatilization. The single particle model for char conversion and reactivity of char are discussed below.

2.1.3.1 Char conversion model

Various models were developed to describe the char conversion process, including uniform char conversion model (UCM), shrinking char conversion model (SCM), progressive char conversion model (PCM). Those models are based on different assumptions summarized in Table 2.5.

The UCM model assumes that the reaction occurs throughout a char particle, and the concentration of gas species and temperature are uniformly throughout a char particle with an assumption of constant particle size. The internal mass and heat transfer are neglected. Therefore, the UCM model is a good approximation of kinetic controlled regime [98], a typical condition is small porous char converted at low temperature. The UCM model is possible used to describe the char conversion rate of a large particle by introducing an effectiveness factor to account for the mass transfer resistance inside the char particle [24,99,100]. It should be noted that the concept of effectiveness factor is derived to model catalytic reactions, which the physical properties (e.g. diameter, density, conductivity, pore size, etc.) of a particle can be considered as constant. However, those physical properties are changed during char conversion [21,22,25,28]. Therefore, a further modification is to couple with the particle size correlation derived from the SCM model [101]. However, it has been proved that the char gasification process does not obey the particle size correlation given by the SCM model [21]. Therefore, it is not suited to a case of a char conversion process dominated by gasification.

The shrinking core conversion model assumes that the char conversion rate is much faster than the mass transfer rate. Consequently, the char conversion only takes place in an infinitely thin layer at the external char particle surface. Therefore, the amount of gas species transferred from bulk gas to the particle is equal to the reaction rate of the char particle. The SCM model can be divided into different particle models: the shrinking core model with ash peel off (SCPM), and shrinking core model without ash peel off (SCRM). In the SCPM model, the char particle density keeps constant and ash peel off immediately once the char consumed. Therefore, the char particle size is described as \( d_p = d_{p0}(1-X_c)^{1/3} \) as shown in Table 2.5. The model is valid for relatively non-porous char [7]. The SCRM model assumes that the remained ash attaches at the external surface of char particle size is constant. Therefore, the density of char core is char particle density, and the ash layer is the density of ash, and the char core diameter is determined by \( d_c = d_{p0}(1-X_c)^{1/3} \). Owing to the existence of the ash layer, the resistance of mass transfer and
heat transfer grows with the increase of ash layer thickness, the overall conversion rate predicted by SCPM is smaller than that of SCRM. The shrinkage core conversion model may be a good approximation of char oxidation dominated process (e.g. char combustion etc.). However, the char CO\textsubscript{2} and H\textsubscript{2}O gasification rates are usually much slower than that of the char oxidation, the SCM model maybe not a good approximation [21].

If the kinetics of char reactions is comparable with the mass transfer rate, the char conversion occurs throughout the whole char particle. It can be handled with a progressive char conversion model (PCM) model [7,12,21,22,28,29,52]. Similar to the SCM model, the PCM model can be classified into the PCPM and PCRM model based on the treatments of the ash layer. PCM model considers the char oxidation and gasification occurs throughout the particle, both the internal and external mass and heat transfer are included. Therefore, the PCM model needs to solve the partial differential equations (mass balance, heat balance) to obtain the overall char conversion rate. Therefore, it is much more difficult to couple a PCM model with a CFD approach. Additionality, the computational cost dramatically increases with an increasing number of particles, it cannot be affordable to model large-scale reactor.
Table 2. 5 A summary of single char particle conversion model

<table>
<thead>
<tr>
<th>Model</th>
<th>Scheme</th>
<th>Features</th>
</tr>
</thead>
</table>
| UCM   | ![UCM Diagram] | - $X_c=X_c(t)$  
- $\rho_c=\rho_c(t)$  
- $d_p=d_{p0}$  
- $X_c=X_c$ |
| SCM   | ![SCM Diagram] | - Reaction at particle surface  
- Ash peels off  
- $d_p=d_{p0}(1-X_c)^{1/3}$  
- $\rho_c$ is constant |
| SCRM  | ![SCRM Diagram] | - Reaction at particle surface  
- Ash layer remains attached  
- $d_p=d_{p0}$  
- $d_p=d_{p0}(1-X_c)^{1/3}$  
- $\rho_c=\rho_c(X_c)$ |
| PCM   | ![PCM Diagram] | - Reaction throughout particle  
- Ash peels off  
- $d_p=d_p(X_c)$  
- $\rho_p=\rho_p(X_c)$  
- Extension of SUPM |
| PCPM  | ![PCPM Diagram] | - Reaction throughout particle  
- Ash layer remains attached  
- $d_p=d_{p0}$  
- $d_p=d_{p0}(X_c)$  
- $\rho_p=\rho_p(X_c)$  
- Extension of SUCM |
| PCRM  | ![PCRM Diagram] | - Reaction throughout particle  
- Ash layer remains attached  
- $d_p=d_{p0}$  
- $d_p=d_{p0}(X_c)$  
- $\rho_p=\rho_p(X_c)$  
- Extension of SUCM |

Since the above mentioned the model requires an input of chemical reaction kinetics, the kinetics of char oxidation and gasification will be discussed in section 2.1.3.2 briefly.

2.1.3.2 Kinetics for char conversion

Char oxidation kinetics

The heterogeneous char oxidation can be lumped as Eq. (2.19) [7,36,98,101–104]:

$$C + \frac{\eta + 2}{2\eta + 2} O_2 \rightarrow \frac{\eta}{\eta + 1} CO + \frac{1}{\eta + 1} CO_2$$  \hspace{1cm} (2.19)

Where $\eta$ is the ratio of produced CO to CO$_2$, which depends on the operating conditions (e.g. Temperature, O$_2$ concentration, etc.) as discussed in Morin et al. [105]. Fig. 2. 5 shows a
comparison of the CO/CO$_2$ ratio reported in the references [105–108]. The CO/CO$_2$ ratio given by Arthur [106] and Linjewile and Agarwal [108] are significantly different, and the CO/CO$_2$ ratio given by Morin et al. [105] and Tognotti et al. [107] are similar. The derivation of the expression probably caused by the experimental material. An artificial graphite coal char was used in the experiment of Arthur [106] and petroleum coke was used by Linjewile and Agarwal [108]. However, both Tognotti et al. [107] and Morin et al. [105] used biomass char as experimental material. The expression developed by Tognotti et al. [107] has been adopted to modelling biomass combustion and gasification in many references and validated in a wide temperature range (670–1670 K) [27,101,105,109–111].

![Fig. 2. 5 CO/CO$_2$ ratio according to Arthur [106], Tognotti et al.[107], Linjewile and Agarwal [108], and Morin et al. [105].](image)

Table 2. 6 summarizes the kinetics of biomass char oxidation, including both volume metric kinetics and the surface area based kinetics. The char oxidation kinetics assumed to be first-order in most of the studies. By plotting the kinetic rate constants in Fig. 2. 6, a large variation of kinetics rate constant was observed. The variation could be caused by experimental conditions, and different value of $n$, as well as different biomass char with significantly different inorganic content.
Table 2. An overview of char oxidation kinetics, including both volume metric kinetics and specific surface area-based kinetics.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>$k_0$ (bar$^{-a}$s$^{-1}$)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$n$</th>
<th>Temperature (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume metric kinetics, $R = k_0 \exp\left(-\frac{E_a}{RT}\right) P^n f(X)^a$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pine wood</td>
<td>$1.0 \times 10^9$</td>
<td>179.4</td>
<td>0.6</td>
<td>1173-1373</td>
<td>[25,112]</td>
</tr>
<tr>
<td>Sewage</td>
<td>$1.16 \times 10^4$</td>
<td>114.0</td>
<td>0.88</td>
<td>673-1173</td>
<td>[113]</td>
</tr>
<tr>
<td>Pine wood</td>
<td>$1.51 \times 10^6$</td>
<td>108.7</td>
<td>1.0</td>
<td>673-873</td>
<td>[114]</td>
</tr>
<tr>
<td>Olive husks</td>
<td>$1.22 \times 10^5$</td>
<td>83.5</td>
<td>1.0</td>
<td>673-873</td>
<td>[114]</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>$1.66 \times 10^4$</td>
<td>71.2</td>
<td>1.0</td>
<td>673-873</td>
<td>[114]</td>
</tr>
<tr>
<td>Grape residues</td>
<td>$6.44 \times 10^4$</td>
<td>78.0</td>
<td>1.0</td>
<td>673-873</td>
<td>[114]</td>
</tr>
<tr>
<td>Beech wood</td>
<td>$9.01 \times 10^5$</td>
<td>144.3</td>
<td>0.59</td>
<td>600-650</td>
<td>[105]</td>
</tr>
<tr>
<td>Douglas</td>
<td>$1.10 \times 10^6$</td>
<td>114.5</td>
<td>0.86</td>
<td>500-873</td>
<td>[115]</td>
</tr>
<tr>
<td>Straw</td>
<td>$1.31 \times 10^8$</td>
<td>134.0</td>
<td>1.0</td>
<td>973</td>
<td>[116]</td>
</tr>
<tr>
<td>Straw</td>
<td>$4.87 \times 10^6$</td>
<td>114.0</td>
<td>1.0</td>
<td>1173</td>
<td>[116]</td>
</tr>
<tr>
<td>Straw</td>
<td>$6.04 \times 10^5$</td>
<td>106.0</td>
<td>1.0</td>
<td>1273</td>
<td>[116]</td>
</tr>
<tr>
<td>Straw</td>
<td>$1.11 \times 10^4$</td>
<td>150.0</td>
<td>1.0</td>
<td>1473</td>
<td>[116]</td>
</tr>
<tr>
<td>Straw</td>
<td>$4.54 \times 10^9$</td>
<td>208.0</td>
<td>1.0</td>
<td>1673</td>
<td>[116]</td>
</tr>
<tr>
<td>Specific surface area based kinetics, $R = k_0 \exp\left(-\frac{E_a}{RT}\right) P^n S(X) f(X)^b$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pine wood</td>
<td>$1.715T$</td>
<td>74.8</td>
<td>1.0</td>
<td>-</td>
<td>[56,117–122]</td>
</tr>
<tr>
<td>Pine wood</td>
<td>$0.658T$</td>
<td>74.8</td>
<td>1.0</td>
<td>-</td>
<td>[22,52,123,124]</td>
</tr>
<tr>
<td>Wood</td>
<td>301.0</td>
<td>149.4</td>
<td>1.0</td>
<td>-</td>
<td>[125]</td>
</tr>
<tr>
<td>Wood</td>
<td>2.3</td>
<td>92.3</td>
<td>1.0</td>
<td>-</td>
<td>[126]</td>
</tr>
<tr>
<td>Wood</td>
<td>$1.04 \times 10^3$</td>
<td>93.1</td>
<td>1.0</td>
<td>-</td>
<td>[127]</td>
</tr>
<tr>
<td>Wood</td>
<td>0.39</td>
<td>47.5</td>
<td>0.29</td>
<td>1173-1473</td>
<td>[128]</td>
</tr>
<tr>
<td>Torrified wood</td>
<td>0.0037</td>
<td>60.0</td>
<td>0.8</td>
<td>1173-1473</td>
<td>[128]</td>
</tr>
<tr>
<td>Wood</td>
<td>$4.0 \times 10^3$</td>
<td>80.0</td>
<td>1.0</td>
<td>-</td>
<td>[31]</td>
</tr>
<tr>
<td>Wood</td>
<td>254</td>
<td>74.8</td>
<td>1.0</td>
<td>-</td>
<td>[129]</td>
</tr>
<tr>
<td>Pine wood</td>
<td>3.01</td>
<td>70.0</td>
<td>1.0</td>
<td>1023-1173</td>
<td>[130]</td>
</tr>
<tr>
<td>Oak</td>
<td>1.01</td>
<td>68.0</td>
<td>1.0</td>
<td>1023-1173</td>
<td>[130]</td>
</tr>
<tr>
<td>Eucalyptus</td>
<td>0.22</td>
<td>55.0</td>
<td>1.0</td>
<td>1023-1173</td>
<td>[130]</td>
</tr>
<tr>
<td>Almond shell</td>
<td>0.68</td>
<td>67.0</td>
<td>1.0</td>
<td>1023-1173</td>
<td>[130]</td>
</tr>
<tr>
<td>Olive stone</td>
<td>0.22</td>
<td>50.0</td>
<td>1.0</td>
<td>1023-1173</td>
<td>[130]</td>
</tr>
<tr>
<td>Wood</td>
<td>4.65</td>
<td>68.0</td>
<td>1.0</td>
<td>-</td>
<td>[131]</td>
</tr>
</tbody>
</table>

$^a$ The $f(X)$ describes the change of char reactivity along with the char conversion. The fitted functions can be found in the listed references.

$^b$ The specific area $S(X)$ depends on the fitted model, it can be found in the listed references.
**CO₂ gasification kinetics**

The CO₂ gasification can be lumped as Eq. (2.20). An overview of char CO₂ gasification kinetics is listed in Table 2.7. The $n^{th}$ order reaction is commonly used in both kinetics, the value is in range of 0-1.0. Similar to char oxidation kinetics, the kinetic rate constants ($k$) are significantly different as shown in Fig. 2.7 for both volume metric kinetics and specific area based kinetic.

\[
C + CO₂ \rightarrow 2CO
\]

(2.20)
An overview of char CO$_2$ gasification kinetics, including both volume metric kinetics and specific surface area based kinetics.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>$k_0$ (bar$^{-n}$s$^{-1}$)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$n$</th>
<th>Temperature (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volume metric kinetics, $R=k_0\exp(-Ea/RT)P^n f(X)^a$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Douglas fir</td>
<td>$2.59 \times 10^8$</td>
<td>200</td>
<td>0.6</td>
<td>973-1173</td>
<td>[132]</td>
</tr>
<tr>
<td>Cotton wood</td>
<td>$4.85 \times 10^7$</td>
<td>196</td>
<td>0.6</td>
<td>973-1173</td>
<td>[132]</td>
</tr>
<tr>
<td>Orujillo</td>
<td>$1.99 \times 10^3$</td>
<td>118.6</td>
<td>0.72</td>
<td>117</td>
<td>[133]</td>
</tr>
<tr>
<td>Wood</td>
<td>$2.08 \times 10^7$</td>
<td>221.0</td>
<td>0.44</td>
<td>-</td>
<td>[134]</td>
</tr>
<tr>
<td>Pine wood</td>
<td>$1.20 \times 10^8$</td>
<td>245.0</td>
<td>0.7</td>
<td>1173-1373</td>
<td>[25,112]</td>
</tr>
<tr>
<td>Sewage</td>
<td>$6.33 \times 10^4$</td>
<td>163.5</td>
<td>0.33</td>
<td>1073-1173</td>
<td>[22,135]</td>
</tr>
<tr>
<td>Pine</td>
<td>$4.47 \times 10^7$</td>
<td>238.0</td>
<td>0.475</td>
<td>1008-1158</td>
<td>[136]</td>
</tr>
<tr>
<td>Eucalyptus</td>
<td>$1.98 \times 10^7$</td>
<td>233.0</td>
<td>0.387</td>
<td>1008-1158</td>
<td>[136]</td>
</tr>
<tr>
<td>Bagasse</td>
<td>$3.15 \times 10^5$</td>
<td>198.0</td>
<td>1.0</td>
<td>1008-1158</td>
<td>[136]</td>
</tr>
<tr>
<td>Beech wood</td>
<td>$2.18 \times 10^5$</td>
<td>141.3</td>
<td>0.683</td>
<td>Up to 1673</td>
<td>[137]</td>
</tr>
<tr>
<td>Pine wood</td>
<td>$4.87 \times 10^6$</td>
<td>217.0</td>
<td>1.0</td>
<td>1000-1170</td>
<td>[138]</td>
</tr>
<tr>
<td>Sewage</td>
<td>$3.1 \times 10^5$</td>
<td>227.0</td>
<td>0.39</td>
<td>973-1173</td>
<td>[113]</td>
</tr>
<tr>
<td>Sawdust</td>
<td>$1.83 \times 10^6$</td>
<td>159.0</td>
<td>0.5</td>
<td>1123</td>
<td>[139]</td>
</tr>
<tr>
<td>Straw</td>
<td>$7.9 \times 10^4$</td>
<td>132.0</td>
<td>0.34</td>
<td>1123</td>
<td>[139]</td>
</tr>
<tr>
<td>Wood</td>
<td>$1.12 \times 10^8$</td>
<td>245.0</td>
<td>0.31</td>
<td>-</td>
<td>[140]</td>
</tr>
<tr>
<td>Pinus densiflora</td>
<td>$1.5 \times 10^4$</td>
<td>172.0</td>
<td>1.0</td>
<td>1123-1323</td>
<td>[141]</td>
</tr>
<tr>
<td><strong>Specific surface area based kinetics, $R=k_0\exp(-Ea/RT)P^n S(X)f(X)^b$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood</td>
<td>$1.07 \times 10^2$</td>
<td>93.9</td>
<td>0.22</td>
<td>1073-1273</td>
<td>[142]</td>
</tr>
<tr>
<td>Wheat</td>
<td>0.01</td>
<td>155.9</td>
<td>1.0</td>
<td>1023-1173</td>
<td>[100]</td>
</tr>
<tr>
<td>Beech wood</td>
<td>$1.56 \times 10^3$</td>
<td>202.19</td>
<td>1.0</td>
<td>1023-1173</td>
<td>[143]</td>
</tr>
<tr>
<td>Pine wood</td>
<td>$3.427^c$</td>
<td>129.7</td>
<td>1.0</td>
<td>-</td>
<td>[52,56,117,119-123,127,129]</td>
</tr>
<tr>
<td>Wood</td>
<td>$6.51 \times 10^3$</td>
<td>217.0</td>
<td>1.0</td>
<td>-</td>
<td>[144]</td>
</tr>
<tr>
<td>Wood</td>
<td>589</td>
<td>222.8</td>
<td>1.0</td>
<td>-</td>
<td>[126]</td>
</tr>
<tr>
<td>Wood</td>
<td>4363</td>
<td>248.12</td>
<td>1.0</td>
<td>-</td>
<td>[26,145]</td>
</tr>
<tr>
<td>Pine wood</td>
<td>148</td>
<td>125.0</td>
<td>1.0</td>
<td>1000-1170</td>
<td>[138]</td>
</tr>
<tr>
<td>Pinus</td>
<td>250</td>
<td>134.0</td>
<td>1.0</td>
<td>1123-1323</td>
<td>[141]</td>
</tr>
<tr>
<td>Pine sawdust</td>
<td>34.9</td>
<td>100.6</td>
<td>1.0</td>
<td>1173-1373</td>
<td>[146]</td>
</tr>
</tbody>
</table>

---

*a The $f(X)$ describes the change of char reactivity along with the char conversion. The fitted functions can be found in the listed references.

*b The specific area $S(X)$ depends on the fitted model, it can be found in the listed references.

**H$_2$O gasification kinetics**

The H$_2$O gasification is commonly lumped as a global reaction as shown in Eq. (2.21). Table 2. 8 shows an overview of char H$_2$O gasification kinetics reported in the references. Similar to char oxidation and CO$_2$ gasification, the kinetics rate constant ($k$) of H$_2$O gasification shown in
Fig. 2. 8 is significantly different. The reaction order of H2O is in a range of 0-1.0 in both volume metric and specific gasification kinetics.

\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2
\]  

(2.21)

Table 2. 8 An overview of char H2O gasification kinetics, including both volume metric kinetics and specific surface area based kinetics.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>(k_0) (bar(^a)s(^{-1}))</th>
<th>(Ea) (kJ/mol)</th>
<th>(n)</th>
<th>Temperature(K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volume metric kinetics, (R=k_0\exp(-Ea/RT))</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pine wood</td>
<td>(3.55 \times 10^5)</td>
<td>170.0</td>
<td>0.8</td>
<td>1173-1373</td>
<td>[25,112]</td>
</tr>
<tr>
<td>Beech wood</td>
<td>(2.54 \times 10^5)</td>
<td>132.1</td>
<td>1.0</td>
<td>Up to 1673</td>
<td>[137]</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>(3.90 \times 10^5)</td>
<td>171.0</td>
<td>0.33</td>
<td>1073-1173</td>
<td>[22,135]</td>
</tr>
<tr>
<td>Birch wood</td>
<td>(2.62 \times 10^8)</td>
<td>237.0</td>
<td>0.57</td>
<td>1023-1173</td>
<td>[147,148]</td>
</tr>
<tr>
<td>Beech wood</td>
<td>(1.71 \times 10^7)</td>
<td>211.0</td>
<td>0.51</td>
<td>1023-1173</td>
<td>[147]</td>
</tr>
<tr>
<td>Wood</td>
<td>(1.79 \times 10^3)</td>
<td>138.0</td>
<td>1.0</td>
<td>-</td>
<td>[147]</td>
</tr>
<tr>
<td>Wood</td>
<td>(1.23 \times 10^7)</td>
<td>198.0</td>
<td>0.75</td>
<td>-</td>
<td>[147]</td>
</tr>
<tr>
<td>Sewage</td>
<td>(1.09 \times 10^6)</td>
<td>193.0</td>
<td>0.3</td>
<td>973-1173</td>
<td>[113]</td>
</tr>
<tr>
<td>Wood</td>
<td>(2.07 \times 10^7)</td>
<td>220.0</td>
<td>0.73</td>
<td>-</td>
<td>[140]</td>
</tr>
<tr>
<td><strong>Specific surface area based kinetics, (R=k_0\exp(-Ea/RT))</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood</td>
<td>(4.78 \times 10^2)</td>
<td>136.0</td>
<td>0.22</td>
<td>1173-1573</td>
<td>[142]</td>
</tr>
<tr>
<td>Pine wood char</td>
<td>(3.427)</td>
<td>129.7</td>
<td>1.0</td>
<td>-</td>
<td>[52,56,117,119– 123,127,129]</td>
</tr>
<tr>
<td>Wood</td>
<td>(4.48 \times 10^4)</td>
<td>217.0</td>
<td>1.0</td>
<td>-</td>
<td>[144]</td>
</tr>
<tr>
<td>Wood</td>
<td>589</td>
<td>222.8</td>
<td>1.0</td>
<td>-</td>
<td>[126]</td>
</tr>
<tr>
<td>Wood</td>
<td>29</td>
<td>175.84</td>
<td>1.0</td>
<td>-</td>
<td>[26]</td>
</tr>
<tr>
<td>Wood</td>
<td>(3.56 \times 10^4)</td>
<td>155.0</td>
<td>1.0</td>
<td>1073-1573</td>
<td>[149]</td>
</tr>
<tr>
<td>Straw</td>
<td>(3.37 \times 10^6)</td>
<td>222.0</td>
<td>1.0</td>
<td>1073-1573</td>
<td>[149]</td>
</tr>
<tr>
<td>Wood</td>
<td>(7.37 \times 10^3)</td>
<td>138.0</td>
<td>1.0</td>
<td>-</td>
<td>[131]</td>
</tr>
</tbody>
</table>

\(a\) The \(f(X)\) describes the change of char reactivity along with the char conversion. The fitted functions can be found in the listed references.

\(b\) The specific area \(S(X)\) depends on the fitted model, it can be found in the listed references.

Fig. 2. 8 A plot of char oxidation kinetics, references listed in Table 2. 8
As mentioned in the above sections, there is a large variation of the reported kinetic rate constant for char oxidation and char gasification with CO₂ and H₂O. The reason is that the measured kinetic is not intrinsic kinetics, which depends on the material and operating conditions. For example, organic contents, sodium, potassium, calcium, and magnesium has been proved to increase the char reactivity and while the silicon has proved to inhabit the char reactivity [7,150–154]. However, the inorganic content in biomass material is significantly different [155]. The influence of inorganic content on char reactivity was rarely studied by a quantitative approach. Besides the effects of the inorganic contents, the fitted function f(X) and S(X) was presented by different models and reaction order assumed by different authors is also different as shown in Table 2. 6-Table 2. 8, which is also resulting in a significant difference of current kinetic models. The physical properties (e.g. particle size, particle density) used by different authors are also diffident, resulting in a significantly different influence degree of intra-particle heat and mass transfer. Since there is a large variation of char oxidation and gasification kinetics, the selected kinetics of char oxidation and conversion in single particle modelling should have similar experimental conditions.

2.1.4 Homogeneous reactions

The homogeneous reactions during biomass combustion are mainly involved with volatile combustion. The composition of volatile produced by devolatilization is generally based on empirical correlations, and only serval important species (e.g. CO, H₂O, CH₄, O₂, H₂, CO₂, C₂H₆, etc.) are considered in terms of simplification [36,103,127,156–162]. Consequently, the homogeneous reactions commonly lumped into a few reactions in both single particle modelling and CFD modelling. Reactions (2.22)-(2.25) are the primary homogeneous reactions used in current simulations.

\[
\begin{align*}
\text{CO} + 0.5\text{O}_2 & \rightarrow \text{CO}_2 \quad (2.22) \\
\text{H}_2 + 0.5\text{O}_2 & \rightarrow \text{H}_2\text{O} \quad (2.23) \\
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (2.24) \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2 + \text{CO}_2 \quad (2.25)
\end{align*}
\]

2.2 CFD modelling biomass combustion and gasification in fluidized bed

The CFD modelling approaches for biomass combustion and gasification in fluidized beds (FB) are classified into different categories based on how the particles and fluid are described, including Direct Numerical Simulation (DNS), Eulerian-Lagrangian (E-L) method, and Eulerian-Eulerian (E-E) approach. Among the three simulation methods, DNS is the most accurate method which directly solves the Naiver-stokes equation without additional
constitutive relation. However, it requires the finest mesh (1/100 to 1/10 of particle size). Consequently, the computational cost is the highest and it is not unaffordable to simulate large-scale fluidized bed reactors for biomass gasification. Thus, the detailed description of this model is not included in this literature review. The E-L and E-E approach has been used to simulate both laboratory-scale to pilot-scale reactors. Both models will be described in the following section.

### 2.2.1 Governing equations

#### 2.2.1.1 E-L method

In the E-L method, the motion of individual particles is tracked, and the fluid is considered as a continuous phase solved by the Eulerian method. In terms of calculating interactions between the particles, two methods: Discrete Element Method (DEM) and Direct Simulation Monte Carlo (DSMC) has been implemented in the E-L method. As compared with the DSMC method, DEM can describe the collision and rotation of individual particles. Therefore, it has been widely used to simulate the gas-solid system [163–172]. The governing equations of DEM based E-L method are listed as below [42]:

Continuous equation of fluid phase:

\[
\frac{\partial (\varepsilon_f \rho_f u_f)}{\partial t} + \nabla \cdot (\varepsilon_f \rho_f u_f) = S_f
\]  

Momentum equation of fluid phase:

\[
\frac{\partial (\varepsilon_f \rho_f u_f)}{\partial t} + \nabla \cdot (\varepsilon_f \rho_f u_f u_f) = -\varepsilon_f \nabla p - \beta (u_f - u_g) - \nabla (\varepsilon_f \tau_f) + \varepsilon_f \rho_f g + S_{mf} \]  

(2.26) (2.27)

Where \( \varepsilon_f \) is the voidage of fluid, \( \rho_f \) is the gas density, kg/m\(^3\), \( u \) is the velocity, m/s, \( P \) is the pressure, Pa, \( S_f \) and \( S_{mf} \) is the source term for continuous equation and momentum equation, respectively. \( \beta \) is the momentum exchange coefficient, kg/(m\(^3\)·s), \( \tau_f \) is the viscous stress tensor, and \( g \) is the gravity acceleration, m/s\(^2\).

The stress-strain tensor can be expressed as follows:

\[
\tau_f = \mu_f \left[ \nabla u_f + (\nabla u_f)^T \right] - \frac{2}{3} \mu_f \nabla \cdot u_f
\]  

(2.28)

The viscosity of bulk gas is expressed as below:

\[
\mu = \mu_{lam} + \mu_t
\]  

(2.29)

Where \( \mu_{lam} \) is laminar viscosity, Pa·s, and \( \mu_t \) is turbulent viscosity, Pa·s, which is determined by the turbulence model.

Species transport equation of fluid phase:
\[
\frac{\partial \left( \kappa_j \rho_j Y_{j,i} \right)}{\partial t} + \left( \nabla \cdot \kappa_j \rho_j \mathbf{u}_j Y_{j,i} \right) = -\nabla \cdot \left( \kappa_j \rho_j \mathbf{D}_j \nabla Y_{j,i} \right) + S_{f,i} \quad (2.30)
\]

Where \( S_{f,i} \) is the source term, kg/(m\(^3\)·s), the diffusion coefficient is expressed as:

\[
D_j = \frac{\mu_j}{\rho_j Sc} \quad (2.31)
\]

Here \( Sc \) is the Schmidt number.

Energy transport equations:

\[
\frac{\partial \left( \kappa_j \rho_j C_p T_j \right)}{\partial t} + \left( \nabla \cdot \kappa_j \rho_j C_p \mathbf{u}_j T_j \right) = \nabla \cdot \left( \kappa_j \lambda_j \nabla T_j \right) + Q_{pf} + Q_R + S_{q,i} \quad (2.32)
\]

Where \( T_j \) is the fluid temperature, K, \( C_{pf} \) is the fluid capacity, J/(kg·K), \( \lambda_j \) is the fluid thermal conductivity, W/(m·K). \( Q_{pf} \) is the heat transfer due to fluid convection, J/(m\(^3\)·s), \( Q_R \) is the heat source due to chemical reactions, J/(m\(^3\)·s), and \( S_{q,i} \) is the heat transported by a mass source of \( S_{f,i} \) in Eq. (2.32). J/(m\(^3\)·s).

The motion of each individual particle is governed by Newton’s second law and angular momentum

\[
\frac{du_i}{dt} = -\frac{\nabla p_i}{\rho_p} + g + \frac{F_{d,i}}{m_p} + F_{e,i} \quad (2.33)
\]

\[
i_i \frac{d\omega_i}{dt} = \Gamma_i \quad (2.34)
\]

Where \( m_i \) is the mass of the particle, kg, and \( F_{e,i} \) is the collision force between the particle and its neighbors as well as the wall, \( N, I_i, m_i, \omega_i \) are the moment of inertia, linear velocity, and angular velocity, \( \Gamma_i \) is the torque arising from tangential components of contact force of particle \( i \), respectively.

Heat balance for the individual particle, \( i \), described by a zero-dimensional model:

\[
\rho_i C_{p,i} \frac{dT_i}{dt} = Q_{pf,i} + Q_{pp,i} + Q_{R,i} + Q_{rad,i} \quad (2.35)
\]

Where \( Q_{pf} \), \( Q_{pp} \), \( Q_R \), \( Q_{rad} \) represent heat transfer between gas and particle, heat transfer between particle and particle, heat from heterogeneous chemical reactions, and radiative heat transfer, J/(m\(^3\)·s).

### 2.2.1.2 E-E Approaches

E-E approaches consider both the solid and fluid phases as interpenetrating mixtures with the continuum theory. Each phase is described by conservation laws. The computational cost of E-E approaches mainly depends on how many meshes used in the simulation, instead of the number of particles. Therefore, it has a lower computational cost, as compared to the E-L approaches. E-E approaches have been used to simulate large-scale fluidized bed reactors by
using a coarse grid [173–180]. The model can be extended to the multi-fluid model by adding governing equations to describe the additional phases. Here, the two-fluid model (TFM) is introduced as an example. The governing equations of the gas phase are the same as the E-L method, which are shown in section 2.2.1.1, the governing equations of the solid phase are shown as follows [181]:

Continuous equation of the solid phase:

\[
\frac{\partial (\varepsilon_p \rho_p u_p)}{\partial t} + \nabla \cdot (\varepsilon_p \rho_p u_p) = S_p
\]  
(2.36)

Momentum equation of the solid phase:

\[
\frac{\partial (\varepsilon_p \rho_p u_p)}{\partial t} + \nabla \cdot (\varepsilon_p \rho_p u_p) = -\varepsilon_p \nabla p - \nabla p_p + \beta (u_f - u_p) - \nabla (\varepsilon_p \tau_p) + \varepsilon_p \rho_p g_p + S_{mp}
\]  
(2.37)

Species transport equation of the solid phase:

\[
\frac{\partial (\varepsilon_p \rho_p Y_{p,i})}{\partial t} + \nabla \cdot (\varepsilon_p \rho_p u_p Y_{p,i}) = -\nabla \cdot (\varepsilon_p \rho_p D_p \nabla Y_{p,i}) + S_{p,i}
\]  
(2.38)

Energy transport equations of the solid phase:

\[
\frac{\partial (\varepsilon_p \rho_p C_{pp} T_p)}{\partial t} + \nabla \cdot (\varepsilon_p \rho_p C_{pp} u_p T_p) = \nabla \cdot (\varepsilon_p \lambda_p \nabla T_p) + Q_{pf} + Q_{rad} + Q_{rg}
\]  
(2.39)

By utilizing Newton’s viscosity law, the stress-strain tensor of the solid phase is expressed as follows:

\[
\tau_p = \mu_p \left[ \nabla u_p + (\nabla u_p)^T + \frac{2}{3} \mu_p \right] \nabla \cdot u_p
\]  
(2.40)

As can be seen from Eq. (2.37) and Eq.(2.40), the concept of solid pressure \(P_p\) and solid viscosity \(\mu_p\) are defined. However, unlike the gas-phase, the viscosity of the solid phase is not a measurable physical variable, it is a concept borrowed from the kinetic theory of gas [182]. Therefore, constitutive relations are required for Eq. (2.37) and Eq. (2.40). The kinetic theory of granular flow (KTGF) has been widely employed to simulate gas-solid systems, with its derivation and formulation given in reference [181].

### 2.2.1.3 Sub-models for E-E and E-L approaches

In the governing equations of E-L and E-E approaches contain sub-models of different source terms, including momentum exchange \(\beta (u_f - u_p)\), source terms of heat balance equation \(Q_{pf}, Q_R, Q_{rad}\) and momentum balance equations \(S_{mp}\), source terms of mass balance equation \(S_f, S_p\) and species transport equations \(S_{s,i}, S_{s,f}\).
**Particle-scale model**

In order to use the E-L and E-E approaches to simulate biomass combustion and gasification, a particle-scale model for biomass combustion and gasification, including drying, devolatilization, and char conversion should be included in the source terms of the momentum balance equation, energy balance equation, mass balance equations, and species transport equations. A zero-dimensional model is commonly used in CFD modelling [37,39,44,45,183–186] to reduce computational cost. The zero-dimensional model is a good approximation for small particles, which the intra-particle mass and heat transfer are negligible. However, for particles with significant internal mass and heat transfer resistance, a more comprehensive model is required (e.g. one dimensional model for biomass devolatilization [117,187–193]). The comprehensive model usually discretizes a biomass particle radially with a large number of grid points (e.g. 50), which results in significant computational demand in CFD modelling [188,193]. It is time-consuming when a comprehensive particle-scale model (e.g. comprehensive biomass devolatilization model [193], progressive char conversion model [7], etc.) is coupled with E-L and E-E approaches. Therefore, it is desirable to develop a model to bridge the comprehensive particle-scale model and CFD approaches.

**Momentum exchange**

The momentum exchange between fluid and solid, \( \beta(u_f - u_p) \), is usually referred to as drag model. It has been reported that a drag model influences significantly the CFD simulation results [176,194–198]. Table 2.9 summarizes the commonly used drag models. The Syamlal-O’Brien drag model [199] has been validated in the simulations of bubbling and turbulent fluidized bed [37]. However, it did not properly simulate a fast fluidized bed [200]. The Wen and Yu drag model [201] is a homogeneous drag model that can be used to simulate dilute systems. The Gidaspow drag model has been widely used in CFD modelling fluidized bed systems. However, it is sensitive to the grid size. To obtain grid-independent results, it was recommended that the grid size should be smaller than 20 times of particle size for Group B particles and 10 time of particle size for Group A particles [202]. Therefore, the Gidaspow drag model is time consuming when it is used to simulate large-scale fluidized beds. The Huilin-Gidaspow drag model is a modification of the Gidaspow drag model, which made a smooth transition between the Wen and Yu drag model and the Ergun drag model. However, it is still sensitive to the grid size used in the CFD simulations.

To develop a grid-independent model, the effects of heterogeneous structure on the momentum exchange between gas and solid have been studied extensively [174,195,196,203–207]. Igci et al. [196,208] introduced a filtered two-fluid model that extracts constitutive models through highly resolved simulations of TFM model in a periodic domain, and applied the model to simulate bubbling fluidized beds or circulating fluidized beds [196,207,209]. A similar method was also used to develop a filtered drag model for the E-L approach [197,210]. However, for
the filtered drag models obtained from CFD simulation of a periodic domain with specific physical properties of fluid and particle, the coefficients may need an update for new conditions by following the procedure of Igci et al. [196,208]. Wang and Li [195] proposed an energy minimum multi-scale (EMMS) method, which is based on the heterogeneous structure (e.g. cluster caused by particle agglomeration) in a fluidized bed, to develop an EMMS/matrix drag model. The theoretical based EMMS drag model is applicable in different operating conditions. The EMMS/matrix model was further modified by Lu et al. [174] with grid-independent results when the grid size is 100 times of the particle size. The EMMS/matrix drag model has been evaluated in different processes, such as fluidized-bed catalytic cracking reactors [211–213], and methanol to olefins fluidized bed reactors [214–216]. The model was extended to model bubbling fluidized beds by Shi et al. [217] and later by Hong et al. [205] and Luo et al. [206]. The developed EMMS/bubbling model has been validated for coarse grid simulations of bubbling and turbulent fluidized beds [206].

Each individual particle is tracked in the E-L approach. Therefore, the momentum exchange between particle and particle can be described by collision force between the particle and its neighbours. However, for the E-E approaches, the momentum exchange between solid and solid phase are commonly described by the Syamlal drag model [218].
Table 2.9 A summary of the commonly used drag models and its applications

<table>
<thead>
<tr>
<th>Ref</th>
<th>Formulations</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syamlal-O’Brien [199]</td>
<td>$\beta = \frac{3\varepsilon \rho_f \nu_f}{4\nu_f^2 \gamma D u_f - u_p}$</td>
<td>Bubbling fluidized bed and turbulent fluidized bed</td>
</tr>
<tr>
<td></td>
<td>$C_D = \left[ 0.63 + \frac{4.8}{\sqrt{Re/v_f}} \right]^2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$v_f = 0.5 \left[ A - 0.06 Re + \sqrt{(0.06 Re)^2 + 0.12 Re (2B - A) + A^2} \right]$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A = \varepsilon_s^{1.14}$, $B = \begin{cases} 0.8\varepsilon_s^{1.28} \quad (\varepsilon_s \leq 0.85) \ \varepsilon_s^{2.66} \quad (\varepsilon_s &gt; 0.85) \end{cases}$</td>
<td></td>
</tr>
<tr>
<td>Wen and Yu [201]</td>
<td>$\beta = \frac{3}{4} C_D \frac{\varepsilon_f \rho_f \nu_f}{\gamma D u_f - u_p} \varepsilon_f^{2.65}$</td>
<td>Dilute gas-solid systems</td>
</tr>
<tr>
<td></td>
<td>$C_D = \frac{24}{\varepsilon_f Re} \left[ 1 + 0.15 (\varepsilon_f Re)^{0.67} \right]$</td>
<td>(Re &lt; 1000)</td>
</tr>
<tr>
<td></td>
<td>$C_D = 0.44$</td>
<td>(Re ≥ 1000)</td>
</tr>
<tr>
<td>Gidaspow [219]</td>
<td>$\beta = \frac{3}{4} C_D \frac{\varepsilon_f \rho_f \nu_f}{\gamma D u_f - u_p} \varepsilon_f^{2.65}$</td>
<td>Bubbling and fast fluidization</td>
</tr>
<tr>
<td></td>
<td>$\left[ 150 \frac{\varepsilon_f \mu_f}{\varepsilon_f \gamma D u_f} + \frac{1.75\varepsilon_f \rho_f}{\gamma D u_f} \right] \varepsilon_f &gt; 0.8$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_D = \frac{24}{\varepsilon_f Re} \left[ 1 + 0.15 (\varepsilon_f Re)^{0.67} \right]$</td>
<td></td>
</tr>
<tr>
<td>Huilin-Gidaspow [220]</td>
<td>$\beta = \frac{3}{4} \phi_f C_D \frac{\varepsilon_f \rho_f \nu_f}{\gamma D u_f - u_p} \varepsilon_f^{2.65}$</td>
<td>Bubbling and fast fluidization</td>
</tr>
<tr>
<td></td>
<td>$\left[ 150 \frac{\varepsilon_f \mu_f}{\varepsilon_f \gamma D u_f} + \frac{1.75\varepsilon_f \rho_f}{\gamma D u_f} \right]$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\phi_f = \arctan \left[ 150 \times 1.75 \left( 0.2 - \varepsilon_f \right) \right] + 0.5$</td>
<td></td>
</tr>
<tr>
<td>EMMS/matrix [174,195]</td>
<td>$\beta = \frac{3}{4} C_D \frac{\varepsilon_f \rho_f \nu_f}{\gamma D u_f - u_p} \varepsilon_f^{2.65} H_D$</td>
<td>Fast fluidization, accounting the effects of meso-scale structure of cluster.</td>
</tr>
<tr>
<td></td>
<td>$H_D = f \left( Re, \varepsilon_f \right)$</td>
<td></td>
</tr>
<tr>
<td>EMMS/bubbling [205,217]</td>
<td>$\beta = \frac{3}{4} C_D \frac{\varepsilon_f \rho_f \nu_f}{\gamma D u_f - u_p} \varepsilon_f^{2.65} H_D$</td>
<td>Bubbling and turbulent fluidization, accounting the effects of meso-scale structure of bubble.</td>
</tr>
<tr>
<td></td>
<td>$H_D = f \left( \varepsilon_f \right)$</td>
<td></td>
</tr>
<tr>
<td>Filtered model [207]</td>
<td>$\beta = \frac{3}{4} C_D \frac{\varepsilon_f \rho_f \nu_f}{\gamma D u_f - u_p} \varepsilon_f^{2.65} H_D$</td>
<td>Bubbling and fast fluidization. Accounting the effects of grid size on CFD simulations</td>
</tr>
<tr>
<td></td>
<td>$H_D = f \left( u_f - u_p, \varepsilon_f \right)$</td>
<td></td>
</tr>
<tr>
<td>Syamlal [218]</td>
<td>$\beta = \frac{3(1+c_0)}{2} \left{ \frac{\pi}{2} + C_{x,y} \pi^2 / 8 \right} \varepsilon_f \rho_f \nu_f \left( d_i + d_p \right)^2 \varepsilon_{ku} \left</td>
<td>u_f - u_p \right</td>
</tr>
</tbody>
</table>
Heat transfer

The heat transfer includes convective heat transfer, radiative heat transfer, and conductive heat transfer.

(1) Convective heat transfer

The convective heat transfer describes the heat exchange between the particle and the surrounding through the following formulation:

\[ Q_{pf} = h_{pf} A_p (T_f - T_p) \] (2.41)

Where \( h_{pf} \) is the convective heat transfer coefficient (W/(m²·K)), which can be determined by Eq. (2.42)

\[ h_{pf} = \frac{6 \lambda_f \varepsilon_f \varepsilon_p Nu}{d_p^2} \] (2.42)

Where \( d_p \) is the diameter of the particle, \( m \), \( Nu \) is the Nusselt number. Nusselt number is usually determined from empirical formulations. The Ranz and Marshall equation [221], which was developed to describe the heat transfer between a single particle and its surrounding flow, is commonly used in both E-E and E-L approaches [164,187–189,222,223]. The expression is given in Eq. (2.43)

\[ Nu = 2.0 + 0.6 Re^{0.4} Pr^{0.33} \] (2.43)

Where \( Re \) is Reynolds numbers, \( Re = \rho d_p |u_f - u_p|/\mu_f \), \( Pr \) is Prandtl number, \( Pr = \mu C_p / \lambda_f \). Since the Ranz and Marshall equation is developed from single particle experiments, it may underestimate the heat transfer between the particle and the surrounding fluid in a fluidized bed, where the collision and agglomeration of particles have significant effects on the heat transfer. To solve this issue, Gunn [224] developed a convective heat transfer model based on fixed-bed experiments and extended its application in fluidized bed reactors. The model is applicable in a wide range of voidage (0.35–1.0) and Reynolds number (up to \( 10^5 \)). The model is commonly used in E-E approaches [39,44,45,184–186,225,226]

\[ Nu = \left( 7 - 10 \varepsilon_f + 5 \varepsilon_f^2 \right) \left( 1 + 0.7 Re^{0.2} Pr^{0.33} \right) + \left( 1.33 - 2.40 \varepsilon_f + 1.2 \varepsilon_f^2 \right) Re^{0.7} Pr^{0.33} \] (2.44)

(2) Conductive heat transfer

The conductive heat transfer between solid and solid particle is usually neglected in the E-E approaches, due to the limitation of the model. The conductive heat transfer can be implemented in the E-L method, where the conductive heat transfer model developed by Zhou et al. [227] is commonly used.

(3) Radiative heat transfer
The radiative heat transfer is expected to have significant effects (contributing 25-45% of total heat transfer) on the biomass combustion and gasification at high temperatures [7]. The radiative heat transfer is commonly described by Stefan-Boltzmann Law. The expression is given in Eq. (2.45)

\[ Q_{rad} = \xi \sigma A_p \left( T_f^4 - T_p^4 \right) \]  

(2.45)

**Mass transfer**

The mass transfer between a particle and the surrounding fluid influences significantly on the biomass combustion and gasification, especially the char conversion [7]. Similar to the convective heat transfer model [221,228], the Ranz and Marshall equation, which was developed based on a single particle, can be also used to describe the mass transfer:

\[ Sh = 2 + 0.6 \text{Re}^{0.5} \text{Sc}^{1/3} \]  

(2.46)

To consider the interaction between particle and particle, Gunn [224] proposed Eq. (2.47) to describe the mass transfer between the fluid and the solid phase in fixed bed and fluidized bed reactors. Other similar expressions are also available in references [229,230].

\[ Sh = \left( 7 - 10 \varepsilon_f + 5 \varepsilon_f^2 \right) \left( 1 + 0.7 \text{Re}^{0.2} \text{Sc}^{0.33} \right) \]

\[ + \left( 1.33 - 2.40 \varepsilon_f + 1.2 \varepsilon_f^2 \right) \text{Re}^{0.7} \text{Sc}^{0.33} \]  

(2.47)

The above equations did not consider the effects of heterogeneous structure on the mass transfer, Dong et al. [230] attempted to develop a structure-dependent mass transfer model to consider the effect of clusters or bubbles. In their model, the gas-solid flow in a fluidized bed is simplified as a dense phase (solid-rich phase) and a dilute phase (gas-rich phase), with the mass transfer rate described for the two phases. The model was verified in modelling ozone decomposition in a fluidized bed [231]. Liu et al. [232] further modified this model which includes the mass transfer between the dilute phase and the dense phase. However, such kinds of the model have not been validated in modelling biomass combustion and gasification in fluidized bed reactors.

### 2.2.2 CFD modelling of biomass combustion and gasification in fluidized beds

#### 2.2.2.1 E-L method

With the rapid development of computer technologies, the E-L approaches have been widely employed in modelling of fluidized bed biomass combustor (FBBC) and fluidized bed biomass gasifier (FBBG) in the recent 10 years. Table 2.10 summarizes the CFD simulation of FBBC and FBBG by using E-L methods. The discussion of Table 2.10 is listed as below:

1. Turbulence model: As compared to other turbulence models, the k-ε model is the simplest and least computation demanded model and it can provide reasonable simulation results [112,170,172,233,234]. Large-eddy simulation (LES) is also employed to describe gas phase
turbulence in MP-PIC (Multiphase particle-in-cell) method which is a coarse grain E-L method [8,171]

(2) Drying process: Six studies have included the drying process in the simulation [8,112,171,172,222,235]. In references [172,222], a heat flux model was used to describe the drying process. Gao et al. [112] employed an equilibrium model to simulate the drying process during biomass gasification. Liu et al. [8,171] used a kinetic model to describe such processes. All three models seem to give reasonable results when compared to measured outlet gas compositions.

(3) Biomass devolatilization: A zero-dimensional model with one-step global mechanism is commonly used to model biomass devolatilization regarding to reducing computational time. The internal mass and heat transfer of a biomass particle is neglected.

(4) Char conversion: Both UCM and SCM models are used to simulate char conversion [21,28]. The progressive char conversion model is rarely used in the E-L approaches due to the heavy computational cost. Therefore, the internal mass and heat transfer of a char particle is neglected in the simulation.

(5) Homogeneous reactions: The homogeneous reactions are commonly presented by CO, H₂, and CH₄ oxidation and water-gas shift reaction [41,235–240], with lumped global reactions kinetics.

(6) Drag model: The most commonly used drag models are the Wen-Yu and the Gidaspow drag models. For fine-grid simulation for laboratory-scale fluidized bed reactor, the Gidaspow, and the Wen and Yu drag model can give reasonable predictions [8,171]. However, for the coarse-grid simulations (e.g. MP-PIC in Barracuda®), the modelling results are sensitive to the choice of drag models [198,241,242]. Kraft et al.[198] compared four drag models in the simulation of an 8 MW dual fluidized bed system for biomass gasification. They found that the EMMS drag model gave the best prediction of pressure and distribution of bed materials, while the Gidapow drag model gave the best prediction of the solid circulation rate.

(7) Heat transfer: Some of the models include all three heat transfer mechanisms (convective, radiative, conductive heat transfer), while some of them only include one or two mechanisms. The Ranz and Marshall Equation [221] is the most commonly used to describe the convective heat transfer. The Stefan-Boltzmann Law is the most commonly used to describe the radiative heat transfer.

(8) Mass transfer: Similar to heat transfer, the Ranz and Marshall Equation[221] is the commonly used method to describe convective mass transfer. However, other models are also available [224,229,243].

(9) Model validation: Various experimental data (e.g. outlet gaseous composition, temperature profiles, particle diameter, etc.) are used to evaluate the E-L models. However, there is no comprehensive validation with both solid distribution and gas species distribution. The
simulation results are only compared to the experimental outlet composition in most of the cases. However, the outlet composition is not enough to reveal both reaction behaviour and hydrodynamic behaviour.

(10) Computational cost: Most of the reported simulations are two-dimensional (2D) or three-dimensional (3D) simulation of laboratory-scale fluidized beds. A few simulations have been achieved for pilot-scale FBBG by using Barracuda® [8,171]. To the author’s knowledge, no 3D simulation of industrial-scale FBBC and FBBG was carried out by E-L method. Ku et al. [168], simulated a laboratory-scale FBBG, which took 14 days to simulate 20s real physical time. Liu et al. [8] achieved simulation of a pilot-scale FBBG by using Barracuda Virtual Reactor®. However, it still needs 4-5 days to simulate one case. Therefore, the E-L method is computational intensive in modelling biomass combustion and gasification in fluidized beds even coupled with a zero-dimensional model (e.g. UCM, SCM, etc.) [244]. A longer simulation time is required when the E-L method is coupled with a comprehensive particle-scale model.
<p>|
|---|---|---|---|---|---|---|
| <strong>Ref</strong> | <strong>Software</strong> | <strong>Particle size (mm)</strong> | <strong>Turbulence model</strong> | <strong>Drying</strong> | <strong>Devolatilization</strong> | <strong>Char conversion</strong> | <strong>Homogeneous reactions</strong> |
| Rong et al.,[164] | Code | 1 | - | - | - | UCM | CO combustion NOx formation CH4 reactions |
| Sofialidis et al.[233] | Fluent | 0.25 | (k-\varepsilon) | - | One step global | UCM | CO combustion NOx formation CH4 reactions |
| Liu et al.[223] | - | 1.5 | - | - | - | SCM | Chaudhry et al.[245] |
| Geng et al.[165] | FORTRAN | 0.5-3.0 | - | - | - | SCM | CO combustion |
| Ku et al.[170] | OpenFOAM | 0.2-0.75 | (k-\varepsilon) | - | One step global | SCM | CO, CH4 reactions |
| Liu et al. [171],[8] | Baracuda | 5.7 | (k-\varepsilon) | Kinetic | One step global | UCM | CO, H2, CH4, C2H6, C3H4 combustion CO, H2 reactions |
| Wiese et al.[172] | Fluent, DEM | Pellet | (k-\varepsilon) | Heat flux | One step global | SCM | CO, H2 reactions |
| Mahmoudi et al.[222] | XDEM | 12 | - | Heat flux | One step global | - | - |
| Zhuang et al. [246] | - | 0.45-1 | - | - | - | SCM | CO, CH4 gasification and combustion CO, H2, CH4, Tar combustion, NOx and SOx formation CO, H2 reactions |
| Zhong et al.[183] | - | 0.56 sand 2.3 biomass | LES | - | One step global | UCM | CO, H2, CH4 reactions |
| Gerber et al.[235] | - | 1, 1.5 coal-char 4 wood | LES | Heat flux | One step global | Hagge et al. [247] | CO, H2, CH4 reactions |
| Oevermann et al.[41] | - | 3 coal-char 4 wood | LES | - | One step global | SCM | CO, H2, CH4 reactions |
| El-Sayed and Noseir [236] | Fluent | ~ 3 | (k-\varepsilon) | - | One step global | UCM | CO, H2, CH4 reactions |
| Xie et al. [237] | Code | 0.3-0.45 | LES | - | One step global | UCM | CO, H2, CH4, C3H4 reactions |
| Stephan et al.[238,239] | Baracuda | 0-24 biomass 0.5-2 sand | - | Kinetic | One step global | UCM | CO, H2, CH4 reactions |</p>
<table>
<thead>
<tr>
<th>Ref</th>
<th>Drag model</th>
<th>Heat transfer model</th>
<th>Mass Transfer model</th>
<th>Validation</th>
<th>Scale</th>
<th>Computational time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yang et al. [240]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Kinetic</td>
<td>One step global</td>
<td>CO, H₂, CH₄</td>
</tr>
</tbody>
</table>

Continued Table 2.10 A summarizes of CFD simulation of FBBG and FBBC by using E-L method

<table>
<thead>
<tr>
<th>Ref</th>
<th>Drag model</th>
<th>Heat transfer model</th>
<th>Mass Transfer model</th>
<th>Validation</th>
<th>Scale</th>
<th>Computational time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sofialidis et al.[233]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Outlet composition</td>
<td>3D-Lab</td>
<td></td>
</tr>
<tr>
<td>Geng et al.[165]</td>
<td>Di Felice</td>
<td>Zhou et al. [227]</td>
<td>Fabrizio Scala [243]</td>
<td>Particle diameter</td>
<td>2D-Lab</td>
<td>0.6 h for 1s</td>
</tr>
<tr>
<td>Ku et al.[170]</td>
<td>Gidaspow</td>
<td>-</td>
<td>Constant diffusion</td>
<td>Outlet composition</td>
<td>3D-Lab</td>
<td>14 days for 20 s</td>
</tr>
<tr>
<td>Liu et al. [8,171]</td>
<td>Wen-Yu, Gidaspow</td>
<td>-</td>
<td>-</td>
<td>Outlet composition</td>
<td>3D-Pio</td>
<td>120 h</td>
</tr>
<tr>
<td>Wiese et al. [172]</td>
<td>Wen-Yu</td>
<td>Wiese et al. [172]</td>
<td>Wiese et al. [172]</td>
<td>Outlet concentration</td>
<td>3D-Lab</td>
<td>-</td>
</tr>
<tr>
<td>Mahmoudi et al.[222]</td>
<td>-</td>
<td>Ranz and Marshall</td>
<td>Ranz and Marshall</td>
<td>Single particle pyrolysis</td>
<td>3D-Lab</td>
<td>-</td>
</tr>
<tr>
<td>Zhuang et al. [246]</td>
<td>Gidaspow</td>
<td>-</td>
<td>La Nauze et al. [229]</td>
<td>-</td>
<td>2D-Lab</td>
<td>-</td>
</tr>
<tr>
<td>Zhong et al.[183]</td>
<td>Wen-Yu &amp; Ergun</td>
<td>-</td>
<td>-</td>
<td>Outlet composition</td>
<td>3D-Lab</td>
<td>-</td>
</tr>
<tr>
<td>Gerber et al.[235]</td>
<td>-</td>
<td>Zhou et al. [249]</td>
<td>-</td>
<td>-</td>
<td>2D-Lab</td>
<td>-</td>
</tr>
<tr>
<td>Oevermann et al.[41]</td>
<td>Oevermann et al.[41]</td>
<td>Stefan–Boltzmann Law (Q₉₆)</td>
<td>-</td>
<td>Outlet composition</td>
<td>2D-Lab</td>
<td>10 s day</td>
</tr>
<tr>
<td>Authors</td>
<td>Non-Spherical Drag Model</td>
<td>Transport Model</td>
<td>Temperature Coefficient</td>
<td>Outlet Composition</td>
<td>Reaction Time</td>
<td></td>
</tr>
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</tr>
<tr>
<td>El-Sayed and Noseir [236]</td>
<td>Non-spherical drag model</td>
<td>P-N model ($Q_{rad}$)</td>
<td>Stefan–Boltzmann Law ($Q_{rad}$)</td>
<td>Temperature dependent</td>
<td>Outlet composition</td>
<td></td>
</tr>
<tr>
<td>Xie et al. [237]</td>
<td>Wen-Yu</td>
<td>-</td>
<td>-</td>
<td>Carbon conversion</td>
<td>3D-Lab</td>
<td></td>
</tr>
<tr>
<td>Stephan et al. [238,239]</td>
<td>Wen-Yu &amp; Ergun</td>
<td>Ranz and Marshall ($Q_{pf}$)</td>
<td>Stefan–Boltzmann Law ($Q_{rad}$)</td>
<td>-</td>
<td>3D-Lab /3D-Pio</td>
<td></td>
</tr>
<tr>
<td>Yang et al. [240]</td>
<td>Gidaspow</td>
<td>Gunn ($Q_{pf}$), Batchelor and O'Brien [250] ($Q_{pf}$), Stefan–Boltzmann Law ($Q_{rad}$)</td>
<td>Outlet composition</td>
<td>3D-Lab</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.5 h for 1s</td>
<td></td>
</tr>
</tbody>
</table>
2.2.2.2 E-E approach

As compared to the E-L method, the E-E approach requires less computational resources, and it is widely employed to simulate multiphase flow systems. Table 2.11 summarizes the application of modelling FBBC and FBBG, including the turbulence model, kinetic model, momentum exchange, heat transfer, mass transfer, coupling method between CFD model and reactions model, model validation, and computational cost. More details are discussed below.

(1) Turbulence model: Similar to E-L method, \( k-\varepsilon \) is also the most favourable model used to describe turbulence behaviour in E-E approaches, due to its low computational cost.

(2) Drying model: The heat flux model [36,251] and the equilibrium model [38,252] have been used to model the drying process. However, the kinetic model is not implemented in the cases listed in Table 2.11.

(3) Devolatilization: Unlike the E-L approaches, besides the one-step global model, one-step multi-reactions model, two-stage semi-global model, chemical structure-based model, and even a comprehensive chemistry scheme was adopted in E-E approaches. Ranganathan and Gu [225] evaluated different kinetic scheme for fast pyrolysis of biomass, they found that the results predicted from a comprehensive chemistry scheme [253] are more reasonable, as compared to one-step global model [13] and chemical structure-based model [89]. The latter two models underestimated the char yield and overestimated volatile and tar yield [225]. However, the comprehensive chemistry scheme resulting in a significant increase in computational cost. By using a comprehensive devolatilization model developed by Mellin et al. [254], a 2D simulation of pilot-scale fluidized bed took 2 months, implying that it is unaffordable to use the model to simulate a 3D large-scale fluidized reactor with current computation capacity.

In CFD simulations, zero-dimensional models are commonly used to describe the biomass devolatilization [39,44,45,87,126,184–186,252,254–257], because it is simple and low computational cost. The model considers the particle having a uniform temperature. Therefore, it is only reasonable for particles with a small Biot number (e.g. \( \text{Bi} < 1 \)) [7,14]. Papadikis et al. [187–189] developed a 1D devolatilization model to describe the intra-particle heat transfer in the CFD model. The model discretized a biomass particle radially in a large number of grid points (e.g. 50), which results in significantly computational demand in CFD [188].

(4) Char conversion: A UCM model is commonly used to describe char conversion process. The intra-particle heat and mass transfer are neglected in the model. Moreover, due to the limitation of the E-E method, the biomass particle is assumed to be a constant particle size in most of the case. Only a few studies considered the particle shrinkage in the modelling [36,252] Nikolopoulos et al. [36] adopted a shrinking core approximation to predict the particle size, and a similar method also was adopted by Ismail et al. [252]. In their models, the particle density is
assumed to be constant. However, it is not a reasonable assumption for char gasification under fluidized conditions [21,28].

(5) Homogeneous reactions: Like the E-L method, the homogeneous reactions described in E-E method are mainly involved with CO, CH₄, H₂, CO₂, O₂, and H₂O, since they are the main components of volatile and products of char conversion.

(6) Drag model: The Gidaspow and Syamlal-O’Brien drag models are the commonly used drag models for describing the momentum exchange between gas and solid. Syamlal et al. [218] drag model is usually adopted to describe the momentum exchange between solid and solid. The simulation results are sensitive to the choice of drag model [39]. Xiong et al. [39] performed CFD modelling of biomass pyrolysis in a fluidized bed by using different drag models. Their results show that the choice of the drag model significantly influences the product yields. The Gidaspow drag model underestimated the tar yield but overestimated the gas and char yield. The Syamlal-O’Brien drag model underestimated the tar and char yield and overestimated the gas yield. The EMMS drag model predicted the most reasonable results. Moreover, there is also evidence showing that the EMMS model has weak grid dependency. Therefore, it is possible to employ the EMMS drag model to simulate FBBC and FBBG with a low computational cost [174]. Moreover, the drag model has the most significant effects on modelling results, as compared to the heat transfer and mass transfer model [39].

(7) Heat transfer model: Similar to the E-E method, the model proposed by Gunn [224] is the most common model used to describe the convective heat exchange between gas and solid phase. The conductive heat transfer between particle and particle is usually neglected, due to the limitation of the E-E method. It has been reported that the heat transfer model has less influence on the modelling of biomass devolatilization, as compared to the drag model [39].

(8) Mass transfer model: The mass transfer part is described by the so-called Ranz and Marshal model in most of the cases. It has been reported that the mass transfer model has less influence on the modelling of biomass devolatilization, as compared to the drag model [39].

(9) Model validation: Similar to E-L method, various experimental data (e.g. outlet gaseous composition, temperature profiles, particle diameter, etc.) are used to evaluate the E-E approaches, but most of the cases only compared the outlet composition with the simulation results. There is a lack of comprehensive validation with both hydrodynamics and reactive behaviours.

(10) Computational cost: Most of the simulations reported in the references are two-dimensional (2D) or three-dimensional (3D) simulation of laboratory-scale fluidized beds. A few simulations have been achieved for pilot-scale FBBG. The computational cost increases sharply with the increase of reaction and species. For example, 10 months are required to simulate a 3D pilot-scale fluidized with 27 reactions, while it can be reduced to 2 months with 5 reactions [36].
Table 2.11 A summary of E-E approaches modelling of FBBC and FBBG.

<table>
<thead>
<tr>
<th>Ref</th>
<th>Code/software</th>
<th>Particle size (mm)</th>
<th>Turbulence model</th>
<th>Drying</th>
<th>Devolatilization</th>
<th>Char conversion</th>
<th>Homogeneous reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Didwania and Cattolica [255]</td>
<td>MFIX</td>
<td>0.334</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Didwania and Cattolica [255]</td>
<td>MFIX</td>
<td>0.425</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Wang et al.[43]</td>
<td>Fluent</td>
<td>0.62</td>
<td>k- Larson-Ericksen</td>
<td>-</td>
<td>One step multi-reaction</td>
<td>UCM</td>
<td>CO, CH₄, and H₂ reactions</td>
</tr>
<tr>
<td>Papadikis et al. [187–189]</td>
<td>Fluent</td>
<td>0.5</td>
<td>-</td>
<td></td>
<td>Two-stage semi-global</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Papadikis et al. [187–189]</td>
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<td>0.44</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gerber et al. [127,160]</td>
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<td>3</td>
<td></td>
<td>-</td>
<td>Two-stage semi-global</td>
<td>SCM</td>
<td>CO, CH₄, H₂ reactions</td>
</tr>
<tr>
<td>Xue et al. [88]</td>
<td>MFIX</td>
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<td></td>
<td>-</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>k- Larson-Ericksen</td>
<td>-</td>
<td>One step multi-reaction</td>
<td>UCM</td>
<td>CO, CH₄, H₂ reactions</td>
</tr>
<tr>
<td>Cornejo and Far [46]</td>
<td>Fluent</td>
<td>0.62</td>
<td>k- Larson-Ericksen</td>
<td>-</td>
<td>One step global</td>
<td>UCM</td>
<td>CO, CH₄, H₂ reactions</td>
</tr>
<tr>
<td>Kurz et al. [251]</td>
<td>AIOLOS</td>
<td>20</td>
<td>k- Larson-Ericksen</td>
<td>Heat flux</td>
<td>One step global</td>
<td>UCM</td>
<td>CO, C₃H₄, H₂ combustion</td>
</tr>
<tr>
<td>Xue et al. [87,126]</td>
<td>MFIX</td>
<td>0.2-0.9</td>
<td></td>
<td>-</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>Figueroa et al. [259]</td>
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<td>0.25</td>
<td></td>
<td>-</td>
<td>Two-stage semi-global</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Couto et al. [260]</td>
<td>Fluent</td>
<td>-</td>
<td>k- Larson-Ericksen</td>
<td>-</td>
<td></td>
<td>UCM</td>
<td>CO, CH₄, H₂ reactions</td>
</tr>
<tr>
<td>Xiong et al. [39,184–186]</td>
<td>MFIX</td>
<td>0.25</td>
<td></td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Melin et al. [261]</td>
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<td>0.7-1.0</td>
<td></td>
<td>-</td>
<td>Two-stage semi-global</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Nikolopoulos et al. [36]</td>
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<td>k- Larson-Ericksen</td>
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<td>One step global</td>
<td>UCM</td>
<td>Nox emissions</td>
</tr>
<tr>
<td>Chen et al. [226]</td>
<td>K-FIX</td>
<td>1.5/2.0</td>
<td></td>
<td>-</td>
<td></td>
<td>UCM</td>
<td>CO, CH₄, H₂ reactions</td>
</tr>
<tr>
<td>Author et al.</td>
<td>Code</td>
<td>k-ε</td>
<td>Equilibrium</td>
<td>Model</td>
<td>UCM</td>
<td>Reactions</td>
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</tr>
<tr>
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<td>RNG</td>
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<td>UCM</td>
<td>CO, CH₄, H₂, C₂H₄ reactions</td>
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<tr>
<td>Mellin et al. [254,256,257]</td>
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<td>0.3,0.85</td>
<td>-</td>
<td>Comprehensive chemistry scheme</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ismail et al. [252]</td>
<td>COMMENT-Code</td>
<td>-</td>
<td>k-ε</td>
<td>Equilibrium</td>
<td>One step global model</td>
<td>UCM</td>
<td>CO, CH₄, H₂ reactions</td>
</tr>
<tr>
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<td>0.3</td>
<td>-</td>
<td>One step global</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Chen et al. [264]</td>
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<td>k-ε</td>
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<td>One step global</td>
<td>UCM</td>
<td>CO, CH₄, H₂ reactions</td>
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<td>-</td>
<td>Two-stage semi-global</td>
<td>-</td>
<td>-</td>
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<td>Ranganathan and Gu [225]</td>
<td>Fluent</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>Different models</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lu et al. [38]</td>
<td>COMMENT-Code</td>
<td>1-2</td>
<td>k-ε</td>
<td>Equilibrium</td>
<td>One step global</td>
<td>UCM</td>
<td>CO, CH₄, H₂ reactions. NOₓ and SOₓ emissions</td>
</tr>
<tr>
<td>Yan et al. [33]</td>
<td>Fluent</td>
<td>2.5</td>
<td>k-ε</td>
<td>-</td>
<td>-</td>
<td>UCM</td>
<td>CO, CH₄, H₂ reactions.</td>
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</table>
Table 2.11 A summarize of E-E approaches modelling of FBBC and FBBG.

<table>
<thead>
<tr>
<th>Ref</th>
<th>Drag model</th>
<th>Heat transfer model</th>
<th>Mass Transfer model</th>
<th>Validation</th>
<th>Scale</th>
<th>Simulation time</th>
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<tbody>
<tr>
<td>Didwania and Cattolica [255]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Outlet composition</td>
<td>2D-Pio</td>
<td>-</td>
</tr>
<tr>
<td>Wang et al. [43]</td>
<td>Gidaspow</td>
<td>Gunn</td>
<td>Ranz and Marshal</td>
<td>Outlet composition</td>
<td>3D-Lab</td>
<td>-</td>
</tr>
<tr>
<td>Papadikis et al. [187–189]</td>
<td>Gidaspow</td>
<td>Ranz and Marshal and Kuipers et al. [265]</td>
<td>-</td>
<td>Outlet composition</td>
<td>3D-Lab</td>
<td>-</td>
</tr>
<tr>
<td>Gerber et al. [127,160]</td>
<td>Wen and Yu</td>
<td>-</td>
<td>Ranz and Marshal</td>
<td>Outlet composition</td>
<td>2D-Lab</td>
<td>Serval days</td>
</tr>
<tr>
<td>Xue et al. [88]</td>
<td>Syamlal-O’Brien</td>
<td>Syamlal and Gidaspow [266]</td>
<td>-</td>
<td>Outlet composition</td>
<td>2D-Lab</td>
<td>-</td>
</tr>
<tr>
<td>Armstrong et al. [44,45]</td>
<td>Gidaspow</td>
<td>Gunn</td>
<td>Ranz and Marshal</td>
<td>Outlet composition</td>
<td>2D-Lab</td>
<td>-</td>
</tr>
<tr>
<td>Cornejo and Far [46]</td>
<td>Wen and Yu</td>
<td>Gunn</td>
<td>Temperature dependent coefficient</td>
<td>Outlet composition</td>
<td>3D-Lab</td>
<td>2 Days</td>
</tr>
<tr>
<td>Kurz et al. [251]</td>
<td>Eurgens’</td>
<td>Wakao and Kagei</td>
<td>Ranz and Marshal</td>
<td>Outlet composition</td>
<td>3D-Lab</td>
<td>2 h, steady simulation profiles</td>
</tr>
<tr>
<td>Xue et al. [87,126]</td>
<td>Syamlal-O’Brien</td>
<td>Gunn</td>
<td>-</td>
<td>Products Yield</td>
<td>2D-Lab</td>
<td>-</td>
</tr>
<tr>
<td>Boateng and Mtui [258]</td>
<td>Gidaspow</td>
<td>Gunn</td>
<td>-</td>
<td>Products Yield</td>
<td>2D-Lab</td>
<td>-</td>
</tr>
<tr>
<td>Couto et al. [260]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Outlet composition</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Xiong et al. [39,184–186]</td>
<td>Syamlal-O’Brien</td>
<td>Ranz and Marshal</td>
<td>-</td>
<td>Products Yield</td>
<td>2D-Lab</td>
<td>-</td>
</tr>
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<td>Study</td>
<td>Gidaspow</td>
<td>Gunn</td>
<td>EMMS/matrix</td>
<td>Li-Mason [269]</td>
<td>Temperature</td>
<td>3D-Lab</td>
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<tr>
<td>-------</td>
<td>--------</td>
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<td>--------</td>
</tr>
<tr>
<td>Chen et al. [226]</td>
<td>Syamlal and O’Brien s-g Morsi [271] and Alexander Syamlal et al.</td>
<td>Gunn</td>
<td>Gunn</td>
<td>Ranz and Marshal</td>
<td>Outlet composition</td>
<td>2D-Pio</td>
</tr>
<tr>
<td>Liu et al. [262]</td>
<td>Gidaspow</td>
<td>Zhou et al. [272]</td>
<td>Temperature dependent coefficient</td>
<td>Outlet composition</td>
<td>2D-Pio</td>
<td>-</td>
</tr>
<tr>
<td>Ismail et al. [252]</td>
<td>Gidaspow</td>
<td>Gunn</td>
<td>Temperature</td>
<td>Outlet composition</td>
<td>2D-Lab</td>
<td></td>
</tr>
<tr>
<td>Azizi and Mowla [263]</td>
<td>Gidaspow</td>
<td>Huilin-Gidaspow</td>
<td>-</td>
<td>Outlet composition</td>
<td>2D-Lab</td>
<td></td>
</tr>
<tr>
<td>Chen et al. [264]</td>
<td>Syamlal-O’Brien</td>
<td>Gunn</td>
<td>Gunn</td>
<td>Products yield</td>
<td>2D-Lab</td>
<td></td>
</tr>
<tr>
<td>Xue and Fox [37]</td>
<td>Gidaspow</td>
<td>Gunn</td>
<td>Temperature dependent coefficient</td>
<td>Outlet composition</td>
<td>2D-Lab</td>
<td></td>
</tr>
<tr>
<td>Ranganathan and Gu [225]</td>
<td>Gidaspow</td>
<td>Gunn</td>
<td>Ranz and Marshal</td>
<td>Products yield</td>
<td>2D-Lab</td>
<td></td>
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<tr>
<td>Lu et al. [38]</td>
<td>Gidaspow</td>
<td>Rosseland model [273]</td>
<td>Temperature</td>
<td>Outlet composition</td>
<td>2D-Lab</td>
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<tr>
<td>Yan et al. [33]</td>
<td>Huilin-Gidaspow</td>
<td>Gunn</td>
<td>-</td>
<td>Outlet composition</td>
<td>3D-Lab</td>
<td></td>
</tr>
</tbody>
</table>
2.3 Summary

At particle-scale, the biomass combustion and gasification is divided into drying, devolatilization, char conversion, and homogeneous reactions. The main conclusions from the literature are:

- The drying process can be described by the heat flux model, equilibrium model, or chemical kinetics model. The heat flux and equilibrium models are based on heat and mass balance of moisture evaporation, which can be used in a wide range of operating conditions. However, the two models may induce numerical problems when they are implemented in particle modelling. Compared to the heat flux and equilibrium model, the chemical kinetics model is the simplest model, which can be easily implemented in the particle model.

- The devolatilization process is complicated. The kinetics used to describe devolatilization is empirical or semi-empirical. The one-step global model is the simplest and easiest one implemented in the particle model.

- The char conversion process is usually slower than biomass devolatilization. Different models have been used to model the char conversion. The PCM model can be used to model various conditions, but it is more complicated and time-consuming. The UCM model is reasonably used in a kinetics transfer controlled regime, while the SCM model is suitable for an external mass transfer controlled case.

- There are large variations of the reported char oxidation and gasification kinetics, the kinetics used in the model should be selected carefully.

- The homogeneous reactions considered in the single particle modelling and CFD modelling are commonly lumped to a few main reactions.

In the CFD modelling, both the E-L and E-E approaches have been used to model biomass combustion and gasification in fluidized beds. The computational cost of the E-E approach is much less than that of the E-L approach. Therefore, it is affordable to simulate a large-scale fluidized bed reactor. However, the following aspects should still be focused on CFD modelling:

- The internal mass and heat transfer and particle shrinkage are commonly neglected in both E-L and E-E approach, in terms of reducing computational time. It indeed needs to be considered in modelling large biomass particle combustion and gasification.

- The commonly used drag models in current CFD simulation of biomass combustion and gasification are homogeneous drag models (e.g. the Gidaspow drag model etc.). However, it has been reported that the heterogeneous structure has a significant effect on the modelling results. Therefore, further evaluation can help the choice of drag model in CFD simulation of biomass combustion and gasification.
• The heat and mass transfer model applied in CFD model are based on single particle experiments and fixed-bed experiments. The simulation results seem less sensitive to the choice of heat and mass transfer model, as compared with the choice of drag model.
• Since CFD simulation of multi-phase flow is time-consuming and computationally intensive, the homogeneous reactions are commonly lumped and decoupled to several global reactions.
3 Modelling of biomass devolatilization in a single particle combustor

The main objective is to develop a comprehensive single particle model for biomass devolatilization which can be used in a wide range of conditions, especially at high temperature conditions. The comprehensive biomass devolatilization model is validated by the experimental results carried out at CHEC research centre, DTU Chemical Engineering.

3.1 Introduction

Biomass devolatilization involves its thermal decomposition coupled with internal and external heat and mass transfer [1,7,30,274]. Devolatilization is an important step for biomass combustion and gasification. Many experimental studies [153,275–278] have been done to investigate biomass devolatilization and found that the devolatilization time of biomass particles decreases with increasing gas temperature and oxygen concentration [275], and increases with increasing particle size [275–278], moisture content [277] and density [153,278]. However, to authors’ knowledge, a comprehensive comparison of the influences of the different factors (e.g. wood types, particle size, moisture content, operating temperature, etc.) on devolatilization time has not been carried out in current existing studies. However, it is important to identify the key parameters controlling the devolatilization time of biomass particles, and to develop reliable modelling tools to describe the devolatilization process.

Comprehensive models have been developed to describe the devolatilization of single biomass particles [12–20]. The existing models have been used to study the effects of particle shape [12], moisture content [12,16], particle size [20], heat flux [19,20] on the biomass devolatilization and validated mainly by experiments under relatively low temperature conditions (T_g < 1273 K). These models have only been validated to a limited extent under high temperature conditions (≥ 1273 K) with respects to the effects of particle shape [131], particle size [1,131,279]. Other important factors, such as the moisture content and density of particles are rarely studied specifically by experiments and modelling. In order to develop a reliable model that is applicable to pulverized biomass combustion. Comprehensive experimental data with different particle density and particle moisture content at high temperature are desirable to validate the model.

Besides the comprehensive models, empirical correlations have also been developed to estimate the devolatilization time of biomass particles [277,280–284]. Most of the existing correlations primarily use a power law to correlate the devolatilization time with particle size with a number of fitting parameters in fluidized bed reactors at relatively low temperatures (< 1273 K) [280–284]. Empirical correlations are rarely reported for biomass devolatilization under pulverized flame conditions. Mason et al. [277] correlated the devolatilization time as a function of particle moisture content, particle size, and particle density at a temperature of 1823 K for 3 different
woody biomass at suspension combustion conditions. However, the obtained coefficients of different woody biomass particles are significant differences, and the developed correlation has only been validated with a limited number of experiments. Thus, a more generic correlation valid for different biomass properties and operating conditions is required.

In this chapter, a comprehensive devolatilization model for a single biomass particle is further improved based on the previous work [1]. The model is validated by the experimental data obtained in a single particle combustor with spherical and cubic wood particles of various density, size, type, and moisture contents. Furthermore, a simple correlation based on the comprehensive devolatilization model is proposed to estimate the devolatilization time of wood particles at high temperatures.

3.2 Model description

3.2.1 Model assumptions

The model used in the present work is originally developed by Johansen et al.[1] to study the influence of intra-particle heat transfer on biomass devolatilization. The model is further improved by including the effects of the heat of devolatilization, and modifying the drying model and the devolatilization kinetics in this work. The model includes phenomena of internal and external heat transfer, moisture evaporation, and devolatilization. The general assumptions are listed as below:

(1) The model is a one-dimensional model for spherical wood particles, which neglects the anisotropy of wood particles, even though the anisotropy of wood is expected to be important when the thermal conductivity along and across the fibre direction of wood particles is significantly different. A 2D or 3D model may be considered to implement the anisotropy of wood particles. However, a 2D or 3D model will result in much more complex and computationally intensive than a 1D model [30]. Moreover, the thermal conductivity along and across the fibre direction is not easily measured from experiments, while there are available and validated the expression of effective dry wood conductivity. Furthermore, previous studies [12–20] have shown that appropriate devolatilization modelling can be obtained without considering the anisotropy of the wood. Thus, the anisotropy of wood is neglected in the present study.

(2) No convective heat transport takes place inside the particle, only heat conduction;

(3) No mass transfer limitation of the released volatile is included;

(4) The reactor walls contribute to the radiative heat flux between the particle external surface and the environment;

(5) A fully devolatilized particle has a shrinkage factor of 0.2 (volume-based) and the particle volume shrinks linearly with the devolatilization degree [1].
(6) The devolatilization time is determined by 99% of conversion (the fraction of the amount of released moisture and volatile);

The above assumptions are commonly applied in the particle modelling literature [1,12,14,16,58].

### 3.2.2 Governing equations

The devolatilization model, which includes both internal and external heat transfer, is described as Eq. (3.1):

\[
C_p \rho_p \frac{\partial T_p}{\partial t} = \left( \frac{b-1}{r} \right) \lambda_{eff} \frac{\partial T_p}{\partial r} + \lambda_{eff} \frac{\partial^2 T_p}{\partial r^2} + \frac{\partial \lambda_{eff}}{\partial r} \frac{\partial T_p}{\partial r} \sum \frac{dX_i}{dt} \rho_{io} Y_{i0} Q_{R,i} \quad (3.1)
\]

Here, \( C_p, \rho_p, \lambda_{eff} \) are the specific heat capacity, J/(kg·K), particle density, kg/m\(^3\), effective thermal conductivity, W/(m·K), of the biomass particle at time \( t \), respectively. \( \rho_{io} \) is the initial particle density, kg/m\(^3\), \( r \) is the radial position, m, \( t \) is time, s, \( T \) is the temperature, K, \( Y_{i0} \) 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. \( dX_i/dt \) is the evaporation rate of moisture or release rate of volatile, which can be determined by drying and devolatilization kinetics as discussed in section 3.2.4. \( b \) is the geometry factor, with 2 and 3 for cylindrical and spherical particles, respectively.

The boundary conditions of the model include both convection and radiation heat transfer are described by Eq. (3.2) and Eq. (3.3).

\[
\left. \frac{\partial T}{\partial r} \right|_{r=0} = 0, \quad \text{all } t \quad (3.2)
\]

\[
\lambda_{eff} \left. \frac{\partial T}{\partial r} \right|_{r=R} = h_c \left( T_g - T_i \right) + \xi \sigma \left( T_w^4 - T_s^4 \right) \quad t > 0 \quad (3.3)
\]

Here, \( h_c \) is the convective heat transfer coefficient, W/(m\(^2\)·K), \( T_g, T_w, \) and \( T_s \) are gas, wall, and particle external surface temperatures, K. \( \xi \) is the particle emissivity, which depends on many factors (e.g. temperature, wood type, surface structure). The typical values of the particle emissivity reported in the literature are in a range of 0.7-1.0 [2]. Due to the difficulties for an accurate determination of the particle emissivity under different conditions, a fixed particle emissivity of 0.85 is selected in the model. The effects of emissivity on modelling results are shown in the section of sensitivity analysis. \( \sigma \) is Stefan-Boltzmann constant (5.6704×10\(^{-8}\) J/(m\(^2\)·K\(^4\)·s)).

The initial conditions are:

\[
T(0,r) = T_{io}, \quad Y_i(0,r) = Y_{i0}, \quad \rho_p(0,r) = \rho_{io} \quad (3.4)
\]
3.2.3 Physical properties

Table 3.1 summarizes the physical properties used in this work. The effective heat conductivity ($\lambda_{eff}$) of the biomass particle is expressed as a sum of the conduction in the solid phase ($\lambda_p$), gas phase ($\lambda_g$), liquid moisture ($\lambda_w$), and radiative conduction ($\lambda_r$) [285]. The solid phase heat conductivity $\lambda_p$ is a function of volatile conversion [1]. The conduction by radiation $\lambda_r$ is a function of particle pore size and particle temperature [1,285], with the particle pore diameter ($d_{pore}$) assumed to vary linearly with the conversion [1]. When the moisture content is larger than $Y_{fsb}$ (fibre saturation point), the heat required for water evaporation is the heat of vaporization, $\Delta_{vap}H$. When it is smaller than $Y_{fsb}$, the heat required is the sum of heat of vaporization and desorption of bound water [1,286]. The convective heat transfer coefficient ($h_c$) of a spherical particle is determined by Ranz and Marshall equation [221]. The shrinkage factor ($\varphi$, volume based), which is dependent on the experimental conditions and wood type as reported in previous studies [12,18,59], is assumed to be 0.2 in this work. All the thermophysical properties described above are summarized in Table 3.1. The bulk gas physical properties are not shown in Table 3.1, but given in Appendix A.
Table 3. A summary of physical properties used in the particle-scale model for wood devolatilization

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Description</th>
<th>Expressions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_b$</td>
<td>W/(m-K)</td>
<td>Dry wood conductivity</td>
<td>$0.13 + 3 \times 10^{-4} (T_p - 273)$, $T_p \leq 1006$ K</td>
<td>[1,287]</td>
</tr>
<tr>
<td>$\lambda_c$</td>
<td>W/(m-K)</td>
<td>Char conductivity</td>
<td>0.071</td>
<td>[1,288]</td>
</tr>
<tr>
<td>$\lambda_g$</td>
<td>W/(m-K)</td>
<td>Gas conductivity</td>
<td>0.0258</td>
<td>[1,289]</td>
</tr>
<tr>
<td>$\lambda_r$</td>
<td>W/(m-K)</td>
<td>Radiative conductivity</td>
<td>$\alpha d_{pore} T_p^2 / \varepsilon$</td>
<td>[1,290]</td>
</tr>
<tr>
<td>$\lambda_w$</td>
<td>W/(m-K)</td>
<td>Water conductivity</td>
<td>$0.6065 \times 1.4845 + 4.1229 (T_p / 298.15 - 1.6387 (T_p / 298.15)^2)$</td>
<td>[1,291]</td>
</tr>
<tr>
<td>$d_{pore}$</td>
<td>M</td>
<td>Wood pore diameter</td>
<td>$3.2 \times 10^{-6}$</td>
<td>[2,292]</td>
</tr>
<tr>
<td>$d_{pore}$</td>
<td>M</td>
<td>Char pore diameter</td>
<td>$1.0 \times 10^{-4}$</td>
<td>[2,293]</td>
</tr>
<tr>
<td>$X$</td>
<td>-</td>
<td>Total particle conversion</td>
<td>$(X_1 Y_1 + X_2 Y_2) / (Y_1 + Y_2)$</td>
<td>[2,294]</td>
</tr>
<tr>
<td>$d_{pore}$</td>
<td>M</td>
<td>Particle pore diameter</td>
<td>$d_{pore} (1 - X) + d_{pore} X$</td>
<td>[2,295]</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>-</td>
<td>Particle porosity</td>
<td>$1 - \rho_0 (1 - X_2 Y_2) / 1500 / (1 - \varphi) - \rho_0 Y_1 (1 - X_2) / 1000 / (1 - \varphi)$</td>
<td>[2,296]</td>
</tr>
<tr>
<td>$\varepsilon_w$</td>
<td>-</td>
<td>Water volume fraction</td>
<td>$\rho_0 Y_0 (1 - X) / 1000 / (1 - \varphi)$</td>
<td>[2,297]</td>
</tr>
<tr>
<td>$\lambda_{eff}$</td>
<td>W/(m-K)</td>
<td>Effective conductivity</td>
<td>$[\lambda_b (1 - X) + \lambda_c X + \lambda_{g,pore} \varphi + \lambda_w \varphi]$</td>
<td>[2,298]</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>kg/m$^3$</td>
<td>Gas density</td>
<td>$p M_w R T_x$</td>
<td>[2,299]</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>kg/m$^3$</td>
<td>Particle density</td>
<td>$\rho_0 (1 + Y_0) / (1 - \varphi)$</td>
<td>[2,300]</td>
</tr>
<tr>
<td>$C_{pc}$</td>
<td>J/(kg-K)</td>
<td>Char heat capacity</td>
<td>$(1000 \rho_r (11.3) (g(380 / T_p) + 2g(1800 / T_p)))$</td>
<td>[1,293]</td>
</tr>
<tr>
<td>$C_{wb}$</td>
<td>J/(kg-K)</td>
<td>Wood heat capacity</td>
<td>$(1000 \rho_r / 7.72) (g(380 / T_p) + 2g(1800 / T_p))$</td>
<td>[1,294]</td>
</tr>
<tr>
<td>$C_{pw}$</td>
<td>J/(kg-K)</td>
<td>Water heat capacity</td>
<td>$4180$</td>
<td>[2,301]</td>
</tr>
<tr>
<td>$C_p$</td>
<td>J/(kg-K)</td>
<td>Particle heat capacity</td>
<td>$\text{Mass averaged}$</td>
<td>[2,302]</td>
</tr>
<tr>
<td>$\Delta_{up}H$</td>
<td>J/kg</td>
<td>Heat of vaporization</td>
<td>$1000 (3179 - 2.5 T_p)$</td>
<td>[2,303]</td>
</tr>
<tr>
<td>$\Delta_{ds}H$</td>
<td>J/kg</td>
<td>Heat of desorption</td>
<td>$0.434 H (1 - Y / Y_0) Y_0$</td>
<td>[2,304]</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>J/kg</td>
<td>Heat of water drying</td>
<td>$\Delta_{up}H (Y_0 &gt; Y_{fb})$ $\Delta_{up}H + \Delta_{ds}H (Y_0 \leq Y_{fb})$</td>
<td>[2,305]</td>
</tr>
<tr>
<td>$Y_{f0}$</td>
<td>-</td>
<td>Fiber saturation point</td>
<td>$\text{Max}(Y_{f0} = 0.598 - 0.0017 T_p, 0.2)$</td>
<td>[2,306]</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>-</td>
<td>Emissivity</td>
<td>0.85</td>
<td>[2,307]</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>J/(m$^2$-K$^4$-s)</td>
<td>Stefan-Boltzmann constant</td>
<td>$5.6704 \times 10^{-8}$</td>
<td>[2,308]</td>
</tr>
<tr>
<td>$h_c$</td>
<td>J/(m$^2$-K$^4$-s)</td>
<td>Convective heat transfer coefficient</td>
<td>$\lambda_0 (2 + 0.6 R e^{0.5} P e^{0.15}) / d_p$</td>
<td>[2,309]</td>
</tr>
<tr>
<td>$d_p$</td>
<td>m</td>
<td>Particle diameter</td>
<td>$d_p (1 - \varphi)^{1/3}$</td>
<td>[2,310]</td>
</tr>
<tr>
<td>$\varphi$</td>
<td></td>
<td>Particle shrinkage</td>
<td>$0.2 X$</td>
<td>[2,311]</td>
</tr>
</tbody>
</table>

3.2.4 Drying and devolatilization models

The drying process is described by a first-order kinetic model as shown in Eq. (3.5) [59]:

$$\frac{dX_1}{dt} = k_1 \left( 1 - X_1 \right)$$  \hspace{1cm} (3.5)

The rate constant $k_1$ follows an Arrhenius expression. The kinetics are shown in Table 3. 2. Based on Johansen et al. [1], the net devolatilization rate is described by Eq. (3.6) and Eq. (3.7):

$$\frac{dX_2}{dt} = k_2 \left( 1 - X_2 \right)$$  \hspace{1cm} (3.6)

47
\[ k_2 = k_v + \min\left(k_t, k_{tv}\right) \]  

(3.7)

\(k_t, k_v,\) and \(k_{tv}\) follow the Arrhenius expression. They are the rate constant of wood to volatile by primary devolatilization, wood to tar by primary devolatilization, and tar to volatile by secondary devolatilization, respectively. The net devolatilization rate constant is lumped as \(k_2\) as defined in Johansen et al. [1]. The kinetic data are derived by Wagenaar et al. [72] and it has been widely used to simulate both small and large wood particles [1,12,296,297]. The kinetic parameters are listed in Table 3.2. Different values of reaction enthalpy, varying from 200 to 600 kJ/kg, have been reported for wood devolatilization [193]. In this work, a value of 418 kJ/kg is used based on reference [12], in which a similar experimental setup was used to study wood devolatilization and combustion.

**Table 3.2 Kinetic parameters of two-step semi-global devolatilization mechanism**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pre-exponential factor (s(^{-1}))</th>
<th>Activation energy (kJ/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1)</td>
<td>(5.13 \times 10^{10})</td>
<td>88</td>
<td>[59]</td>
</tr>
<tr>
<td>(k_v)</td>
<td>(1.11 \times 10^{11})</td>
<td>177</td>
<td>[72]</td>
</tr>
<tr>
<td>(k_t)</td>
<td>(9.29 \times 10^{9})</td>
<td>149</td>
<td>[72]</td>
</tr>
<tr>
<td>(k_{tv})</td>
<td>(4.28 \times 10^{6})</td>
<td>107.5</td>
<td>[74]</td>
</tr>
</tbody>
</table>

### 3.3 Experiments for model validation

A brief introduction of single particle experiments for biomass devolatilization is given below.

#### 3.3.1 Single particle combustor

A single particle combustor (SPC), designed for combustion of a single fuel particle with local conditions similar to that in pulverized fuel combustor was used [275]. Detailed descriptions of the SPC and experimental procedures can be found elsewhere [153,275,278]. In the experiments, a wood particle was loaded to a 0.3 mm titanium wire on a ceramic sample holder and suspended in the flue gas from the hydrogen flame. The combustion process of the single wood particle was recorded by a video camera. In the present work, the devolatilization time is the sum of ignition and pyrolysis time. The method to estimate the ignition and pyrolysis time and the detailed image post-processing for determining the devolatilization time is described in reference [275].

#### 3.3.2 Materials

In a pulverized wood-fired power plant, particles fed to the burners are in a size range of from 10 µm to 5 mm wood particles [298]. The millimetre-sized wood particles in a pulverized biomass combustor may result in unburned carbon in both bottom and fly ash, and therefore need special attention [299]. In the present study, two series experiments were performed with millimetre-sized wood particles in the single particle combustor. Three types of biomass, pine,
beech, and bamboo, were selected as raw materials in the experiment series I. The particles used in this series are spherical and having two sizes of ~4 mm and ~3 mm. The proximate analyses and the inorganic compositions are shown in Table 3. 3. The mass and diameter of individual particles were measured by a microbalance (±0.01 mg) and a sliding calliper (±0.05 mm). For ~4 mm biomass particles, the measured mean particle diameters of pine, beech, and bamboo particles were 4.00 mm, 4.13 mm and 3.97 mm, respectively. In the case of ~3 mm spherical biomass particles, the mean diameters were 3.12 mm and 3.03 mm of pine and beech wood, respectively. To investigate the effects of density on devolatilization time, particles with significantly different mass were selected in the experiments. The corresponding density ranges were 400-900, 600-1100, and 400-900 kg/m³ for pine, beech, and bamboo, respectively. The “density” in the present work refers to “particle density on dry basis”. To produce wetted wood particles with different moisture content, selected particles were submerged into deionized water, and then exposed to air to obtain a specified moisture content (as received based: ~15.0 ar%, ~30.0 ar%, ~50.0 ar%). The actual moisture content of individual wetted particle varies slightly (< 4 ar%) from the averaged moisture content.

In the series II experiments, particles (~3 mm cubic) from five wood types with and without torrefaction pretreatment were used. The torrefaction was made using a 3-zone electrically heated tubular furnace at a temperature of 563 K for 1 hour [278]. The proximate analyses and other properties of particles with and without torrefaction are shown in Table 3. 4. The wood particles have small differences and variations in length, between 2.78 and 3.03 mm with a maximum standard derivation of 0.03 mm. The apparent wood particle densities are in a range from 184 to 698 kg/m³ based on the measured mass and volume of particles.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Pine</th>
<th>Beech</th>
<th>Bamboo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture Content</td>
<td>ar%</td>
<td>6.9</td>
<td>4.9</td>
<td>5.2</td>
</tr>
<tr>
<td>Ash</td>
<td>db%</td>
<td>0.2</td>
<td>0.6</td>
<td>1.9</td>
</tr>
<tr>
<td>Volatile</td>
<td>db%</td>
<td>86.6</td>
<td>83.7</td>
<td>79.0</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>db%</td>
<td>13.2</td>
<td>15.7</td>
<td>19.1</td>
</tr>
<tr>
<td>Al</td>
<td>mg/kg, db</td>
<td>10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Fe</td>
<td>mg/kg, db</td>
<td>42</td>
<td>29</td>
<td>38</td>
</tr>
<tr>
<td>P</td>
<td>mg/kg, db</td>
<td>82</td>
<td>70</td>
<td>82</td>
</tr>
<tr>
<td>Ti</td>
<td>mg/kg, db</td>
<td>&lt;3</td>
<td>&lt;3</td>
<td>&lt;3</td>
</tr>
<tr>
<td>K</td>
<td>mg/kg, db</td>
<td>150</td>
<td>1700</td>
<td>8700</td>
</tr>
<tr>
<td>Na</td>
<td>mg/kg, db</td>
<td>20</td>
<td>&lt;10</td>
<td>22</td>
</tr>
<tr>
<td>Ca</td>
<td>mg/kg, db</td>
<td>530</td>
<td>2000</td>
<td>&lt;200</td>
</tr>
<tr>
<td>Mg</td>
<td>mg/kg, db</td>
<td>75</td>
<td>290</td>
<td>490</td>
</tr>
<tr>
<td>Si</td>
<td>mg/kg, db</td>
<td>&lt;100</td>
<td>&lt;100</td>
<td>290</td>
</tr>
</tbody>
</table>
Table 3.4 Properties of ~3 mm cubic wood particles with and without torrefaction

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Balsa</th>
<th>Paulownia</th>
<th>Pine</th>
<th>Beech</th>
<th>Sapele</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood without torrefaction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture ar%</td>
<td></td>
<td>5.0</td>
<td>4.9</td>
<td>6.4</td>
<td>6.3</td>
<td>7.7</td>
</tr>
<tr>
<td>Ash db%</td>
<td></td>
<td>2.1</td>
<td>0.6</td>
<td>0.1</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>Volatile db%</td>
<td></td>
<td>81.1</td>
<td>80.2</td>
<td>82.1</td>
<td>80.4</td>
<td>74.3</td>
</tr>
<tr>
<td>Fixed carbon db%</td>
<td></td>
<td>16.8</td>
<td>19.1</td>
<td>17.8</td>
<td>19.1</td>
<td>24.8</td>
</tr>
<tr>
<td>K mg/kg</td>
<td></td>
<td>5522</td>
<td>2122</td>
<td>85</td>
<td>1060</td>
<td>65</td>
</tr>
<tr>
<td>Na mg/kg</td>
<td></td>
<td>189</td>
<td>30</td>
<td>9</td>
<td>64</td>
<td>64</td>
</tr>
<tr>
<td>Ca mg/kg</td>
<td></td>
<td>2318</td>
<td>467</td>
<td>250</td>
<td>1032</td>
<td>3399</td>
</tr>
<tr>
<td>Mg mg/kg</td>
<td></td>
<td>644</td>
<td>27</td>
<td>61</td>
<td>203</td>
<td>457</td>
</tr>
<tr>
<td>Si mg/kg</td>
<td></td>
<td>737</td>
<td>526</td>
<td>321</td>
<td>427</td>
<td>758</td>
</tr>
<tr>
<td>Mass mg</td>
<td></td>
<td>6.70±0.25</td>
<td>9.30±0.35</td>
<td>11.70±0.10</td>
<td>17.50±0.41</td>
<td>19.00±0.69</td>
</tr>
<tr>
<td>Cube lengths mm</td>
<td></td>
<td>3.02±0.03</td>
<td>3.03±0.02</td>
<td>2.97±0.03</td>
<td>2.96±0.03</td>
<td>3.01±0.03</td>
</tr>
<tr>
<td>Apparent density kg/m³</td>
<td></td>
<td>243</td>
<td>335</td>
<td>446</td>
<td>673</td>
<td>698</td>
</tr>
<tr>
<td>Wood with torrefaction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture ar%</td>
<td></td>
<td>3.0</td>
<td>2.6</td>
<td>3.0</td>
<td>3.8</td>
<td>3.9</td>
</tr>
<tr>
<td>Ash db%</td>
<td></td>
<td>3.0</td>
<td>0.8</td>
<td>0.1</td>
<td>0.8</td>
<td>1.1</td>
</tr>
<tr>
<td>Volatile db%</td>
<td></td>
<td>69.0</td>
<td>76.4</td>
<td>78.5</td>
<td>73.5</td>
<td>68.6</td>
</tr>
<tr>
<td>Fixed carbon db%</td>
<td></td>
<td>28.0</td>
<td>22.8</td>
<td>21.4</td>
<td>25.7</td>
<td>30.3</td>
</tr>
<tr>
<td>Mass mg</td>
<td></td>
<td>4.25±0.18</td>
<td>6.51±0.18</td>
<td>8.26±0.21</td>
<td>12.67±0.24</td>
<td>14.00±0.50</td>
</tr>
<tr>
<td>Cube lengths mm</td>
<td></td>
<td>2.85±0.12</td>
<td>2.94±0.06</td>
<td>2.77±0.14</td>
<td>2.78±0.14</td>
<td>2.89±0.10</td>
</tr>
<tr>
<td>Apparent density kg/m³</td>
<td></td>
<td>184</td>
<td>256</td>
<td>389</td>
<td>589</td>
<td>583</td>
</tr>
</tbody>
</table>

3.3.3 Operating conditions

The operating conditions of the experiment series I and II are shown in Table 3.5. The Series I experiment has been carried out in the single particle combustor with different temperatures of 1481/1494/1630/1673/1714 K, and oxygen concentrations of 0.0/4.4 vol%, while the series II experiment has been carried out using a temperature of 1529 K and an oxygen content of 2.8 vol%. The extracted flue gas samples from the reactor outlet were dried and the O₂ concentrations were measured. The averaged gas velocity in the single particle combustor was about 1.5 m/s as shown in Table 3.5. The wall temperature is assumed to be 200 K (estimated from the measured radial temperature distribution of our previous work [275,278]) lower than the gas temperature in our devolatilization model.
Table 3.5 Operating conditions of single particle combustor

<table>
<thead>
<tr>
<th>No.</th>
<th>Measured gas temperature (K)</th>
<th>Calculated gas velocity (m/s)</th>
<th>O₂ concentration (wet basis, vol%)</th>
<th>H₂O concentration (wet basis, vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0% O₂ / 1487 K</td>
<td>1494</td>
<td>1.49</td>
<td>0.0</td>
<td>26.8</td>
</tr>
<tr>
<td>0% O₂ / 1630 K</td>
<td>1630</td>
<td>1.50</td>
<td>0.0</td>
<td>39.7</td>
</tr>
<tr>
<td>0% O₂ / 1673 K</td>
<td>1673</td>
<td>1.42</td>
<td>0.0</td>
<td>39.1</td>
</tr>
<tr>
<td>0% O₂ / 1714 K</td>
<td>1714</td>
<td>1.40</td>
<td>0.0</td>
<td>41.8</td>
</tr>
<tr>
<td>4.4%O₂ / 1483 K</td>
<td>1481</td>
<td>1.43</td>
<td>4.4</td>
<td>25.7</td>
</tr>
<tr>
<td>Series II</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.8% O₂ / 1529 K</td>
<td>1529</td>
<td>1.50</td>
<td>2.8</td>
<td>27.0</td>
</tr>
</tbody>
</table>

3.4 Results and Discussion

3.4.1 Particle evolution

In order to analyze the particle evolution during drying and devolatilization, the radial distribution of particle temperature, moisture conversion, and volatile conversion with specified global particle conversion (defined as \((X_1Y_{10} + X_2Y_{20})/(Y_{10} + Y_{20})\) of 0.01, 0.5, and 0.9 are obtained at the conditions of \(T_g = 1487\) K with 4 mm wood particle. As shown in Fig. 3.1 (a), when the total conversion is 0.01, the temperature of the particle outer layer between a radius of 1.2 mm and 2.0 mm is in a range of 373-873 K. A large amount of moisture is evaporated, while only a small amount of volatile is released. When the particle conversion is 0.5, the temperature of the entire particle is higher than 373 K as shown in Fig. 3.1 (b), and the drying process is almost finished. With a particle surface temperature of \(~1123\) K and a centre temperature of \(~473\) K, significantly different conversion degrees are observed at different radius positions. When the particle conversion is 0.9, the particle centre temperature is higher than 673 K. All moisture is evaporated, and the volatile matters only remain in the particle centre. From Fig. 3.1, it is also seen that the moisture front propagates inward to the centre of the particle, followed by the volatile released front. The results are consistent with other studies [52,58,193].
Fig. 3.1 Radial distribution of wood particle temperature ($T$), conversion of moisture ($X_w$) and conversion of volatile ($X_{vol}$) under different particle conversion (0.01, 0.5, and 0.9 corresponding to a residence time of 0.27 s, 3.37 s, and 7.77 s. Simulation conditions: $d_p = 4$ mm, $M_C = 4.9$ ar%, $Vol = 83.7$ db%, $FC = 15.7$ db%, $T_g = 1487$ K, $T_w = 1287$ K, 0.0% $O_2$, $\rho_{DB} = 700$ kg/m$^3$.)
3.4.2 Devolatilization time

In Fig. 3. 2 (a)-(c), the experimental and predicted devolatilization times at different temperatures (1487/1630/1673/1714 K) are compared for ~4 mm beech, pine, and bamboo. The devolatilization time decreases with increasing gas temperature due to an enhanced heat transfer, consistent with the results of other studies [14,60,275,281,300,301]. The predicted results agree with the experiments within about ±25% for all three types of biomass particles.

In Fig. 3. 2 (d)-(f), the experimental and predicted devolatilization times of beech, pine, and bamboo with moisture content from 4.9-6.9 ar% (raw wood particle) to ~50 ar% at 1481 K are compared. An increased devolatilization time is observed with an increase of moisture content. A higher moisture content results in a large heat consumption for the drying process and thereby delays devolatilization. Again, the predicted devolatilization time agrees with the experimental data within ±25%.

The effect of density on devolatilization time can also be observed in Fig. 3. 2 (a)-(f). The devolatilization time increases with an increase of the particle density. A higher density of the particles results in a lower heating rate, mainly due to increased heat capacity of the particles, and thereby increases the devolatilization time. Moreover, both the experimental and the model predicted results show that the devolatilization time increases linearly with an increase in the density, consistent with the study of Haseli et al. [20]. The results suggest that under the studied conditions, the density is the primary parameter that influences the devolatilization time of the biomass particles.
Fig. 3. 2 A comparison between the experimental and model predicted devolatilization time with a variation of gas temperature, moisture content and particle density for three different wood (beech, pine, bamboo) in series I experiments (spherical particle). Fig. 3. 2 (a)-(c) show received particles devolatilized at different temperatures (1487/1630/1673/1714 K), Fig. 3. 2 (d)-(f) show particles with different moisture content (as received particle basis, \(\sim 15\) ar\%, \(\sim 30\) ar\%, \(\sim 50\) ar\%) devolatilized at 1481 K.

Fig. 3. 3 presents the experimental and predicted devolatilization time of \(\sim 3\)mm spherical wood particles (pine and beech) devolatilized with and without the presence of oxygen. With the presence of oxygen, the released volatile is combusted near the particle, supplying extra heat and thereby leading to a small decrease in devolatilization time. However, the experimental results in Fig. 3. 3 show that the presence of 4.4 vol\% O$_2$ only decreases the devolatilization time slightly, compared to the case with 0.0 vol\% O$_2$. The particle density is still a key parameter affecting the devolatilization time almost in a linear trend as shown in Fig. 3. 3.
Fig. 3. A comparison between the experimental and model predicted devolatilization time with variation of wood types (Pine, Beech) and oxygen concentration (0.0 vol% O$_2$, 4.4 vol% O$_2$) in series I experiments (spherical particles), the particle diameter of pine and beech is 3.12 mm and 3.03 mm, respectively.

Fig. 3. 4 shows the experimental and predicted devolatilization time of different woods with or without torrefaction in series II experiments (~3 mm cubic particles). The particle size used in modelling is based on the equivalent particle volume. The volume equivalent method is simple approximation which is proposed in previous studies [1,299]. The predicted devolatilization time for different wood types, torrefaction treatment, particle moisture content, and particle size conditions is in good agreement with measurements. The tendency in Fig. 3. 4 further implies the significant influence of particle density on devolatilization time.

Fig. 3. 4 A comparison between predicted and experimental devolatilization time of different wood with or without torrefaction in series II experiments (cubic particles), the oxygen concentration of bulk gas is about 2.8 vol% and the temperature is 1529 K.
3.4.3 Parameter sensitivity analysis

3.4.3.1 Physical properties

There are several parameters in the model that may affect the predicted devolatilization time, such as emissivity ($\varepsilon$), gas conductivity ($\lambda_g$), char conductivity ($\lambda_c$), raw wood conductivity ($\lambda_B$), heat of devolatilization ($Q_{pyro}$), convective heat transfer coefficient ($h_c$), char pore size ($d_{porec}$), raw wood pore size ($d_{poreB}$), raw wood thermal capacity ($C_{pB}$), char thermal capacity ($C_{pc}$), wood true density ($\rho_{true}$), shrinkage coefficient ($\varphi$), and fixed carbon content (FC).

Fig. 3. 5 shows the results of a sensitivity analysis done by decreasing and increasing each parameter by 50% for a 4 mm wood particle devolatilized in 26.8 vol% H$_2$O/73.2 vol% N$_2$ at $T_g = 1487$ K. The internal heat transfer related parameters ($\lambda_c$, $\lambda_B$, $C_{pB}$) and the heat of devolatilization show significant influences (> 10%) on the devolatilization time, the external heat transfer related parameters ($\varepsilon$, $h_c$) show a limited effects (5-10%) on the predicted devolatilization time. Therefore the devolatilization process is internal heat transfer dominated and partially controlled by external heat transfer for 4 mm particles [7,297]. Therefore, the assumption of using a constant emissivity in the modelling is reasonable in this work. The devolatilization time turned out to be insensitive to char pore size, gas conductivity, and raw wood pore size, due to its small contribution (< 20%) to particle effective conductivity during the devolatilization process. The shrinkage coefficient also shows an insignificant impact on devolatilization time for the 4 mm wood particle, which is consistent with a previous study [290]. The fixed carbon content is found to have no significant influence on devolatilization time, and the results are consistent with the study of Bu et al. [15,17] as well as the experimental data are shown in Fig. 3. 3.
3.4.3.2 Devolatilization kinetics

The influence of devolatilization kinetics is shown in Fig. 3. 6, with Fig. 3. 6 (a) showing the kinetic data and Fig. 3. 6 (b) comparing the conversion history predicted by different kinetics. The kinetics of Wagenaar et al. [72] is derived by fast pyrolysis of pine wood sawdust in a drop tube reactor at low temperatures (573-873 K) and commonly used in single particle modelling [1,12,296,297]. The devolatilization kinetics of Johansen et al. [35] (HT) is derived from small wood particles (< 0.1 mm) devolatilization in an entrained flow reactor at high temperatures (1473-1873 K). To cover a wide range of temperatures, Johansen et al. [1] proposed a combination of the low temperature kinetics (T < 800 K, Wagenaar et al. [72]) and the high temperature kinetics (T ≥ 800 K, Johansen et al. (HT) [1]). The devolatilization kinetics of Roberts and Clough [302] was derived from a single beech wood particle devolatilization with a heating rate of 20 K/min at low temperatures (548-708 K). The devolatilization kinetics of Johansen et al. [35] (TGA) was derived by TGA using a heating rate of 2 K/min. According to Fig. 6 (b), the kinetics of Johansen et al. (HT) [1] underestimate the devolatilization time, because it is too fast at low temperatures (it is 10⁶ times faster than that of Wagenaar et al. [72] when the temperature is < 673 K). The devolatilization kinetics of Wagenaar et al. [72] and Johansen et al. (Two) [1] lead to a similar particle conversion history. This implies that the volatile is almost fully released at low temperatures (< 873 K) during the devolatilization of the 4 mm particle. Therefore, it is more reasonable to use the kinetics derived at low temperatures (< 873 K) in the single particle model for large particles. Although the devolatilization kinetics of low temperature (Wagenaar et al. [72], Roberts and Clough [66], and Johansen et al. [35] (TGA)) are significantly different (a magnitude of -2 to 7, Wagenaar et al. [72] as basis), the devolatilization times predicted by different devolatilization kinetics (Wagenaar et al. [72]: 9.50s, Roberts and Clough [66]: 11.71s, Johansen et al. [35] (TGA): 12.45s) have a maximum difference of 31%. Therefore, for the devolatilization of large particles at high temperatures, low-temperature devolatilization kinetics should be chosen in the modelling, and the modelling results are not sensitive to the selected low-temperature devolatilization kinetics.
Fig. 3. 6 (a): five devolatilization kinetics (Wagenaar et al. [72], Johansen et al.[35] high temperature kinetic: Johansen et al. (HT), Johasnen et al.[1] two regime kinetics ($T \geq 800$ K, Johansen et al. (HT), $T < 800$ K, Wagenaar et al.); Johasnen et al. (Two), Johansen et al. [35] TGA kinetic: Johansen et al. (TGA), and Roberts and Clough’s kinetic [66]); (b): The effects of five devolatilization kinetics on modelling results. (Beech wood, $T_s = 1487$ K, $T_w = 1287$ K, $M_c = 4.9$ ar%, Vol = 83.7 db%, FC = 15.7 db%, Ash = 0.6 db%, $d_p = 4$ mm, $\rho_{DB} = 800$ kg/m$^3$).

Fig. 3. 7 shows the results of a variation of the devolatilization rate by 0.1 and 10 times of the Wagenaar et al. [72] for different size wood particles devolatilized at 1487 K. Again, the devolatilization rate has limited impact on the devolatilization time of large particles ($d_p = 1$ mm ($\leq \pm 25\%$) and $d_p = 10$ mm ($\leq \pm 15\%$)). The influence of the devolatilization rate on devolatilization time becomes larger for a small particle (up to $\pm 60\%$). It indicates that the regime of biomass devolatilization transits from the heat transfer dominated regime to a kinetically controlled regime with decreasing particle size from 10 mm to 0.1 mm.

Fig. 3. 7 Sensitivity analysis of the influence of devolatilization rate and particle size on devolatilization time. The dash (---) line are the $\pm 25\%$ deviation line based on the results of using Wagenaar et al. kinetics ($T_s = 1487$ K, $T_w = 1287$ K, $M_c = 4.9$ ar%, Vol = 83.7 db%, FC = 15.7 db%, Ash = 0.6 db%).
3.5 Simple correlation for devolatilization time

According to the results and discussion in section 3.4, the devolatilization time is sensitive to gas/wall temperature, moisture content, particle density, gas temperature, and particle size, and insensitive to volatile content. The devolatilization time is found to increase linearly with the increase of particle density. A range of material properties (such as particle density, size) can influence the devolatilization time. However, the different wood species seem to be relatively similar with respect to their material properties. If a change in wood density is accounted for, the devolatilization time can be calculated. Therefore, it is possible to derive a theoretical based simple correlation to estimate the devolatilization time based on our detailed devolatilization model. In this way, the devolatilization time can be estimated by readily measurable properties (such as particle density, size, and operation conditions).

3.5.1 Parametric analysis

To derive a correlation to predict devolatilization time, a parametric analysis of gas velocity, gas temperature, and moisture content is described in the following section.

3.5.1.1 Effects of gas velocity

According to Fig. 3. 5, it seems that by changing the convection heat transfer coefficient by ±50%, the predicted devolatilization time is changed only by about 10%. A change in the gas velocity influences the external convective heat transfer coefficient and thereby the devolatilization time. Fig. 3. 8 shows an analysis of the influence of gas velocity. The devolatilization time is insensitive to gas velocity for 10 mm particles, because the contribution of convection is small compared to radiative heat transfer. The gas velocity seems to have a maximum of 18% effect on the predicted devolatilization time for small wood particles with \( d_p = 1 \) mm and 0.1 mm. However, such a difference is acceptable due to the shorter devolatilization time (< 2s) for particle sizes smaller than 1 mm.
3.5.1.2 Effects of gas temperature

Fig. 3. 9 shows the influence of gas temperature on predicted devolatilization time for different particle size \( (d_p = 0.1 \text{ mm}, 1 \text{ mm}, 10 \text{ mm}) \) with a various of particle density. The predicted devolatilization times decrease with an increase of gas temperature, consistent with other studies \([1,281,283,303]\). Moreover, the predicted devolatilization time increases linearly with the increase of particle density for all selected temperatures.

3.5.1.3 Effects of moisture content

Fig. 3. 10 show the results of model calculations for different particle size \( (d_p = 0.1 \text{ mm}, 1 \text{ mm}, 10 \text{ mm}) \) and moisture content \( (0.0 \text{ db\%}, 20.0 \text{ db\%}, 50.0 \text{ db\%}) \) devolatilized at \( T_g = 1473 \text{ K} \).
With the increase of moisture content from 0.0% to 50.0%, the devolatilization time is delayed 45%, 54%, and 68% for \( d_p = 0.1 \text{ mm} \), \( d_p = 1 \text{ mm} \), and \( d_p = 10 \text{ mm} \), respectively. The predicted devolatilized times increase with moisture content as also reported in previous studies [12,16,277].

3.5.2 Simple devolatilization time model

According to the sensitivity analysis in section 3.4.3 and the parametric analysis in section 3.5.1, we can conclude that the devolatilization time is sensitive to particle size, gas temperature, moisture content, and particle density. According to the sensitivity analysis shown in Fig. 3. 5, it is seen that changing the fixed carbon content of 20% by ±10% does not have a significant influence on devolatilization time. The reason is that the devolatilization of millimetre-sized biomass particles is controlled by internal and external heat transfer and the heat of devolatilization, which is not significantly affected by volatile content. The devolatilization time is relatively insensitive to gas velocity as shown in Fig. 3. 8, and the devolatilization kinetics have a limited influence on the predicted devolatilization time for large particles. According to the experimental results in section 3.4.2 and the parametric analysis in section 3.5.1, the devolatilization time increases linearly with the particle density when the gas temperature, moisture content, and particle size are constant. Therefore, it is possible to derive a simple correlation to predict devolatilization time,

\[
\tau_{\text{dev}} = f\left(d_p, M_c, T_g\right) \rho_{DB}
\]  

(3.8)

Here, \( f(d_p, M_c, T_g) \) is a function to correlate particle density and devolatilization time. To correlate the function of \( f(d_p, M_c, T_g) \), a series of data with changing particle density, particle size, gas temperature, and moisture content are generated by using the comprehensive

Fig. 3. 10 Parameter analysis influence of moisture content on modelling results of different particle sizes. (\( V_g = 3 \text{ m/s} \), \( T_g = 1473 \text{ K} \), Vol = 88.0 db%, FC = 12.0 db%, Ash = 0.0 db%)
devolatilization model in section 3.2. Then \( f(d_p, M_c, T_g) \) is fitted from the data based on Eq. (3.8). The variation of particle density, particle size, gas temperature, and moisture content used to generate database are listed as below:

1. Particle density: 50-800 kg/m\(^3\) with an increment step of 50 kg/m\(^3\), 900-1200 kg/m\(^3\) with an increment step of 100 kg/m\(^3\), the number of points is 20.
2. Particle size: 0.1-1 mm with an increment of 0.1 mm, 1.5-10 mm with an increment step of 0.5 mm, the number of points is 37.
3. Gas temperature: 1073, 1273, 1373, 1473, 1573, 1673, 1773, and 1873 K
4. Moisture content: 6 moisture contents as dry basis: 0%, 10%, 20%, 30%, 40%, 50%.

The matrix size of the generated database is 20×37×8×6.

3.5.3 Discussion of \( f(d_p, M_c, T_g) \)

Fig. 3.11 (a) presents the effect of gas temperature on the value of \( f(d_p, M_c, T_g) \). The \( f(d_p, M_c, T_g) \) monotonically and nonlinearly decreases with temperature. A monotonically nonlinear function with the formulation of \( (a+b/(T_g c)) \) is selected to represent the influence of gas temperature. Fig. 3.11 (b) shows that the value of \( f(d_p, M_c, T_g) \) monotonically and nonlinearly increases with moisture content. Thus, a polynomial function with the formulation of \( (dM_c + eM_c^2) \) is selected to represent the influence of particle moisture content. According to Fig. 3.11 (a) and Fig. 3.11 (b), \( f(d_p, M_c, T_g) \) monotonically and nonlinearly increases with particle size. A typical power-law expression: \( f_d p n \), as reported in references [281,283,303], is selected to represent the influence of particle size. The value of the coefficient \( n \) is in a range of 1-2 as discussed by Diego et al. [283]. Finally, the Eq. (3.9) is suggested to be used for the calculation of devolatilization time.

\[
\tau_{dev} = f \left( d_p, M_c, T_g \right) \rho_{DB} = \left( a + \frac{b}{T_g} + dM_c - eM_c^2 \right) f_d p \rho_{DB} \quad (3.9)
\]

Here, \( a, b, c, d, e, f \), and \( n \) are coefficients that are fitted from the devolatilization time calculated by using the devolatilization model. With a rearrangement, the simple correlation to predict the devolatilization time can be expressed by Eq. (3.10).

\[
\tau_{dev} = 0.0209 \left( 1000 d_p \right)^{1.86} \left( 0.0072 + \frac{0.0591}{(T_g/1000)^{0.3}} \right) + 0.0440M_c - 0.0117M_c^2 \rho_{DB} \quad (3.10)
\]

Here, \( d_p \) is particle size, \( m \), \( T_g \) is gas temperature, \( K \), \( M_c \) is particle moisture content (dry based), and \( \rho_{DB} \) is particle density, kg/m\(^3\).

The value of \( n \) is 1.86 in good agreement with the range found in other studies [281,283,303]. Since the correlation is used to describe a spherical wood particle, \( d_p \) should be the equivalent particle diameter (diameter of a sphere having the same volume as the particle) multiplied by the shape factor (surface area of a sphere having the same volume as the initial particle/initial...
surface area of the particle) for non-spherical particle as suggested by Diego et al. [283]. In some cases, when the gas temperature is different from the wall temperature, a modification of using the average temperature of the gas and the wall is recommended.

![Fig. 3.11](image)

(a) Gas Temperature  
(b) Moisture Content

\[ f(d_p, M_c, T_e) \]

3.5.4 Model validation

To evaluate the simple correlation, the devolatilization time calculated by Eq. (3.10) were compared with experimental data from other studies as shown in Fig. 3. 12. The experimental data include both single particle experiments with temperature higher than 1273 K [131,153,275,278,279] and lower than 1273 K [12,279]. Even though the experimental data from Lu et al. [153,278] were obtained from various conditions (e.g., wood with and without torrefaction, torrefaction temperature and time, KCl content, etc.), the correlation gives a reasonable estimation of the devolatilization time. Although the generated database used to obtain Eq. (3.10) is for temperature higher than 1273 K, it still gives a reasonable estimation of devolatilization time in single particle combustor for the low-temperature cases as shown in Fig. 3. 12 (b). Generally, the predicted results agree with the experiments within about ±25%, it is acceptable in engineering applications. While other empirical correlations [277,281,283,303] were obtained in specified experimental conditions, this simple correlation based on the comprehensive model validated by experimental data obtained from different experimental setup with different operating conditions, it appears to be applicable in a wide range of conditions with known operating temperature (1273-1873 K), particle size (0.1-10 mm), particle density (50-1200 kg/m³) and moisture content (0-50 db%). It should be noted that the simple correlation is only validated with the experimental particle size (1-10 mm.) in this work, the uncertainty of the simple model may increase for small particle size (e.g. 0.1 mm) which the effects of kinetics on devolatilization become significant.
Fig. 3. 12 Comparison of single particle experimental and predicted devolatilization time from various references: Fig. 13 (a): Momeni et al. [275] ($d_p$: 1.65-3.0mm, $T_g$ = 1473 K, $T_w$ = 1273 K (estimated)), Lu et al. (2016) [278] ($d_p$: 3.00-5.00 mm, $T_g$ = 1504 K, $T_w$ = 1304 K (estimated)), Cereijo et al. [131] ($d_p$: 1.0-5.0 mm, $T_g$ = 1823 K, $T_w$=1123 K), Lu et al. (2017) [153] ($d_p$: 3.00-5.00mm, $T_g$ = 1498 K, $T_w$ = 1298 K (estimated)); Fig. 13 (b): Anca-Couce et al. [304] ($d_p$: 9.9 mm, $T_g$ = $T_w$=823-1223 K); Remacha et al. [279] ($d_p$: 3.0-15.0mm, $T_g$ = 1653 K, $T_w$ = 723 K), Lu et al. [12] ($d_p$: 9.5 mm, $T_g$ =1050 K, $T_w$ = 1276 K).

3.6 Summary

A comprehensive biomass devolatilization model based on the work of Johansen et al. [1] was improved to simulate single particle devolatilization experiments at temperatures from 1473 to 1723 K. The model accounts for internal and external heat transfer, water evaporation and devolatilization kinetics. The comprehensive devolatilization model was validated by the experimental data. Both experiments and modelling show that the devolatilization time increases linearly with the increase of particle density.

A sensitivity analysis showed that the devolatilization time predicted by the comprehensive model is influenced significantly by material thermal properties, such as particle heat capacity, particle conductivity and enthalpy of pyrolysis reactions. The devolatilization kinetics have limited effects on the simulated devolatilization time for large wood particles (> 1mm), suggesting that the devolatilization process is mainly heat transfer controlled. The particle density, size, gas temperature, and moisture content have significant effects on the devolatilization time, while parameters, such as the mass fraction of volatile, gas velocity, only have small influences. Therefore, the devolatilization time is reasonably well predicted using one set kinetics by changing the moisture content, particle density, particle size, and gas temperature for different woody biomass particles.

Based on the finding that the devolatilization time increases linearly with the increase of particle density, a simple devolatilization correlation was derived from the 1D model and validated by experimental data from other references. The results show that the correlation can be used to predict the devolatilization time with an accuracy of ±25% for millimeter-sized woody biomass particles under different operating conditions.
4 Modelling char conversion in a single particle combustor

The main objective is to develop a comprehensive char conversion model for woody biomass. The comprehensive char conversion model is validated by the experimental results carried out at the CHEC researcher centre, DTU Chemical Engineering.

4.1. Introduction

In biomass combustion, the heterogeneous char reactions, i.e. char oxidation and gasification with H2O and CO2, occur simultaneously [30,52]. The char oxidation is commonly in a mass transfer limited regime [7]. However, the char gasification rate and the intra-particle mass transfer rate may be comparable, with the char gasification process controlled by intra-particle mass transfer, external mass transfer, and gasification kinetics [22]. As a result, the progressive char conversion model [21–26] is commonly used to model with both combustion and gasification reactions, while the shrinking particle model is commonly used in modelling char combustion [101,305]. Mermoud et al. [21] have carried out an experimental and numerical study of steam gasification of biomass char particles under a gas temperature of 1100-1300 K and steam partial pressure of 0.1-0.4 atm. They found that the gasification process was controlled by both intra-particle mass transfer and gasification kinetics [21]. Van de steene et al. [25] found that the oxidation of biomass char particle was limited by external mass transfer. Fatehi and Bai [22] developed a model including both char oxidation and gasification, with the effects of pore size distribution on intra-particle transport included.

The homogeneous reactions (e.g. CO oxidation, water-gas shift reaction, H2 oxidation) in the particle boundary layer were ignored in the above-mentioned models. It may be a reasonable assumption at low temperatures (< 1273 K) when the gas phase reaction rates are relatively slow. However, the oxygen transferred from bulk gas to the external particle surface may be consumed by CO and H2 oxidation in the boundary layer, resulting in a reduced char oxidation rate [110]. The water-gas shift reaction may affect the CO2 and H2O concentration on the particle surface, and thereby influence the gasification rates. According to a progressive char conversion model for coal combustion [110,306–311], CO oxidation in the particle boundary layer inhabits the char conversion process. Bhunia et al. [110] investigated the combustion of single coal char particles under a gas temperature of 1100 K and oxygen concentration of 40-60%, and found that the CO oxidation in the boundary layer consumed approximately 30% O2 transferred from bulk gas to char particle. Singer and Ghoniem [27] developed a comprehensive model for char conversion with validation of experiments with small char particles (~100 µm), but they neglect the water-gas shift reactions in the modelling. Karlström et al. [28,29] developed a char conversion model for 6-10 mm biomass char particles and validated the model by using experimental data from a single particle combustor with relatively low temperature
(1073-1323 K). However, the existing models have been mainly focused on the combustion of biomass char particles under conditions relevant for fluidized bed combustion. In pulverized biomass fired power plants, the biomass particles usually have a size of 100 µm to several millimetres. The char conversion takes place at high temperature conditions (> 1273 K) with a lower oxygen concentration (< 5%) and high steam and CO₂ concentration (> 10%). Based on the fuel properties and the reaction conditions, it is expected that both char oxidation and gasification are important for char conversions. A validated model that can describe the conversion of biomass char particles under pulverization conditions is rarely reported.

This chapter presents a comprehensive progressive char conversion model for biomass char conversion that is applicable in pulverized biomass combustion conditions. Experiments with spherical wood char particles were carried out in a single particle combustor under different temperatures (1473-1723 K) and gas atmosphere conditions (Oxygen concentration of 0.0-10.5 vol% and steam concentration of 25-40 vol%). The model was validated by the experimental data. Finally, a sensitivity analysis of the developed char conversion model was carried out.

4.2 Model description

4.2.1 Model assumption

Both char oxidation (Char-O₂) and gasification (Char-H₂O and Char-CO₂) are assumed to take place in the internal char particle, and homogeneous reactions (CO oxidation, H₂ oxidation, and water-gas shift reaction) are assumed to only occur in the particle boundary layer. The external and internal heat and mass transfer, and the particle shrinkage are considered in the model. The other assumptions of the model are listed below:

(1) A one-dimensional model for spherical wood char particle, since the wood char particle is assumed to be isotropic.

(2) The effect of Stefan flow on the heat transfer is neglected, because the heat transfer in a char conversion process is dominated by radiation at high temperatures [12,30].

(3) Since the internal pressure gradient is small during char conversion [312], the velocity of outflow gas is much smaller than that of the bulk gas flow. Therefore, the effect of Stefan flow on mass transfer is also neglected [308].

(4) The specific surface area for wood chars spreads over a large range as summarized by Haberle et al. [313], and it also changes along with the char conversion [22]. For simplicity, it is assumed to a constant specific surface area of 1.0×10⁶ m²/m³ [12].

(5) The ash content of the char particle is assumed to be 1.5%, because of low ash content of woody biomass and the ash content in the char particle does not measure directly during the experiments.
According to our experiments, the char particle size decreases along with the char conversion. The shrinkage of a char particle is modelled by assuming ash peeling off when the char conversion is over 0.95.

The char conversion time is determined by 95% conversion of char particle.

4.2.2 Kinetics of heterogeneous reactions

The following heterogeneous reactions of char oxidation (R₁), CO₂ gasification (R₂), and H₂O gasification (R₃) are included in the model:

\[
\begin{align*}
C + \frac{\eta + 2}{2\eta + 2}O_2 &\rightarrow \frac{\eta}{\eta + 1}CO + \frac{1}{\eta + 1}CO_2, \quad \Delta H_1 = -\frac{110.5\eta}{\eta + 1} - \frac{393.5}{\eta + 1} \text{ kJ/mol} \\
C + CO_2 &\rightarrow 2CO, \quad \Delta H_2 = 172.5 \text{ kJ/mol} \\
C + H_2O &\rightarrow CO + H_2, \quad \Delta H_3 = 131.0 \text{ kJ/mol}
\end{align*}
\]

The CO/CO₂ ratio (\(\eta\)) depends on the temperature and oxygen concentration. The expression, Eq. (4.1), derived by Tognotti et al. [107] is used, because it is validated at high temperatures up to 1670 K which is close to our experimental conditions.

\[
\eta = 69.39\exp\left(\frac{-3070}{T_p}\right)
\]

(3.11)

The kinetics of heterogeneous reactions can be expressed as below:

\[
r_i = -\frac{1}{m_c} \frac{dm}{dt} = k_i P_i^m F\left(X_i\right)
\]

(3.12)

Here, \(m_c\) is the mass of char particle, kg, \(t\) is time, s, \(P_i\) is the partial pressure of gaseous component (\(i\)), bar, \(k_i\) is followed by Arrhenius equations as shown in Eq. (4.3), bar·s⁻¹, \(F(X_i)\) is a char reactivity function which describes the effect of char structure change on its reactivity.

\[
k_i = k_{i,0} \exp\left(\frac{-Ea_i}{RgT_p}\right)
\]

(3.13)

Here, \(Ea_i\) is the activation energy of reactions \(i\), \(R_g\) is the gas constant, J/(mol·K), \(T_p\) is the temperature, K.

It has been reported that the inorganic elements (especially potassium, K) have significant effects on char reactivity [153,154]. In our experiments, the beech wood (1700 mg/kg) has much higher potassium content than that of the pine wood (150 mg/kg) as shown in Table 3.3, implying the gasification reactivity of beech wood char is higher than the pine wood char.

Therefore, the char oxidation and gasification kinetics of the pine [25] and beech char [314] are selected accordingly, as shown in Table 4.1. The kinetics are derived from the wood char particles produced under a high heating rate, which is similar to our experiments. For the
combustion kinetics of beech wood char, the kinetics of Di Blasi et al. [315] was selected, since it was validated by previous studies [24, 159, 170].

### Table 4. 1 kinetic parameter for char combustion and gasification

<table>
<thead>
<tr>
<th></th>
<th>n</th>
<th>$E_a$ (kJ/mol)</th>
<th>$k_0$ (bar$^{n}$s$^{-1}$)</th>
<th>$F(X_i)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Kinetics of pine wood char</td>
</tr>
</tbody>
</table>
| O$_2$ | 0.6| 179.4         | $1.0\times10^9$           | $F(X_i) = 94.95X_i + 190.37X_i + 143.28X_i$  
|       |    |               |                            | $- 47.08X_i + 6.14X_i + 0.29$ |
| CO$_2$| 0.7| 245.0         | $1.2\times10^8$           | $F(X_i) = 94.90X_i - 187.23X_i + 135.12X_i$  
|       |    |               |                            | $- 40.59X_i + 5.55X_i + 0.65$   |
| H$_2$O| 0.8| 170.0         | $3.55\times10^5$          | $F(X_i) = 64.16X_i - 129.72X_i + 94.35X_i$  
|       |    |               |                            | $- 29.39X_i + 4.51X_i + 0.29$   |

|       |    |               |                            | Kinetics of beech wood char |
| O$_2$ | 1.0| 228.6         | $4.85\times10^{14}$       | $F(X_i) = (1 - X_i)^{1.16}$ |
| CO$_2$| 0.55| 154.0         | $5.52\times10^4$          | $F(X_i) = -0.00823X_i + 0.02038X_i + 0.11367X_i$  
|       |    |               |                            | $+ 0.23074X_i + 0.56013X_i + 1.12488$ |
| H$_2$O| 0.64| 139.0         | $2.63\times10^4$          | $F(X_i) = 0.014422X_i + 0.081024X_i + 0.1379X_i$  
|       |    |               |                            | $+ 0.2142X_i + 0.5254X_i + 1.1175$     |

### 4.2.3 Kinetics of homogeneous reactions

The CO oxidation (R$_4$), water-gas shift reaction (R$_5$), and H$_2$ oxidation (R$_6$) have been selected to represent the homogeneous reactions in the particle boundary layer. The reaction rates of R$_4$-R$_6$ are expressed by using the global kinetics as listed in Table 4. 2.

$$
\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2, \quad \Delta H_4 = -283.0 \text{ kJ/mol} \quad (R_4)
$$

$$
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2, \quad \Delta H_5 = -41.0 \text{ kJ/mol} \quad (R_5)
$$

$$
\text{H}_2 + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O}, \quad \Delta H_6 = -242.0 \text{ kJ/mol} \quad (R_6)
$$

### Table 4. 2 The global reaction kinetics of CO oxidation, water-gas shift reaction, and H$_2$ oxidation

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Expressions (kmol/m$^3$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$_4$</td>
<td>$r_i = 1.3\times10^3 \exp \left(\frac{-126000}{R_i T} \right) C_5^{1.5} C_i$</td>
<td>[7]</td>
</tr>
<tr>
<td>R$_5$</td>
<td>$r_i = 2.78\times10^4 \exp \left(\frac{-126000}{R_i T} \right) \left( C_5 C_i - \frac{C_i C_4}{0.0265 \exp(3968/T)} \right)$</td>
<td>[7]</td>
</tr>
<tr>
<td>R$_6$</td>
<td>$r_i = 5.16\times10^3 T^{-1.5} \exp \left(\frac{-28500}{R_i T} \right) C_5^{1.5} C_i$</td>
<td>[7]</td>
</tr>
</tbody>
</table>

$C$ is the molar concentration of gaseous species, $i = 1, 2, 3, 4, 5, 6$ represents O$_2$, CO$_2$, H$_2$O, H$_2$, CO, and N$_2$, respectively.

### 4.2.4 Governing equations

The conservation equation of the gaseous species $i$ inside a char particle is,
\[
\frac{\partial (\varepsilon_g \rho_g Y_{g,i})}{\partial t} = \frac{\partial}{\partial r} \left( r^2 \varepsilon_g \rho_g D_{\text{eff}} \frac{\partial Y_{g,i}}{\partial r} \right) + S_{g,i}, \quad \left( 0 \leq r < \frac{d_r}{2} \right) \quad (3.14)
\]

The conservation equation of the gaseous species \( i \) in the boundary layer is,
\[
\frac{\partial (\rho_g Y_{g,i})}{\partial t} = \frac{\partial}{\partial r} \left( r^2 \rho_g D_{m,i} \frac{\partial Y_{g,i}}{\partial r} \right) + S_{g,i}, \quad \left( \frac{d_r}{2} < r \leq \delta + \frac{d_r}{2} \right) \quad (3.15)
\]

The conservation equation of heat balance inside a char particle is,
\[
\frac{\partial \left( \rho_g \sum_{i=1}^{N_y} Y_{g,i} C_{pg,i} T \right)}{\partial t} = \frac{\partial}{\partial r} \left( r^2 \rho_g \lambda_{\text{eff}} \frac{\partial T}{\partial r} \right) + \sum_{i=1}^{N_y} r_i \Delta H_i, \quad \left( 0 \leq r < \frac{d_r}{2} \right) \quad (3.16)
\]

The conservation equation of heat balance in the boundary layer is,
\[
\frac{\partial \left( \rho_g \sum_{i=1}^{N_y} Y_{g,i} C_{pg,i} T \right)}{\partial t} = \frac{\partial}{\partial r} \left( r^2 \rho_g \lambda_{\text{eff}} \frac{\partial T}{\partial r} \right) + \sum_{i=1}^{N_y} r_i \Delta H_i, \quad \left( \frac{d_r}{2} < r \leq \delta + \frac{d_r}{2} \right) \quad (3.17)
\]

At the particle external surface, \( r = d_r/2 \), the mass and heat balance are calculated as follows:
\[
\varepsilon_g \rho_g \Delta V_s \frac{\partial Y_{g,i}}{\partial t} + \rho_g \Delta V_g \frac{\partial Y_{g,i}}{\partial t} = D_{m,i} \rho_g S_p \frac{\partial Y_{g,i}}{\partial r} + S_{s,i} \Delta V_s + S_{g,i} \Delta V_g - \varepsilon_g D_{\text{eff},i} \rho_g S_p \frac{\partial Y_{g,i}}{\partial r} \quad (3.18)
\]

\[
\frac{\partial}{\partial t} \left( \rho_c C_{pc} + \rho_a C_{pa} + \varepsilon_g \rho_g \sum_{i=1}^{N_y} Y_{g,i} C_{pg,i} \right) \Delta V_s \frac{\partial T}{\partial t} + \rho_g \sum_{i=1}^{N_y} Y_{g,i} C_{pg,i} \frac{\partial T}{\partial r} \Delta V_g = \lambda_s S_p \frac{\partial T}{\partial r} + \sum_{i=1}^{N_y} r_i \Delta H_i \Delta V_s + \sum_{i=1}^{N_y} r_i \Delta H_i \Delta V_g + Q_{\text{rad}} - \lambda_{\text{eff}} S_p \frac{\partial T}{\partial r} \quad (3.19)
\]

Here, \( S_p \) is particle external surface, \( \Delta V_s \) and \( \Delta V_g \) is the volume of solid and gas at the particle external surface layer. If Eqs. (4.4)-(4.9) are discretized with grid size \( \Delta r_s \) and \( \Delta r_g \), respectively, \( \Delta V_s \) and \( \Delta V_g \) is approximated as Eq. (4.10) and Eq. (4.11) by using centre difference method,
\[
\Delta V_s = \frac{\pi d_r^2 \Delta r_s}{2} \quad (3.20)
\]
\[
\Delta V_g = \frac{\pi d_r^2 \Delta r_g}{2} \quad (3.21)
\]

The mass balance of char and ash inside wood char particle is,
\[
\frac{\partial \rho_c}{\partial t} = - \sum_{i=1}^{N_y} \varepsilon_i \quad (3.22)
\]
\[
\frac{\partial \rho_a}{\partial t} = 0 \quad (3.23)
\]

69
In Eqs. (4.4)-(4.13), \( \rho_c \) is the char density, kg/m\(^3\), \( \rho_a \) is ash density, kg/m\(^3\), \( \rho_g \) is the gas density, kg/m\(^3\), \( r_i \) is the reaction rate of reaction \( R_1-R_6 \), \( \varepsilon_g \) is the particle voidage. \( T \) is the temperature, K, \( \lambda_{ef} \) is the effective heat conductivity of char particle, W/(m-K). \( \lambda_g \) is the heat conductivity of gas mixtures, W/(m-K). \( \delta \) is the averaged boundary layer thickness, m. \( D_{ef,i} \) is the effective mass diffusion coefficients in char particle, m\(^2\)/s. \( D_{m,i} \) is the mass diffusion coefficient of component \( i \) in gas mixtures. \( C_{pc}, C_{pa}, \) and \( C_{pg,i} \) is the heat capacity of char, ash and gas species \( i \), respectively, J/(kg·K). \( S_{si} \) and \( S_{gi} \) is the source term of gas species \( i \) in the char particle and the particle boundary layer, respectively, kg/m\(^3\)/s, which can be found in Appendix B. \( Y_{g,i} \) is mass fraction of gas species \( i \) in gas mixtures, \( i = 1, 2, 3, 4, 5, 6 \) represents \( \text{O}_2, \text{CO}_2, \text{H}_2\text{O}, \text{H}_2, \text{CO}, \) and \( \text{N}_2 \), respectively.

The sum of all gas species in the gas phase should be unity,

\[
\sum_{i=1}^{6} Y_{g,i} = 1 \tag{3.24}
\]

The effective diffusion coefficients for each gas species inside a char particle can be obtained based on the combined Knudsen and bulk diffusion coefficients with considering the influence of the porous structure of the particle [22].

\[
D_{ef,i} = \frac{\varepsilon_g}{\tau} \left( \frac{1}{D_{Kn,i}} + \frac{1}{D_{m,i}} \right)^{-1} \approx \varepsilon_g^2 \left( \frac{1}{D_{Kn,i}} + \frac{1}{D_{m,i}} \right)^{-1} \tag{3.25}
\]

The Knudsen diffusion coefficient for species \( i \) is calculated based on the following expression,

\[
D_{Kn,i} = \frac{d_{pore}}{3} \sqrt{\frac{8RT}{\pi M_i}} \tag{3.26}
\]

Where \( M_i \) is the molecular weight of species \( i \), and \( R_g \) is the universal gas constant. \( d_{pore} \) is the pore diameters, which can be calculated by assuming the pore inside a wood char particle is cylindrical pore,

\[
d_{pore} = \frac{4\varepsilon_g}{S_r} \tag{3.27}
\]

Here, \( S_r \) is the specific surface area, m\(^2\)/m\(^3\), which is assumed to be a constant value 1.0×10\(^6\) m\(^2\)/m\(^3\) as discussed in model assumptions.

The particle voidage is calculated by assuming wood real density of 1500 kg/m\(^3\).

\[
\varepsilon_g = \frac{\rho_c + \rho_a}{1500} \tag{3.28}
\]

The binary diffusion coefficient of species \( i \) in the mixture depends on the gas composition and temperature, which can be calculated as below [22,23],

\[
D_{m,i} = \frac{1-Y_{g,i}}{\sum_{j=1}^{N} X_{g,j}/D_{g,j}} \tag{3.29}
\]
Where \( D_{ij} \) is the binary diffusion coefficient, which is calculated by Lennard-Jones Equation [316]. \( N \) is the total number of gas species, \( X_{g,i} \) is the mass fraction of other gas species \( i \) in the gas mixtures.

The density of the gas is calculated by ideal gas law,

\[
\rho_g = \frac{\rho \bar{M}}{R_g T}
\]  

(3.30)

\( P \) is the pressure which is assumed to the same as bulk gas pressure, Pa, and \( \bar{M} \) is the molecular weight of gas mixtures, kg/mol.

The boundary layer thickness for the concentration of gas species, \( \delta_{m,i} \) \((i=1-6)\) and the temperature \( \delta_T \) is defined as below [28]:

\[
\delta_{m,i} = \frac{d_p}{Sh_i - 2}
\]  

(3.31)

\[
\delta_T = \frac{d_p}{Nu - 2}
\]  

(3.32)

Here, \( Sh \) is the Sherwood number, and \( Nu \) is the Nusselt number. The temperature and each species have different boundary layer thicknesses [28]. The Sherwood number and Nusselt number of a single particle are determined by the Ranz and Marshall equation [221].

\[
Nu = 2 + 0.6Re^{0.5}Pr^{1/3}
\]  

(3.33)

\[
Sh_i = 2 + 0.6Re^{0.5}Sc_i^{1/3}
\]  

(3.34)

Where the Reynolds number, Prandtl number, and Schmidt number are calculated as,

\[
Re = \frac{d_p \mu_s \rho_b}{\mu_b}, \quad Pr = \frac{C pb \mu_b}{\lambda_b}, \quad Sc_i = \frac{\mu_b}{D_{mb,i} \rho_b}
\]  

(3.35)

Where \( u_s, \rho_b \), and \( \mu_b \) is the slip velocity, gas density, and viscosity of bulk gas, \( \mu_b \) and \( D_{mb,i} \) is the viscosity and mass diffusion coefficient of gas species \( i \).

According to Eq. (22) and (23), the boundary layer thickness of temperature and each gas species is different. The averaged boundary layer thickness, \( \bar{\delta} \), defined as Eq. (4.26), is adopted to simplify the implementation of a numerical method for solving the governing equations, Eq.(4.4)-Eq. (4.14),

\[
\bar{\delta} = \frac{\sum_{i=1}^{6} \delta_{m,i} + \delta_T}{7}
\]  

(3.36)

The heat conductivity of the char particle is obtained from Johansen et al. [1], as shown in Eq. (4.27). The heat conductivity in the boundary layer is equal to the heat conductivity of gas mixture (\( \lambda_g \)), which is calculated by the mass weighted heat conductivity of gas species. The
heat conductivity of gas species can be found in the database of DIPPR system (https://dippr.aiche.org/).

\[ \lambda_{\text{eff}} = \lambda_c + \lambda_g \varepsilon_g + \frac{d_{\text{pore}} T^3}{\xi} \]  

(3.37)

Here, \( \lambda_c \) is the heat conductivity of char, it is assumed to be 0.071 W/(m\(^2\) K) [12,18,288,289]. \( \xi \) and \( \sigma \) are emissivity (0.85) and Stefan-Boltzmann constant (5.6704\times 10^{-8} J/(m\(^2\) K\(^4\) s)), respectively.

The heat capacity (J/(kg K)) of char [1,12,293] and ash [101] can be described as Eq. (4.28) and (4.29), respectively.

\[ C_{pc} = \frac{1000 R_g}{11.3} \left( g \left( \frac{380}{T} \right) + 2 g \left( \frac{1800}{T} \right) \right) \]

(3.38)

\[ C_{pa} = 594 + 0.586T \]

(3.39)

Where,

\[ g(x) = \frac{x^2 \exp(x)}{\left( \exp(x) - 1 \right)^2} \]

(3.40)

The heat capacity of gas species \( i \) can be found in the database of NIST Chemistry Webbook (https://webbook.nist.gov/chemistry/). The heat capacity of gas is based on mass weighted method.

Followed by Karlström et al. [28], the radiation heat transfer is calculated by adding a source term,

\[ Q_{\text{rad}} = S_p \sigma \xi (T_w^4 - T_s^4) \]

(3.41)

Here, \( T_w \) is the wall temperature of the single particle combustor, and \( T_s \) is the temperature of the external surface of the particle. The wall temperature of the SPC is estimated to be 200 K lower than the gas temperature in the SPC centre, according to radial temperature distribution measured in our previous experiments [275,278].

The boundary conditions for the governing equations, Eq. (5)-Eq. (10), are

\[ T_{r=\delta+d_s/2} = T_{b,i}, \quad Y_{r=\delta+d_s/2} = Y_{b,i} \]

(3.42)

At the centre of the particle, the gradient of pressure, temperature and all species are zero due to particle symmetry:

\[ \frac{\partial T}{\partial r}_{r=\delta+d_s/2} = 0, \quad \frac{\partial Y}{\partial r}_{r=\delta+d_s/2} = 0 \]

(3.43)

The initial char particle temperature is assumed to be 873 K, because the drying and devolatilization process ends at this temperature according to the studies of Chapter 3, and the char oxidation and gasification rates are relatively slow below this temperature.
4.2.5 Numerical method

A fully implicit finite difference method [317] is employed to solve the governing equations with their initial and boundary conditions. The discretized governing equations at each grid point are presented as a set of linear algebraic equations by using the central difference method [317]. The linear algebraic equations are solved by using Tri-Diagonal Matrix Algorithm. The char particle is divided into 900 cells inside the particle and 100 cells in the particle boundary layer in the radial direction. The time-step size is set to $10^{-3}$ s. According to our modelling results shown in Appendix B, the above grid and time-step size can obtain grid and time-step size independent results for millimeter-size char particle. The time-step size may reduce for modelling smaller particles (e.g. 0.1 mm), since its total conversion time is much shorter than that of millimeter-size particles.

4.3. Experiments for model validation

4.3.1 Single particle combustor

Char conversion experiments were conducted in the single particle combustor presented in Chapter 3. In the experiments, an individual wood particle was held by a 0.3 mm titanium wire on a ceramic sample probe and suspended in the flue gas from the hydrogen flame. The combustion process of the single wood particle was recorded by a video camera. The char conversion begins after the biomass devolatilization determined by the extinguished of volatile combustion. The image post-processing to determine the start of char conversion is provided in references [153,275,278]. The image post-processing method developed to determine the particle size evolution can be found in Appendix B.

4.3.2 Materials

The spherical pine and beech wood particles of ~4 mm size were selected as the raw materials with the proximate analysis (as received) and ultimate analysis is given in Table 3. 3.

4.3.3 Operating conditions

The experiments were conducted according to the operating conditions as shown in Table 4. 3. The gas velocity at the centre of the SPC was estimated to be 2 times of bulk gas velocity by assuming a fully developed laminar flow.
Table 4.3 The operating condition of single particle combustion experiments

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th>Measured gas temperature (K)</th>
<th>Bulk gas velocity (m/s)</th>
<th>O₂ concentration (wet basis, vol%)</th>
<th>H₂O concentration (wet basis, vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0% O₂ / 1494 K</td>
<td>1494</td>
<td>1.49</td>
<td>0.0</td>
<td>26.8</td>
</tr>
<tr>
<td>4.4% O₂ / 1483 K</td>
<td>1481</td>
<td>1.43</td>
<td>4.4</td>
<td>25.7</td>
</tr>
<tr>
<td>10.5% O₂ / 1484 K</td>
<td>1484</td>
<td>1.51</td>
<td>10.4</td>
<td>24.9</td>
</tr>
<tr>
<td>0.0% O₂ / 1630 K</td>
<td>1630</td>
<td>1.50</td>
<td>0.0</td>
<td>39.7</td>
</tr>
<tr>
<td>4.4% O₂ / 1722 K</td>
<td>1722</td>
<td>1.50</td>
<td>4.5</td>
<td>39.0</td>
</tr>
<tr>
<td>10.5% O₂ / 1702 K</td>
<td>1702</td>
<td>1.44</td>
<td>10.6</td>
<td>41.8</td>
</tr>
</tbody>
</table>

4.3.4 Char yield

To estimate the initial density of char particle, selected char particles were sampled when the flame of volatile extinguished, with the particle mass measured by a microbalance (±0.01 mg). It was repeated 6 times for each specific operating condition. The char yield was calculated from the mass of char particle divided by the initial mass of the wood particle (as received basis). The char yields of the raw wood char particles and wet wood char particles obtained under different experimental conditions are shown in Table 4.4 and Table 4.5, respectively. The particle shrinkage factor of particle diameter during drying and devolatilization is assumed to be 0.2 according to our previous work [278]. Thereby the initial diameter of the pine and beech char is 3.20 mm and 3.31 mm, respectively. Then the initial char particle density can be calculated by following equations

\[ \rho_{c0} = \frac{6m_{\rho0}v_c}{\pi(\varphi d_{\rho0})^3} \]  

Here, \( \rho_{\rho0} \) is the initial char density, kg/m³, \( m_{\rho0} \) is the mass of a raw wood particle, \( v_c \) is the char yield of a raw wood particle, \( \varphi \) is the shrinkage factor during drying and devolatilization, \( d_{\rho0} \) is the initial diameter of wood particle, m.

Table 4.4 The char yield of raw wood particles under different experimental conditions.

<table>
<thead>
<tr>
<th>Operational conditions</th>
<th>Pine (%)</th>
<th>Beech (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0% O₂ / 1494 K</td>
<td>9.1±1.3</td>
<td>9.7±0.5</td>
</tr>
<tr>
<td>4.4% O₂ / 1483 K</td>
<td>8.9±0.3</td>
<td>9.4±0.4</td>
</tr>
<tr>
<td>10.5% O₂ / 1484 K</td>
<td>8.5±0.4</td>
<td>9.5±0.2</td>
</tr>
<tr>
<td>0.0% O₂ / 1630 K</td>
<td>6.3±0.7</td>
<td>5.9±0.8</td>
</tr>
<tr>
<td>4.4% O₂ / 1722 K</td>
<td>7.3±0.3</td>
<td>6.6±1.0</td>
</tr>
<tr>
<td>10.5% O₂ / 1702 K*</td>
<td>6.8</td>
<td>6.3</td>
</tr>
</tbody>
</table>

*Using averaged char yield of the case of 0.0%/1630 K and 4.4%O₂ / 1722 K
Table 4.5 The char yield of wet wood particles with different moisture content.

<table>
<thead>
<tr>
<th>Moisture content (ar)</th>
<th>Pine (%)</th>
<th>Beech (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0%</td>
<td>8.9±0.3</td>
<td>9.4±0.4</td>
</tr>
<tr>
<td>~15%</td>
<td>8.5±1.0</td>
<td>8.4±0.1</td>
</tr>
<tr>
<td>~30%</td>
<td>8.0±0.5</td>
<td>8.4±1.1</td>
</tr>
<tr>
<td>~50%</td>
<td>7.3±0.8</td>
<td>8.5±0.5</td>
</tr>
</tbody>
</table>

4.4 Results and Discussion

4.4.1 Model analysis

Four cases, as shown in Table 4.6, have been simulated to evaluate the model. The difference between those four cases is the bulk gas compositions. The other operating conditions (e.g. temperature, particle size, etc.) are the same.

Table 4.6 The operating conditions of four cases used to evaluate the model

<table>
<thead>
<tr>
<th>Items</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas composition (vol%)</td>
<td>4.4% O₂</td>
<td>4.4% O₂</td>
<td>25.7% H₂O</td>
<td>4.4% O₂ + 25.7% H₂O + 10.0% CO₂</td>
</tr>
<tr>
<td></td>
<td>+25.7% H₂O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle diameter (mm)</td>
<td>3.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slip velocity (m/s)</td>
<td>2.86</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Char density (kg/m³)</td>
<td>120</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>Reactor wall: 1283 K, Gas: 1483 K.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash composition (wt%)</td>
<td>1.5%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle temperature (K)</td>
<td>873</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.4.1.1 Char conversion and particle size evolution

Fig. 4.1 (a) shows the computed char conversion profiles of the four cases. With the presence of oxygen (case 1, case 2, case 4), the char conversion rate is much faster than that of steam gasification (case 3). A comparison of case 1, 2 and 4 show that the char conversion is slightly prompted by the gasification reaction. A plot of char particle shrinkage versus char conversion is shown in Fig. 4.1 (b) and compared with the analytical solution of the shrinking core model (SCM, \( \frac{d_d}{d_{d0}} = (1-X_c)^{1/3} \)). For case 1 where only char oxidation is involved, the char particle size evolution is expected to be in good agreement with a profile of shrinking core model, because the char oxidation is mass transfer limited at high temperatures and only occurs at the external char particle surface. For the cases with presence of \( \text{O}_2/\text{H}_2\text{O} \) or \( \text{O}_2/\text{CO}_2/\text{H}_2\text{O} \) (case 2, 4), the particle size reduction rate along with char conversion is smaller than that of the shrinking core model. A probable reason is that the gasification reactions occur throughout the whole particle. For the case of \( \text{H}_2\text{O} \) gasification, the char particle size keeps constant at the beginning and then reduces with the increase of char conversion. Similar results are also reported by previous studies [21,22].
Fig. 4.1 (a) char conversion versus reaction time of the four cases; (b) char particle shrinkage versus char conversion of different cases. Case 1: 4.4% O$_2$, Case 2: 4.4% O$_2$ + 25.7% H$_2$O, Case 3: 25.7% H$_2$O, Case 4: 4.4% O$_2$ + 25.7% H$_2$O + 10.0% CO$_2$. Simulating conditions: pine wood, $d_p = 3.2$ mm, $T_g = 1483$ K, $T_w = 1283$ K, $\rho_{ic} = 120$ kg/m$^3$, $u_s = 2.86$ m/s.

4.4.1.2 Radial concentration profiles

Fig. 4.2 shows the computed radial concentration profiles when the char conversion is 0.1. For the case of char oxidation (case 1), the oxygen concentration at the char particle external surface is near zero, implying that the reaction is mass transfer limitation. A peak CO$_2$ concentration is also observed at the particle surface. The CO$_2$ concentration is gradually decreased when CO$_2$ diffuses from the external char particle surface to the particle centre, because the CO$_2$ is consumed by gasification reaction. For the case of H$_2$O gasification (case 3), a steam concentration gradient inside the char particle is observed, implying that the char gasification is limited by both H$_2$O gasification kinetics and mass transfer. Both H$_2$ and CO concentration decreases with an increase of the distance from the centre of the particle. The CO$_2$ concentration is close to zero in the particle boundary layer, indicating that the reaction rate of water-gas shift reaction is low, because the reaction is limited by thermodynamic equilibrium at high temperature ($K_{eq} = 0.386 < 1$ for $T_g = 1483$ K). For the case 2 and the case 4, the O$_2$ concentration is close to zero at the particle external surface. The peak of CO$_2$ concentration is moved from the particle external surface to the boundary layer of the particle, suggesting that the CO oxidation occurs inside the particle boundary layer. The importance of CO oxidation in the particle boundary layer on char combustion has also been observed by Gonzalo-Tirado et al. [306].
Fig. 4. 2 Radial gas species concentration profiles of the four cases when the char conversion is 0.1. Case 1: 4.4% O₂, Case 2: 4.4% O₂ + 25.7% H₂O, Case 3: 25.7% H₂O, Case 4: 4.4% O₂ + 25.7% H₂O + 10.0% CO₂. Conditions: pine wood, \(d_p = 3.2\) mm, \(T_g = 1483\) K, \(T_w = 1283\) K, \(\rho_{c0} = 120\) kg/m³, \(u_s = 2.86\) m/s.

Fig. 4. 3 shows the radial gas concentration profiles of beech wood char particle when the char conversion is 0.1. Compared to pine wood, the steam gasification rate of beech wood is about 2 times faster. As a result, the concentration gradient of H₂O is larger than that of the case 2 as shown in Fig. 4. 2 (c), and the CO concentration inside the particle is also higher than that of pine wood.

Fig. 4. 3 The radial profiles of gas species concentration of beech wood char particle when char conversion is 0.1. Simulating conditions: \(d_p = 3.2\) mm, \(T_g = 1483\) K, \(T_w = 1283\) K, \(\rho_{c0} = 120\) kg/m³, \(u_s = 2.86\) m/s, 4.4% O₂ + 25.7% H₂O.
4.4.1.3 Radial temperature and char conversion profiles

Fig. 4. 4 shows the radial temperature and char conversion profiles of temperature and char conversion of the four cases. Due to the exothermic char oxidation and endothermic char gasification reactions, the particle temperature of case 1 (char oxidation) is about 50 K higher than that of case 3 (steam gasification). For case 2 and case 4, a peak temperature is observed outside the particle, due to the CO oxidation in the boundary layer. The conversion profile of case 1 shows that the char oxidation occurs at the particle external surface. A probable reason is that the char oxidation is limited by mass transfer at high temperatures. The conversion profile of steam gasification (case 3) shows that conversion takes place throughout the whole particle, implying that the char gasification rate is controlled by both kinetics and mass transfer.

![Radial profiles of temperature (a) and char conversion (b) of the four cases when char conversion is 0.1. Case 1: 4.4% O\textsubscript{2}, Case 2: 4.4% O\textsubscript{2} + 25.7% H\textsubscript{2}O, Case 3: 25.7% H\textsubscript{2}O, Case 4: 4.4% O\textsubscript{2} + 25.7% H\textsubscript{2}O + 10.0% CO\textsubscript{2}. Simulating conditions: pine wood, d\textsubscript{p} = 3.2 mm, T\textsubscript{g} = 1483 K, T\textsubscript{w} = 1283 K, p\textsubscript{c0} = 120 kg/m\textsuperscript{3}, u\textsubscript{s} = 2.86 m/s.](image)

4.4.2 Model validation

The experimental data from the single particle combustor are used to evaluate the comprehensive char combustion model.

4.4.2.1 Char conversion time

Fig. 4. 5 (a) and (b) show the computed and measured char conversion time of the pine wood char particles at the low temperatures bulk gas with ~25.0% H\textsubscript{2}O (1494/1483/1484 K, 0.0/4.4/10.5% O\textsubscript{2}) and the high temperatures bulk gas with ~40.0% H\textsubscript{2}O (1630/1722/1702 K, 0.0/4.4/10.5% O\textsubscript{2}), respectively. The measured char conversion times scatter a lot for the case of gasification (0.0% O\textsubscript{2}), while the repetition of experimental data with the presence of O\textsubscript{2} is much better. Since the single particle combustor is heated by the flue gas from H\textsubscript{2} combustion, there is small fluctuation of local O\textsubscript{2} concentration observed in the experiments. The small fluctuation of local O\textsubscript{2} concentration may lead to significantly different char conversion times for the gasification case. The computed and measured char conversion time decrease with an
increase of oxygen concentration and gas temperature, and increases with an increase of char particle density. The computed char conversion times are in good agreement with the experimental data for both the pine and beech wood char particles. For the case of steam gasification (0.0% O₂), the conversion times predicted for the pine wood are in good agreement with experimental data at the low temperature. However, the conversion time is underestimated at high temperatures, probably because the kinetics derived at 973-1173 K is not suitable to be used at high temperature conditions. Fig. 4. 5 (c) shows a comparison of computed and measured char conversion time of the wetted pine wood char particles, which are also in good agreement.

Fig. 4. 5 (d) and (e) show the computed and measured char conversion time of the beech wood char particles. Similar to the pine wood char particles, both computed and measured char conversion times decrease with an increase of oxygen concentration and gas temperature. The computed char conversion times are generally in good with experimental data for both raw beech wood char and wetted beech char particles as shown in Fig. 4. 5 (d-f). However, the model slightly overestimates the char conversion time for the case of gasification. Compared to pine wood char, the char conversion time of beech wood char particles is shorter, which is most likely because the char reactivity of beech wood char is higher than that of pine wood char due to a higher K content. The modelling results suggest that the gasification reaction has a larger contribution to beech wood char than to pine wood char, evidence is that the surrounding gas of beech wood char particle is much brighter than that of pine wood according to the experiments, probably caused by a higher CO oxidation rate due to higher CO concentration caused by gasification reactions. Fig. 4. 5 (a)-(f) show that the char conversion time increases with an increase of char particle density, similar results are also reported in our previous studies [153,278].
Fig. 4. The computed and experimental char conversion time of the pine and beech wood char particles under different conditions: (a) pine wood char particles at the low temperatures (1494/1483/1484 K), (b) pine wood char particles at high temperature (1630/1722/1702 K), (c), wet pine wood char at operating conditions of 4.4% O_2/1483 K, (d) beech wood char particles at low temperatures (1494/1483/1484 K), (e) beech wood char particles at high temperatures (1630/1722/1702 K), (f), wet pine wood char at operating condition: 4.4% O_2/1483 K.

4.4.2.2 Particle size evolution

Fig. 4. 6 shows the computed and experimental particle size evolution of pine and beech wood char particles during combustion and gasification at low temperatures (1494/1483/1484 K) and high temperatures (1630/1722/1702 K). The initial char particle density used in the modelling is the averaged particle density of the tested particles. For the gasification cases with 0.0% O_2
(Fig. 4. 6 (a), (b), (d), (e)), the experiments show that the particle size changes slowly at the beginning and then decreases quickly along with the conversion time. However, the computed char particle size is kept constant at the beginning and then decreases fast along with conversion time. A probable reason is that the assumption of immediate ash peeling off once the char conversion reaches 0.95, which may not suit the case of gasification. The collapse of the char particle may occur at a lower conversion degree of char conversion. A better agreement with experimental data may be obtained by considering the particle collapse mechanism in the current model. For the cases with the presence of O₂, the computed particle size evolutions are in good agreement with the experimental data. It is conceivable that the CO produced by H₂O and CO₂ gasification is not enough to consume all the O₂ transferred from bulk gas to the char particle. Thus, the char oxidation occurs at the external surface of the char particle. The char particle size evolution can be well predicted, if the mass transfer is predicted correctly. In Fig. 4. 6 (d) and (e), the predicted particle size evolution of beech wood char particle agrees better with experimental data of 10.5% O₂, as compared to that of 4.4% O₂, emphasizing that the char oxidation is dominated by external mass transfer. For the wetted wood char particle converted under 4.4% O₂ and 25.7% H₂O with bulk gas temperature 1483 K, the model gives reasonable results. Based on the results of char conversion time and particle size evolution, it is concluded that the comprehensive char conversion model can give reasonable results under both oxidation and gasification conditions.
Fig. 4.6 The computed and experimental particle size evolution of the pine and beech wood char particles under different conditions: (a) pine wood char particles at low temperature (1494/1483/1484 K), the averaged initial char densities are 111.4, 121.5, 111.7 kg/m³ for 0.0%, 4.4%, 10.5% O₂, respectively, (b) pine wood char particles at high temperature (1630/1722/1702 K), the averaged initial char densities are 88.8, 101.3, 94.8 kg/m³ for 0.0%, 4.4%, 10.5% O₂, respectively, (c) wet pine wood char at operating condition: 4.4 vol% O₂ / 1483 K, the averaged initial char density is 115.6 kg/m³, (d) beech wood char particles at low temperature (1494/1483/1484 K), the averaged initial char densities are 162.6, 149.0, 159.8 kg/m³ for 0.0%, 4.4%, 10.5% O₂, respectively, (e) beech wood char particles at high temperature (1630/1722/1702 K), the averaged initial char densities are 96.0, 111.3, 103.3 kg/m³ for 0.0%, 4.4%, 10.5% O₂, respectively, (f) wet pine wood char at operating condition: 4.4% O₂ / 1483 K, the averaged initial char density of the tested char particles is 144.1 kg/m³.

4.4.3 Sensitivity analysis

There are several parameters in the model that may affect the predicted char conversion time, such as the specific area ($S_r$), the critical conversion ($X_c$) that results in ash peel off, wood true
density ($\rho_{\text{m}}$), char conductivity ($\lambda_c$), emissivity ($\varepsilon$), slip velocity ($u_s$), temperature difference between wall and gas ($\Delta T$), initial char particle temperature ($T_{p0}$), particle shrinkage during devolatilization ($\phi$), the heterogeneous reaction kinetics (char oxidation ($r_1$), CO$_2$ gasification ($r_2$), and H$_2$O gasification ($r_3$)), and the homogeneous reaction kinetics (CO combustion ($r_4$), water-gas shift reaction ($r_5$), H$_2$ combustion ($r_6$)). Fig. 4. 7 (a) shows the sensitivity analysis results obtained by decreasing and increasing each modelling parameter by 50% and by scaling heterogeneous and homogeneous reactions kinetics by 0.1 and 10 times for a 3.2 mm pine wood char particle converted in 4.4 vol% O$_2$ and 25.7 vol% H$_2$O at $T_g = 1483$ K. Among the modeling parameters, the char conversion time is insensitive to specific surface area, the critical conversion for ash peel off, wood true density, char conductivity, because the reaction is controlled by both internal and external mass and heat transfer and kinetics, and these parameters influence limitedly on its. The initial char particle temperature also has a limited effect, because the char oxidation and CO$_2$/H$_2$O gasification reactions are relatively slow at low temperatures (873 K). However, the predicted char conversion time is sensitive to other modelling parameters, such as, emissivity, the temperature difference between gas and wall, and slip velocity. Changing the slip velocity by $\pm 50\%$ influences the char conversion time by 20-30%, the significant effect of the slip velocity is because the char conversion is partially controlled by external mass transfer. Among the kinetics for heterogeneous reactions, the kinetics of char oxidation rate has limited effects, since the char oxidation rate is controlled by the external mass transfer rate of oxygen at high temperatures, as shown in Fig. 4. 2. The predicted char conversion is significantly affected by the kinetics of H$_2$O gasification, indicating that the char gasification is at least controlled by the kinetics. The kinetics of CO$_2$ gasification is less pronounced as compared to the kinetics of H$_2$O gasification, because the bulk gas does not contain CO$_2$. Among the homogeneous kinetics, the predicted char conversion time is the most sensitive to the kinetics of CO oxidation, compared to water-gas shift reaction and H$_2$ oxidation. A probable reason is that when reducing the kinetics by 10 times, the water-gas shift reaction can still achieve thermodynamic equilibrium almost instantaneously. Therefore, it has limited effects on the modelling results. For H$_2$ oxidation, H$_2$ concentration is relatively low due to a low gasification rate thereby resulting in a limited effect on gas temperature by H$_2$ oxidation.

Fig. 4. 7 (b) and (c) shows the sensitivity analysis of 3.2 mm and 0.32 mm pine wood char particle converted at 1473 K with a bulk gas composition of biomass combustion in a pulverized furnace (4 vol% O$_2$, 13 vol% CO$_2$, 13 vol% H$_2$O) [10,35,318]. For a 3.2 mm pine wood char particle, the slip velocity, CO$_2$ and H$_2$O gasification kinetics, and CO oxidation kinetics have significant effects on the modelling results, while other parameters are insignificant. For the 0.32 mm pine wood char particles, implying that char oxidation is controlled by both kinetics and external mass diffusion for small char particles. Since the modelling results are sensitive to
the kinetics related parameters (e.g. temperature, gasification kinetics) and mass transfer related parameters (e.g. slip velocity and char particle size), these factors will be further studied in following sections.

Fig. 4. 7 Sensitivity analysis of the model with respect to its modelling parameters, solid phase kinetics and gas phase kinetics. (a) pine wood char particle under experimental conditions \(T_g = 1483 \text{ K}, T_w = 1283 \text{ K}, d_p = 3.2 \text{ mm}, \rho_{c0} = 120 \text{ kg/m}^3, 4.4 \text{ vol}\% \text{ O}_2, 25.7 \text{ vol}\% \text{ H}_2\text{O} \). 3.2 mm (b) and 0.32 (c) mm pine char particle under a pulverized furnace condition \(T_g = T_w = 1473 \text{ K}, \rho_{c0} = 120 \text{ kg/m}^3, 4 \text{ vol}\% \text{ O}_2, 13 \text{ vol}\% \text{ CO}_2, 13 \text{ vol}\% \text{ H}_2\text{O} \). For the emissivity of the particle, the maximum value with reasonable physical meaning is 1. Therefore, it is not 50% increase of the parameter.
4.4.3.1 Effects of gasification kinetics

Fig. 4.8 (a) and (b) show the effects of CO$_2$ gasification kinetics on the conversion of pine wood char under a condition of 4.4% O$_2$ and 25.7% CO$_2$ at $T_g=1483$ K. The char conversion time decreases with an increase of CO$_2$ gasification rate. When the CO$_2$ gasification kinetics is scaled by 0.01, the char conversion is mainly contributed by char oxidation. The contribution of char oxidation decreases with an increase of the CO$_2$ gasification rate. Fig. 4.8 (c) and (d) shows the effects of H$_2$O gasification kinetics on the char conversion under a condition of 4.4% O$_2$ and 25.7% H$_2$O. Similarly, the char conversion time and the contribution of char oxidation decreases with an increase of H$_2$O gasification rate. The contribution of char oxidation on char conversion reduces from 90% to 10%, when scaling the steam gasification kinetics from 0.01 to 100 times of the base kinetics, the effect of steam gasification kinetics is more pronounced than the CO$_2$ gasification kinetics due to O$_2$ consumed by CO oxidation.

![Graphs showing effects of gasification kinetics](image)

**Fig. 4.8** The effects of CO$_2$ ($r_2$)/H$_2$O ($r_3$) gasification rates on char conversion time and contribution of char reactions by using the gasification kinetics of pine wood char as shown in Table 4.1. Simulating conditions: (a) and (b), ($T_g = 1483$ K, $T_w = 1283$ K, $d_p = 3.2$ mm, $\rho_{c0} = 120$ kg/m$^3$, 4.4% O$_2$, 25.7% CO$_2$), (c) and (d), ($T_g = 1483$ K, $T_w = 1283$ K, $d_p = 3.2$ mm, $\rho_{c0} = 120$ kg/m$^3$, 4.4% O$_2$, 25.7% H$_2$O).

Fig. 4.9 (a)-(c) shows the effects of CO$_2$ gasification kinetics on the radial concentration of CO$_2$, CO, and O$_2$. At a low gasification rate (0.01 $r_2$), the CO$_2$ concentration inside the char particle is almost constant and is slightly higher than bulk gas concentration. By increasing the CO$_2$ gasification kinetics to 100$r_2$, the CO$_2$ concentration inside the char particle is much lower than that in the bulk, with a significant concentration gradient in the boundary layer. This indicates that the char CO$_2$ gasification change from a kinetically controlled regime to a regime
limited by both kinetics and external and internal mass transfer. The CO concentration inside the char particle increases with an increase of char gasification rate as shown in Fig. 4. 9 (b). For a 3.2 mm particle under conditions of 4.4% O\(_2\) and 25.7% CO\(_2\) at \(T_g = 1483\) K, the char oxidation occurs at the particle external surface and is limited by mass transfer, as shown in Fig. 4. 9 (c). An increase of H\(_2\)O gasification kinetics also increases the concentration of CO in the boundary layer. However, the O\(_2\) concentration near the particle external surface is lower than that of Fig. 4. 9 (c). Because O\(_2\) transferred from bulk gas to char external particle surface is consumed by CO oxidation in the particle boundary layer. That also explains why the contribution of H\(_2\)O gasification is higher than that of CO\(_2\) gasification.

Fig. 4. 9 The effects of CO\(_2\) (\(r_2\))/H\(_2\)O (\(r_3\)) gasification rates on radial gas species concentration profiles by using the gasification kinetics of pine wood char which shown in Table 5. Simulating conditions: (a), (b) and (c), \((T_g = 1483\) K, \(T_w = 1283\) K, \(d_p = 3.2\) mm, \(\rho_{c0} = 120\) kg/m\(^3\), 4.4% O\(_2\), 25.7% CO\(_2\)), (d), (e) and (f), \((T_g = 1483\) K, \(T_w = 1283\) K, \(d_p = 3.2\) mm, \(\rho_{c0} = 120\) kg/m\(^3\), 4.4% O\(_2\), 25.7% H\(_2\)O).
Fig. 4. 10 (a) and (b) shows the effects of the CO$_2$ and H$_2$O gasification rates on radial temperature profiles. No peak temperature is observed in the particle boundary layer, implying no CO oxidation occurring in the particle boundary layer. However, with the presence of H$_2$O in the bulk gas, a peak temperature is observed due to the homogeneous reactions of CO oxidation. The peak temperature increases with an increase of H$_2$O gasification kinetics. In both figures, the particle temperature decreases with an increase of gasification rate, because the CO$_2$ and H$_2$O gasification are endothermic reactions.

![Fig. 4. 10 The effects of CO$_2$ (r$_2$)/H$_2$O (r$_3$) gasification rates on radial particle temperatures profiles by using the gasification kinetics of pine wood char which shown in Table 5. Simulating conditions: (a), (T$_g$ = 1483 K, T$_w$ = 1283 K, d$_p$ = 3.2 mm, $\rho_{c0}$ = 120 kg/m$^3$, 4.4% O$_2$, 25.7% CO$_2$), (b), (T$_g$ = 1483 K, T$_w$ = 1283 K, d$_p$ = 3.2 mm, $\rho_{c0}$ = 120 kg/m$^3$, 4.4% O$_2$, 25.7% H$_2$O).](image)

### 4.4.3.2 Effects of gas temperature

The effects of gas temperature on the char conversion time and the relative contributions heterogeneous reactions are shown in Fig. 4. 11 (a) and (b), respectively, for pine and beech wood char particle. As expected, the char conversion time decreases with an increase of gas temperature. At $T_g = 1273$ K, char oxidation contributes over 80% and 60% of char conversion for pine and beech wood char particle, respectively. The contribution is less for beech wood char, because the gasification reactivity of the beech wood char is higher than that of the pine wood char. At $T_g = 1673$ K and $T_g = 1873$ K, the char oxidation almost has no contribution, because O$_2$ is total consumed by CO/H$_2$ oxidation in the particle boundary layer.
The effects of gas temperature on char conversion time (a) and contribution of different char reactions (b) on char conversion of pine and beech wood char particles. Simulating conditions: \( d_p = 3.2 \text{ mm} \), \( \rho_{c0} = 120 \text{ kg/m}^3 \), 4% \( \text{O}_2 \), 13% \( \text{CO}_2 \), 13% \( \text{H}_2\text{O} \), \( u_s = 3 \text{ m/s} \).

According to Fig. 4. 12 (a), a peak \( \text{CO}_2 \) concentration is observed for different gas temperatures, because of the occurrence of \( \text{CO} \) oxidation in the particle boundary layer. Compared to the \( \text{CO}_2 \) concentrations profiles, no significant \( \text{H}_2\text{O} \) concentration peak is observed in the char particle boundary layer. At low temperatures, the \( \text{CO} \) produced by \( \text{CO}_2/\text{H}_2\text{O} \) gasification is not enough to consume all the \( \text{O}_2 \) diffusion from the bulk gas to the particle surface, as shown in Fig. 4. 12 (c). Therefore, at low temperatures, a considerable fraction of \( \text{O}_2 \) is consumed by heterogeneous reactions with char. The increasing gasification rate leads to a higher \( \text{CO} \) (according to our calculation, it is about 40% mol) concentration inside particle at high temperature, facilitating \( \text{CO} \) diffusion from the char particle to the particle boundary layer. The \( \text{CO} \) transferred to the boundary layer consumes all the \( \text{O}_2 \) diffused from the bulk gas. \( \text{O}_2 \) cannot reach the particle external surface as shown in Fig. 4. 12 (c). This is the reason why the char particle is almost all converted by \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) gasification as shown in Fig. 4. 12 (b).
Fig. 4.12 The effects of gas temperature on radial profiles of CO$_2$ (a), H$_2$O (b), O$_2$ (c) concentration and particle temperature of pine wood char particle. Simulating conditions: $\rho_0 = 3.2$ mm, $\rho_c = 120$ kg/m$^3$, 4% O$_2$, 13% CO$_2$, 13% H$_2$O, $u_s = 3$ m/s.

4.4.3.3 Effects of slip velocity

Fig. 4.13 shows the effects of slip velocity on char conversion time and relative contribution heterogeneous reactions of 3.2 mm pine and beech wood char particles placed in a typical pulverized furnace conditions (4 vol% O$_2$, 13 vol% CO$_2$, 13 vol% H$_2$O, $T_g = T_w = 1473$ K). The char conversion time decreases with an increase of slip velocity, due to an enhanced external mass transfer between the surrounding gas and the char particle. Since the gasification rate of beech wood char is faster than that of pine wood char at the simulated temperature, the char conversion time of beech wood char particle is shorter than that of pine wood char. Due to an increase of external mass transfer between gas and char particle, the contribution of char oxidation increases from 2% to 50% by increasing slip velocity from 0.1 m/s to 9.0 m/s.
4.4.3.4 Effects of char particle size

The effect of char particle size on char conversion time and relative contributions heterogeneous reactions of pine and beech wood char particle placed in a typical pulverized furnace conditions (4 vol% O$_2$, 13 vol% CO$_2$, 13 vol% H$_2$O, $T_g = 1473$ K) are shown in Fig. 4.14 (a) and (b), respectively. The char conversion time increases with an increase of particle size for both pine and beech wood char particles. According to Fig. 4.14 (b), the char particle size has a significant effect on the contribution of char reactions, the contribution of char oxidation decreases with an increase of char particle size, due to a decrease of external mass transfer of O$_2$ between the bulk gas and char particle. For particle size smaller than 1 mm, the char oxidation contributes over 60% for both pine and beech wood char particle, it can decrease to be lower than 5% when the char particle size reaches 10.0 mm.

Fig. 4.14 The effects of particle size on char conversion time (a) and contribution of char reactions (b) of pine and beech wood char particles. Simulating conditions: $T_g = T_w =1473$ K, $\rho_o = 120$ kg/m$^3$, 4% O$_2$, 13% CO$_2$, 13% H$_2$O, $u_s = 3$ m/s.
4.5 Summary

A comprehensive char conversion model, which includes heterogeneous reactions, and homogeneous reactions in the particle boundary layer, particle shrinkage, and external and internal heat and mass transfer, was developed. The model was compared and validated by single particle combustion experiments of 3.20 mm pine and 3.31 mm beech wood char particle under conditions of 1473-1723 K with 0.0-10.5\% O_2 and 25-42\% H_2O. Under the experimental conditions, the modelling results show that the char oxidation is controlled by mass transfer and the char gasification is limited by both mass transfer and gasification kinetics. The predicted results are in good agreement with the experiments containing oxygen in the bulk gas. However, the model underestimated char conversion time of pine wood char at high temperature (>1673 K) without oxygen, suggesting that the kinetics for gasification and the assumption of immediate ash peel off needs a further investigation.

A sensitivity analysis shows that the CO oxidation in the boundary layer has a significant effect on char conversion, while water-gas shift reaction and H_2 oxidation have smaller influences. The gasification kinetics also have significant effects on the modelling results. The effects of the important parameters have been investigated under a typical pulverized biomass combustion conditions (1473 K, 4\% O_2, 13\% CO_2, 13\% H_2O). The results show that the char reactivity (gasification kinetics), operating conditions (gas temperature and slip velocity), and particle size have significant effects on the contribution of char conversion. The increase of char reactivity results in an increase of relative char conversion contribution from char gasification. The char gasification is important and should be included in the model under PF conditions, especially for millimetre-sized biomass char particles.
5 A heat transfer corrected isothermal model for devolatilization of thermally-thick biomass particles

The main objective is to develop a sub-model for CFD modelling devolatilization of thermally-thick biomass particles. The main method utilized here is to simplify the comprehensive single particle model developed in Chapter 3.

5.1 Introduction

In CFD modelling of biomass devolatilization in fluidized beds, the biomass particles are usually described by an isothermal model [7,35,39–42], due to its simplicity and low computational cost. However, the isothermal assumption is only reasonable for particles with a small Biot number (e.g. Bi < 1) [7,14,279]. For biomass particles with a large Biot number, a significant particle internal temperature gradient exists, requiring the use of a non-isothermal model or a kinetics-modified isothermal model to describe the devolatilization accurately [7,12,13,16,129,279,290,319,320].

Non-isothermal models have been implemented in CFD to predict the heating and devolatilization of biomass particles [117,187–190,192,193,321]. A common approach is to discretize a biomass particle radially in a large number of mesh grid points (e.g. 50), which results in significant computational demand in CFD [188,193]. To reduce the computational cost, Thunman et al. [56] proposed a model to discretize a biomass particle into four layers (moist wood, dry wood, char, and core layers) in a radial direction, with additional equations to describe the heat transfer between the layers. This approach reduces significantly the discretized grid points, and thereby improves the computational efficiency in CFD, compared to other non-isothermal models [188,321]. However, it is still complicated to apply the four-layer model to CFD for simulation of biomass devolatilization in fluidized beds due to highly diverse boundary conditions in fluidized bed reactors [30], and the computational cost still higher than that of the conventional isothermal model.

Compared to non-isothermal models, an isothermal model requires much less computational cost and is easier to implement in CFD. Johansen et al. [35] modified the devolatilization kinetic parameters by fitting CFD modelled biomass particle temperature history versus experimental conversion in an entrained flow reactor. Simone et al.[322] also modified the kinetic parameters based on CFD modelled results for a drop tube reactor. In this way, the performance of CFD modelling has been improved compared to use a TGA determined kinetic parameters [35,322]. However, both CFD simulations and experimental data are required to obtain the modified kinetics, and the kinetics should be updated with changing operating conditions (e.g. temperature and gas velocity). Additionally, the internal heat transfer is still neglected in those models. However, it has a significant effect on devolatilization of thermally-thick biomass
particles [1,12,13,58,247,279]. Therefore, an improvement is needed to include the effects of internal heat transfer on devolatilization rates.

In this chapter, a heat transfer corrected isothermal model is developed to facilitate CFD modelling of the devolatilization of thermally-thick biomass particles. Correction coefficients of reaction rates \((H_{R,i})\) and external heat transfer, which use to modify a conventional isothermal model, are introduced by comparing the difference between a conventional isothermal model and the comprehensive devolatilization model developed in Chapter 3. The results of the three models have been compared to the experimental data. The heat transfer corrected isothermal model is further implemented in CFD to simulate biomass devolatilization in a batch bubbling fluidized bed.

5.2 Particle-scale model for biomass devolatilization

5.2.1 Model description

The conventional isothermal model, the non-isothermal model, and the heat transfer corrected isothermal model are described below. The general assumptions of different models are listed in Table 5.1

<table>
<thead>
<tr>
<th>Items</th>
<th>Model assumptions</th>
</tr>
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| Conventional isothermal model | (1) Zero-dimensional model, the particle temperature, and the fraction of water and volatile is uniform.  
(2) The reactor walls contribute to the radiative heat flux between particle external surface and the environment for single particle experiments |
| Non-isothermal model | The same as section 3.2.1 |
| Heat transfer corrected isothermal model | Since the heat transfer corrected derived from the non-isothermal model, the other assumptions of the non-isothermal model are also used in this model, except the assumption of the one-dimensional model. |

5.2.1.1 Conventional isothermal model

The heat balance equation and the reaction rate of the conventional isothermal model (i.e. drying rate and devolatilization rate) are given as:

\[
C_p m_p \frac{dT_p}{dt} = h_c A_p (T_g - T_p) + \xi \sigma A_p (T_w - T_p^4) - \sum_i R_{iso,i} Q_{R,i} \quad (4.1)
\]

\[
R_{iso,i} = \frac{dX_i}{dt} \rho \beta Y_{0.i} \frac{V_p}{V} \quad (4.2)
\]

\[
q_{iso} = h_c (T_g - T_p) + \xi \sigma (T_w - T_p^4) \quad (4.3)
\]
Where $i$ represents different components ($i = 1$ and 2 represents water and volatile, respectively); $\rho_{DB}$ is initial particle density, kg/m$^3$; $Y_{0,i}$ is an initial mass fraction of component $i$ in the particle. $T_p$ and $X_i$ is the particle temperature, and conversion of volatile and water. $dX_i/dt$ can be determined by drying and devolatilization kinetics which has been discussed in section 3.2.4.

5.2.1.2 Non-isothermal model

The non-isothermal devolatilization model is the same as the one developed in Chapter 3. The global reaction rate predicted by the non-isothermal model for a spherical particle is given as:

$$ R_{\text{non-iso},i} = \int_0^R 4\pi r^2 \frac{dX_i}{dt} \rho_{DB} Y_{0,i} dr $$  \hspace{1cm} (4.4)

Where $r$ is the radius position, m, $R$ is the particle radius, m. The heat flux predicted by the non-isothermal model is given as:

$$ q_{\text{non-iso}} = h_i \left( T_s - T_i \right) + \xi \sigma \left( T_w^4 - T_i^4 \right) $$  \hspace{1cm} (4.5)

The average particle temperature, conversion of water and volatile are calculated follows,

$$ T_{\text{aver},i} = \frac{\int_0^R 4\pi r^2 T_i dr}{\int_0^R 4\pi r^2 dr} $$  \hspace{1cm} (4.6)

$$ X_{\text{aver},i} = \frac{\int_0^R 4\pi r^2 X_i dr}{\int_0^R 4\pi r^2 dr} $$  \hspace{1cm} (4.7)

5.2.1.3 Heat transfer corrected isothermal model

To take into account the effect of the internal heat transfer on particle heating-up and devolatilization, two correction coefficients, $H_T$ and $H_{R,i}$, are proposed to describe the difference between the conventional isothermal and the non-isothermal model. The assumptions of the heat transfer corrected isothermal model are given in Table 5.1. According to the definition of corrected coefficients, for a particle with average temperature ($T_{p,\text{aver}}$), and surface temperature ($T_{\text{surf}}$), and boundary condition with a convective heat transfer coefficients ($h_c$), the two coefficients, $H_T$ and $H_{R,i}$ can be expressed as:

$$ H_T = \frac{q_{\text{non-iso}}}{q_{\text{iso}}} = \frac{h_i \left( T_s - T_i \right) + \xi \sigma \left( T_w^4 - T_i^4 \right)}{h_i \left( T_s - T_{\text{aver}} \right) + \xi \sigma \left( T_w^4 - T_{\text{aver}}^4 \right)} $$  \hspace{1cm} (4.8)
Thus, the heat balance equation for the corrected isothermal model is:

\[ C_p m_p \frac{dT}{dt} = H_T \left( h_A \left( T_g - T_{\text{avg}} \right) + \zeta \sigma A_p \left( T_w - T_{\text{avg}} \right) \right) - \sum_{i=1}^{n} R_{\text{cor},i} Q_{\text{cor},i} \]  

(4.10)

And the reaction rate of the corrected isothermal model is:

\[ R_{\text{cor},i} = H_{R,i} R_{\text{iso},i} \]  

(4.11)

With predefined \( T_w, T_g \) and \( h_c \), the heat transfer boundary condition of a biomass particle is determined, the internal particle temperature distribution, and conversion distribution of volatile and moisture content can be calculated, according to Eq. (5.8) and Eq. (5.9). The average particle temperature \( T_{\text{avg}} \), the average conversion of volatile and water \( (X_{\text{avg},i}) \), the heat flux, the drying and devolatilization rate \( (R_{\text{non-iso},i}) \), and the heat flux \( (Q_{\text{non-iso}}) \) can be further calculated based on Eq. (5.4)-(5.7), respectively. With known internal particle temperature distribution, and conversion distribution of volatile and moisture content from the solutions of non-isothermal model, a series data of \( (T_{\text{avg}}, T_w, X_{\text{avg},i}, Q_{\text{non-iso},i}, R_{\text{non-iso},i}) \) are obtained with above procedures. Then, \( T_w, X_{\text{avg},i}, Q_{\text{non-iso},i}, \) and \( R_{\text{non-iso},i} \) can be determined by corresponding \( T_{\text{avg}} \). By assuming an isothermal particle with the same \( T_{\text{avg}} \) and predefined \( T_w, T_g \) and \( h_c \), the valued of \( Q_{\text{iso},i}, \) and \( R_{\text{iso},i} \) can be determined by using Eq. (5.2) and (5.3). Therefore, the corresponding \( H_T \) and \( H_{R,i} \) can be simplified as a function of \( T_{\text{avg}} \). For the case with dynamically changed convective heat transfer conditions (e.g. biomass devolatilization in fluidized bed etc.), \( h_c \) dynamically changes along with time \( t \). Since the model is derived with a predefined \( h_c \), the \( H_T \) and \( H_{R,i} \) are further extended as a binary function of \( (T_{\text{avg}}, h_c) \). In order to implement the corrected isothermal model to CFD easily, a dimensionless temperature \( \theta \) is defined by Eq.(5.12), \( H_T \) and \( H_{R,i} \) can be expressed as a function of \( (\theta, h_c) \) after the arrangement.

\[ \theta = \frac{T_p - T_{p0}}{\max(T_w, T_g) - T_{p0}} \]  

(4.12)

### 5.2.2 Physical properties

The physical properties shown in section 3.2.3 are used in the modelling. The convective heat transfer coefficient \( (h_c) \) of the spherical particle is determined by Ranz and Marshall equation [221], while the correlation of Churchill and Bernstein [323] is adopted for cylinder particles.

### 5.2.3 Heat transfer corrected coefficients

The solution steps to obtain \( H_T \) and \( H_{R,i} \) are illustrated in Fig. 5.1, and are explained as follows:
(1) With given input parameters of gas and wall temperature \( (T_g, T_w) \), particle dry density \( (\rho_{DB}) \), diameter \( (d_p) \) and particle initial temperature \( (T_{p0}) \), and proximate analysis of biomass. Defining a trial value of \( h_c \). The \( h_c \) starts with a minimum \( h_{c\text{min}} \) and ends with a maximum \( h_{c\text{max}} \) value. The range of \( h_{c\text{min}} \) and \( h_{c\text{max}} \) covers the possible value of convective heat transfer coefficient under the specified operating conditions, \( m \) is the number of \( h_c \) value used to calculate \( H_T \) and \( H_{R,i}, j \) is current iteration number.

(2) With the given \( h_c \) from Step 1 and the physical properties determined by Table 3. 1, and the drying and devolatilization model, solving the non-isothermal model, the local particle temperature, local conversion of water and volatile, and particle surface temperature can be obtained. Based on the above data, the average particle temperature \( (T_{\text{aver}}) \), and the average conversion of water and volatile \( (X_{\text{aver},i}) \), and dimensionless temperature \( (\theta) \) can be calculated by Eq. (5.6), Eq. (5.7), and Eq. (5.12), respectively. The heat flux \( (q_{\text{non-iso}}) \), and reaction rate \( (R_{\text{non-iso},i}) \) of the non-isothermal model are calculated by Eq. (5.5) and (5.4), respectively. A series of data \( (\theta, q_{\text{non-iso}}, R_{\text{non-iso},i}) \) can be obtained.

(3) Assuming an isothermal particle with the same average particle temperature \( (T_{\text{aver}}) \), and average conversion of water and volatile \( (X_{\text{aver},i}) \) of the non-isothermal model, the heat flux \( (q_{\text{iso},i}) \) and reaction rate \( (R_{\text{iso},i}) \) of the conventional isothermal model are calculated by Eq. (5.3) and Eq.(5.2) , respectively. A series of data \( (\theta, q_{\text{iso}}, R_{\text{iso},i}) \) of the conventional isothermal model can be obtained.

(4) Based on the data of non-isothermal data \( (\theta, q_{\text{non-iso}}, R_{\text{non-iso},i}) \) and isothermal model\( (\theta, q_{\text{iso}}, R_{\text{iso},i}) \), calculating \( H_T \) and \( H_{R,i} \) by Eq. (9) and Eq. (10) at the same dimensionless temperature \( (\theta) \). When the dimensionless temperature and conversion of components are larger than 0.999, both \( H_T \) and \( H_{R,i} \) are specified as 1 to avoid numerical problems.

(5) Repeating Step 1 to Step 4 with a new \( h_c \) until \( h_c > h_{\text{cmax}} \), namely the current iteration number \( j > m \). After finishing the calculation of all \( h_c \) from \( h_{\text{cmin}} \) to \( h_{\text{cmax}} \), a matrix with \( (\theta, h_c, H_T, H_{R,i}) \) is saved.

(6) The saved matrix can be used in either CFD modelling or single particle modelling by data post-processing. A two-dimensional linear interpolation method [324] is used to fit \( H_T \) and \( H_{R,i} \) as a binary function of \( (\theta, h_c) \).
Fig. 5. 1 The calculation steps for obtaining $H_T$ and $H_{R,i}$ of the heat transfer corrected isothermal model (an example of the calculation is given in Appendix C).
Based on the solving scheme in Fig. 5.1, the two heat transfer corrected coefficients, $H_T$ and $H_{R,i}$, for a 10 mm spherical wood particle with convective heat transfer coefficients range from 10 to 1000 W/(m$^2$-K) (corresponding to the Biot numbers in a range from 3.71 to 57.26) are shown in Fig. 5.2. The values of the corrected coefficients of external heat transfer, drying, devolatilization rate increase with an increase of convective heat transfer coefficient. $H_T$ decreases with the increase of $\theta$, because of the increasing of difference between particle surface temperature and the average particle temperature. $H_{R,i}$ increases firstly with the increase of $\theta$, representing the drying and devolatilization occurs at particle external surface layer when the average particle temperature is relatively low, and then decreases to the value lower than unity, due to the fact that the drying and devolatilization only occur in the core layer described by the non-isothermal model, while they occur throughout the whole biomass particle by using the conventional isothermal model. $H_{R,i}$ finally reaches 1 when the drying and devolatilization is completed. Because the drying process occurs at a much lower temperature than the biomass devolatilization, $H_{R,i}$ reaches 1 with a smaller $\theta$. At $\theta = 0$, both $H_T$ and $H_{R,i}$ is 1, because the temperature is uniformly distributed with initial particle temperature, and the drying and devolatilization do not occur at room temperature. At $\theta = 1$, $H_T$ and $H_{R,i}$ is also 1, because of uniform temperature and a completed drying and devolatilization process.

Fig. 5.2 The heat transfer corrected coefficients ($H_T$ and $H_{R,i}$) for isothermal model (Gas: N$_2$, spherical particle, $d_p = 10$ mm, $\rho_{DB} =$ 580 kg/m$^3$, Vol = 90.0 db%, $M_i =$ 6.3 db%, $T_g = T_w =$ 1173 K, $h_c =$ 10-1000 W/(m$^2$-K), $Bi =$ 3.71- 57.26).

Fig. 5.3 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/(m$^2$-K). For the small particle, both $H_T$ and $H_{R,i}$ are close to 1 with $h_c =$ 10, 100, and 1000 W/(m$^2$-K). However, for the large particle, the corrected coefficients for external heat transfer, drying rate, and devolatilization rate, are in a range of $0$-$1$, $10^{-4}$-$10^2$, $10^{-4}$-$10^{10}$, respectively. This implies a significant difference between the isothermal model and the non-isothermal model for large particles. The results are in agreement with previous studies [1,7,14,58], showing the conventional isothermal and non-isothermal models predict similar results for thermally-thin particles, but resulting in large differences for thermally-thick particles.
5.3 Evaluation of the corrected isothermal model

In this part, the heat transfer corrected isothermal model is evaluated by comparing a series of experimental results with particle size ranged from 0.079 mm to 10 mm. The conventional isothermal model, non-isothermal model, and the corrected isothermal model are compared. A sensitivity analysis of modelling parameters is done to evaluate the uncertainty of modelling results.

5.3.1 Experimental data for model validation

Table 5. 2 presents an overview of the experiments used for model validation. The experiments are categorized according to the biomass particle size. For small-size 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 [35]. For the cases of medium-size particles (1 mm-5 mm), two series of experimental data are used with a reactor temperature of 1284-1873 K, and a slip velocity of 2.76-5 m/s [275,278]. For the case of the large particle (> 5 mm), the experimental data of Lu et al [12] is used to evaluate the model. In their experiments, 9.5 mm particle was put in a single particle combustor with gas and wall temperatures of 1050 K and 1276 K, respectively. Both particle surface and centre temperatures were measured by thermocouples, and the weight loss was measured by weighted the particle mass at different times. The proximate analysis of the fuels is given in Appendix C.
Table 5.2 Overviews of the experimental setup and operating conditions used for model validation

<table>
<thead>
<tr>
<th>Cases</th>
<th>Fuel type</th>
<th>Diameter (mm)</th>
<th>Moisture (db%)</th>
<th>Density (kg/m³) (dry basis)</th>
<th>Shapes</th>
<th>$T_{p0}$ (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small</td>
<td>Pine wood</td>
<td>0.079</td>
<td>0.0</td>
<td>1180</td>
<td>Sphere</td>
<td>298</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>Pine wood</td>
<td>1.31-3.0</td>
<td>10.3</td>
<td>544</td>
<td>Sphere/Cylinder</td>
<td>298</td>
<td>[275]</td>
</tr>
<tr>
<td>Medium</td>
<td>Schima wood</td>
<td>3.5</td>
<td>1.0-5.0</td>
<td>520-720</td>
<td>Sphere</td>
<td>298</td>
<td>[278]</td>
</tr>
<tr>
<td>Large</td>
<td>Poplar wood</td>
<td>9.5</td>
<td>6.38/66.67</td>
<td>580</td>
<td>Sphere/Cylinder</td>
<td>298</td>
<td>[12]</td>
</tr>
</tbody>
</table>

5.3.2 Results and discussion

5.3.2.1 Small-size particles

Fig. 5.4 shows a comparison of the measured and the predicted particle total conversion \((m_0 - m)/m_0\) (\(m_0\): initial wood particle mass, \(m\): particle mass at time \(t\), \(m_\infty\): particle mass after devolatilization) of devolatilization of small pinewood particles \((d_p = 0.079 \text{ mm}, \text{Bi} < 1)\) at 1405 K and 1667 K. Non-isothermal and corrected isothermal models predict similar results, and the conventional isothermal model predicts a slightly faster devolatilization rate, indicating the heat transfer corrected method is reasonable and consistent with previous studies [7,14,319].

Fig. 5.4 A comparison between the predicted particle total conversion history by using different models and experimental data [35]. (Con-iso: conventional isothermal model, Non-iso: non-isothermal model, Cor-iso: corrected isothermal model. The brevities used in here is also used in other figures).

5.3.2.2 Medium-size particles

Fig. 5.5 shows the devolatilization time (defined as the time needed to release 99% of the volatile) predicted by different models, and its comparison with the experimental data of Momeni et al. [275]. For the case of Fig. 5.5 (a), the particles are devolatilized at \(T_g = T_v = 1473\) K [275]. Non-isothermal and corrected isothermal models predict similar results, which are in good agreement with experimental data. However, the conventional isothermal model underestimates the devolatilization time. The deviations between the conventional isothermal
model and the other two models are decreased with the decrease of particle size. Fig. 5. (b) presents the devolatilization time of \( d_p = 1.65 \) mm cylinder particles under different bulk gas temperatures. The conventional isothermal model predicts the shortest devolatilization time, while non-isothermal and corrected isothermal model predicts similar results that are in better agreement with experimental data.

\[ \text{Fig. 5. 5 The devolatilization time of wood particle predicted by different models and its comparison with experimental data [275]: (a) different particle size, the particle size with } d_p = 3.0 \text{ mm is spherical particles, while the others are cylindrical particles, (b) different bulk gas temperature.} \]

Another comparison of the devolatilization time predicted by the different models and experimental data of Lu et al. [278] based on 3-5 mm raw and torrefied spherical wood particles is shown in Fig. 5. 6. Both non-isothermal and corrected isothermal models predict reasonably the devolatilization time compared to the experimental data. However, the devolatilization time is underestimated by the conventional isothermal model, especially for the larger particles.

\[ \text{Fig. 5. 6 The devolatilization time predicted by different models and its comparison with experimental data (Raw represents wood without torrefaction, 230C1h, 260C1h, and 290C1h represent the wood was torrefied at 230, 260, and 290 °C with 1 hour, respectively. 290C4h represents the wood was torrefied at 290 °C with 4 hours, Gas: 3% O}_2 \text{ and 97% N}_2; 1503 \text{ K).} \]
5.3.2.3 Large-size particles

Fig. 5. 7 (a) and (c) show the particle conversion profiles predicted by different models and their comparison with experimental data of a near-spherical particle and a cylindrical particle [12], respectively. The conversion predicted by the corrected isothermal and non-isothermal model is in good agreement with experimental data, while the conventional isothermal model underestimates the conversion at the beginning and overestimates the conversion later. In Fig. 5. 7 (b) and (d), the corrected isothermal model can predict similar particle average temperature profiles as the non-isothermal model, while the conventional isothermal model overestimates the heating rate, resulting in overestimate the devolatilization rate. A similar trend was also reported by Lu et al.[12]. Fig. 5. 8 (a) and (b) shows the particle conversion profiles of a spherical and cylindrical wood particle with the moisture content of 66.67 db%, it also shows that the conventional isothermal model over predicts the conversion rate.

![Graphs showing particle conversion and temperature profiles](image)

Fig. 5. 7 Total conversion (a) and temperature (b) comparison of a near-spherical wood particle during devolatilization in nitrogen. Total conversion (c) and temperature (d) comparison of cylindrical wood particle (Length/d_p = 4) during devolatilization in nitrogen. (Conditions: d_p = 9.5 mm, M_c = 6.38 db%, 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 model parameters on non-isothermal model

A sensitivity analysis of model parameters under high temperature conditions has been shown in section 3.4.3.1. An additional analysis under a fluidized bed reactor condition is shown in Fig. 5.9. It should be noted that the radiative heat transfer is neglected in the sensitivity analysis. The devolatilization time is selected as the indicator to show the influence of the parameters. Fig. 5.9 shows the results of a sensitivity analysis done by decreasing and increasing each parameter by 50% for a 5 mm biomass particle devolatilized in 100% $N_2$ at $T_g = 1173$ K. The particle pore size, gas conductivity, 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, thereby, it is reasonable to assume the fixed carbon content as char yield in the modelling. The shrinkage coefficient also shows an insignificant impact on devolatilization time for the 5 mm wood particle. The drying and devolatilization rate also show limited effects on the modelling results, because the devolatilization process is heat transfer dominated for 5 mm particles [7]. The effect of char conductivity on the predicted devolatilization is smaller than 10%, it is reasonable to use a constant value for all kinds of biomass in the modelling. The predicted devolatilization time is sensitive to the particle dry density, but it can be easily measured by experiments and it is also the input of the three models. The biomass conductivity, biomass thermal capacity and the heat of devolatilization also show significant influences on the modelling results. Therefore, those parameters should be modified accordingly for the biomass particles that have significantly different values, compared to Table 3.1.
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3.2. Effects of convective heat transfer coefficient

In a fluidized bed, the surrounding conditions (e.g. slip velocity, gas composition, solid concentration, etc.) of the biomass particles are varied dynamically, which causes the dynamical change of convective heat transfer coefficient ($h_c$) during biomass drying and devolatilization. However, the heat transfer corrected coefficients $H_T$ and $H_{R,i}$ is determined with a constant $h_c$ in biomass particle drying and devolatilization life. To test whether the derived $H_T$ and $H_{R,i}$ determined by the corrected isothermal model can be used in a dynamically changed surrounding conditions of a biomass particle, two scenarios are designed for simulation. It should be noted that the radiative heat transfer is neglected in the modelling for simplification.

In Scenario I, it is assumed that the convective heat transfer coefficient varies alternately of two values with a frequency of 0.025 Hz as illustrated in Fig. 5. 10 (a). Fig. 5. 10 (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 history. However, the conventional isothermal model predicts a much faster devolatilization rate and particle heating rate. In Scenario II, a random time variated convective heat transfer coefficient, shown in Fig. 5. 10 (d), is used. The conclusion is the same as Scenario I according to Fig. 5. 10 (e) and (f).

Therefore, the results in Fig. 5. 10 imply that the corrected isothermal model is applicable to model biomass devolatilization in a fluidized bed where the convective heat transfer coefficient is dynamically changed.
5.4 Implementation of heat transfer corrected isothermal model in CFD modelling of biomass devolatilization

In section 5.3, the corrected isothermal model is validated at particle-scale. In this section, a CFD model based on Eulerian multiphase flow model is applied to simulate the 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. A two-dimensional domain is selected, because it saves computational time and gave similar results, as compared to three-dimensional simulations [87].

5.4.1 Model description

5.4.1.1 Model assumptions

Besides the assumptions used in Table 5. 1, the following additional assumptions are applied to simplify CFD simulation:

(1) Constant particle diameter during devolatilization.

(2) The biomass is assumed to be a dry particle, therefore, the correction of drying is not included in the CFD modelling.
(3) Since the devolatilization biomass particle is either floating on the bed surface or immersed in the particle surface, and only occasionally in contact with bubble, and the fluidized bed reactor for biomass combustion and gasification is usually operated at low temperature range (1023-1273 K), the radiative heat transfer is not significant and thus is not included in the current CFD model as done Xue et al. [88] and Xiong et al. [184].

5.4.1.2 Governing Equations

The Eulerian multiphase flow model in ANSYS Fluent® 18.0 is used to simulate biomass devolatilization in a batch fluidized bed [88]. The gas phase, biomass, and sand particles are treated as inter-penetrating continuums. The gas phase includes 2 species: N₂ and volatile, the biomass phase also includes two species: char and raw wood. The kinetic theory of granular flow (KTGF) is applied to close the solids stress [181]. The momentum exchange between gas and solid phase was derived by Gidaspow [181], which has been applied to model biomass devolatilization in bubbling fluidized bed reactors [87,187,189]. 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 by Syamlal et al. [218]. The heat exchange between the fluid and solid phase is determined by the model derived by Gunn [224], applicable to a porosity range of 0.35-1.0 and Reynolds number of up to 10⁵ [325]. The Nusselt Number (\( \text{Nu}_{gm} \)) is calculated as [325]:

\[
\text{Nu}_{gm} = \left( 7 - 10\varepsilon_g + 5\varepsilon_g^2 \right) \left( 1 + 0.7 \frac{\text{Re}_{sm}}{\text{Pr}^{1/3}} \right) + \left( 1.33 - 2.4\varepsilon_g + 1.2\varepsilon_g^2 \right) \frac{\text{Re}_{sm}}{\text{Pr}^{1/3}}
\]

(4.13)

Where \( m \) represents a different solid phase, \( m = 1 \), biomass phase, \( m = 2 \), sand phase.

For the conventional isothermal model, the convective heat transfer coefficient for biomass particle is given as [300,326]:

\[
h_{gm} = \frac{6\lambda_g \varepsilon_g \varepsilon_{sl} \text{Nu}_{gr1}}{d_{sl}^2}
\]

(4.14)

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

\[
h_{gm} = \frac{6\varepsilon_g \varepsilon_{sl}}{d_{sl}} \left( H_T \frac{\lambda_g \text{Nu}_{gr1}}{d_{sl}} \right)
\]

(4.15)

Where \( H_T \) is obtained from the heat transfer corrected isothermal model.

The devolatilization model is defined as a source term by using User Defined Functions (UDFs) in ANSYS Fluent® 18.0 as shown in Appendix C.
5.4.2 Geometry and operating conditions

Fig. 5. 11 shows the two-dimensional (2D) domain of the batch fluidized bed. The diameter and height of the fluidized bed 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 at a uniform temperature of 1173 K inlet stream, bed material, and reactor wall. More details of operating conditions and biomass properties are shown in Table 5. 3 and Table 5. 4, respectively.

---

**Fig. 5. 11 2D domain and initial conditions of CFD modelling the batch fluidized bed**

**Table 5. 3 Operating conditions of the batch fluidized bed**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$ inlet, m/s</td>
<td>0.65</td>
</tr>
<tr>
<td>Initial patched bed height, m</td>
<td>1.0</td>
</tr>
<tr>
<td>Solid volume fraction of sand particles, vol/vol</td>
<td>0.5</td>
</tr>
<tr>
<td>Diameter of sand particles, mm</td>
<td>0.5</td>
</tr>
<tr>
<td>Density if sand particles, kg/m$^3$</td>
<td>2600</td>
</tr>
<tr>
<td>Diameter of biomass particles, mm</td>
<td>1/3/6/10</td>
</tr>
<tr>
<td>Operating pressure, Pa</td>
<td>101325</td>
</tr>
<tr>
<td>Bed temperature, K</td>
<td>1173</td>
</tr>
<tr>
<td>Wall temperature, K</td>
<td>1173</td>
</tr>
</tbody>
</table>
### Table 5.4 Properties of the biomass particles used in CFD simulation

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, kg/m³</td>
<td>580</td>
</tr>
<tr>
<td>Volatile, wt%</td>
<td>90</td>
</tr>
<tr>
<td>Fixed carbon, wt%</td>
<td>9.5</td>
</tr>
<tr>
<td>Ash, wt%</td>
<td>0.5</td>
</tr>
<tr>
<td>Moisture, wt%</td>
<td>0.0</td>
</tr>
<tr>
<td>Char density, kg/m³</td>
<td>58</td>
</tr>
</tbody>
</table>

### 5.4.3 Simulation procedure and parameters

The CFD simulations are performed in two stages. At the first stage, only the sand particles are loaded to the bed with a height of 1 m, and the simulation starts with temperature of 1173 K without biomass particle. The solid flux at different heights and bed height is monitored to determine when the simulation reaches the quasi-steady state. The simulations show that it reaches a quasi-steady state after 10 seconds of fluidization. The results at the moments of 10 seconds after fluidization are used as the initial condition for the second stage. In the second stage, the biomass particles are fed into the fluidized bed reactor by patching in a region (0.5 m × 1 m with a centre coordinate (2.5, 2.5)). The solid volume fraction of patched biomass is 0.02, and the initial temperature of biomass particle is 298 K. The devolatilization rate can be affected by the amount of the patch of biomass particles, because a longer time is required to heat more biomass particles from the ambient temperature to the devolatilization temperature. However, this will not influence the results for a qualitative comparison between the corrected and the conventional isothermal models.

To improve the computational efficiency and numerical convergence, the algebraic form of the granular temperature model is chosen for both sand and biomass particles instead of the full granular energy balance model [206,327,328]. The no-slip and the partial-slip boundary conditions are applied to the gas phase and solid phase, respectively. The specularity coefficient is set as 0.001, as suggested by Vashisth et al. [329]. The correlation of physical properties is the same as those in Table 3.1, except for the particle shrinkage coefficient of zero.

To compare the results of the conventional and corrected isothermal models, 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 stored by using “Execute on Demand” UDFs in ANSYS Fluent® 18.0. The two-dimensional linear interpolation method [324] is used to calculate $H_T$ 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 sizes is given in Appendix C. The grid size adopted here is 15 mm × 30 mm and the number of meshes is approximately 9000. The grid size is 24 times of sand size, which is fine enough for coarse grid simulation of Group B particle as discussed by Li et al. [330]. The fraction of released volatile and the average temperature of biomass particles are monitored.
when devolatilization completes and the average temperature of biomass particles reaches a steady value, the CFD simulation will be stopped. The methods and parameters used in the simulation are summarized in Table 5.5.

Table 5.5 Methods and parameters for the simulation of the batch fluidized bed [206]

<table>
<thead>
<tr>
<th>Method/Parameter</th>
<th>Method/Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsteady formulation</td>
<td>Unsteady, 2nd-order Implicit</td>
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<td>Granular viscosity</td>
<td>Gidaspow</td>
</tr>
<tr>
<td>Granular bulk viscosity</td>
<td>Lun et al.</td>
</tr>
<tr>
<td>Frictional viscosity</td>
<td>Schaeffer</td>
</tr>
<tr>
<td>Granular temperature</td>
<td>Algebraic</td>
</tr>
<tr>
<td>Frictional pressure</td>
<td>Based KTGF</td>
</tr>
<tr>
<td>Solid pressure</td>
<td>Lun et al.</td>
</tr>
<tr>
<td>Radial distribution</td>
<td>Lun et al.</td>
</tr>
<tr>
<td>Angle of internal friction</td>
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<tr>
<td>Drag model</td>
<td>Gidaspow</td>
</tr>
<tr>
<td>Timestep</td>
<td>0.0005 s</td>
</tr>
</tbody>
</table>

5.4.4. Results and discussions

5.4.4.1 Devolatilization rate

Fig. 5.12 shows a comparison of the CFD results of biomass devolatilization rate in the batch fluidized bed by using the heat transfer corrected isothermal model and the conventional isothermal model. For the 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 predicted by the corrected isothermal model starts at a lower temperature and ends at higher particle temperature. At the particle average temperature of 600 K, the corrected isothermal model predicts a higher devolatilization rate than the conventional isothermal model, consequently, the corresponding volatile fraction in the gas phase is higher. The corrected isothermal model predicts a lower devolatilization rate and lower volatile concentration at the particle temperature of 800 K, as shown in Fig. 5.12. The results are consistent with what we observed from the particle-scale modelling, as well as the conclusions of the previous studies that the conventional isothermal model overestimates the devolatilization rate [89,319]. Such differences also reflect the importance of internal heat transfer.
Fig. 5. 12 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.

5.4.4.2 Conversion

Fig. 5. 13 shows the simulated conversion of biomass devolatilization in the batch fluidized bed by using the conventional and corrected isothermal models. The overall devolatilization rate predicted by the corrected isothermal model is lower than that of the conventional isothermal model for all particle size, the degree of the deviation between those two models depends on the biomass particle size. When $d_p = 1$ mm, the conventional isothermal model predicts slightly shorter devolatilization time than the corrected isothermal model, with a deviation of about 10%. With the increase of biomass particle size, the deviation of the predicted devolatilization time between those two models is over 30%.
Fig. 5. 13 Biomass conversion history of different particle size (1/3/6/10 mm) predicted by using the conventional and corrected isothermal models in CFD simulations.

5.4.4.3 The average temperature of biomass particles

Fig. 5. 14 shows the predicted the average temperature of biomass particles in the batch fluidized bed. For all particle sizes, the conventional isothermal model predicts a higher particle temperature than the corrected isothermal model. The reason is that under practical non-isothermal conditions, the particle surface temperature is higher than the particle average temperature, which means the heat flux between gas and particle is smaller than that described by the conventional isothermal model. Additionally, the deviation between the conventional and corrected isothermal model becomes large with the increase of particle size, because the effect of the internal particle temperature gradient becomes more significant on the devolatilization of thermally-thick biomass.
5.4.4.4 Computational time

The simulations have been carried out by using 16 cores in the HPC system of the Technical University of Denmark. All simulations were finished within 1 week for different particle sizes (1/3/6/10 mm) by using both the conventional and heat transfer corrected isothermal models. There is no significant difference in the computation time between the two models. For a 2D case with 100000 meshes and a time-step 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 simulation of pilot-scale or large-scale fluidized bed. Compared to the models in the literature (e.g. Papadikis et al. [187,189], and Ström and Thunman [193], and Lattice Boltzmann method [321], etc.), it is not necessary for the biomass particle to be discretized radially in a number of grid points by using the corrected isothermal model. Thus, it is expected that the corrected isothermal model would have a better performance with respect to computational efficiency when implemented in CFD modelling, compared to the non-isothermal models.

Fig. 5. 14 The average temperature of biomass particles of different particle size (1/3/6/10 mm) predicted by using the conventional and corrected isothermal models in CFD simulations.
5.5 Summary

In this chapter, a heat transfer corrected model for CFD simulation of devolatilization of thermal-thick biomass in fluidized beds is presented. Two heat transfer corrected coefficients, $H_T$-correction of heat transfer and $H_{R, i}$-correction of reaction rates are introduced. The model exhibited good accuracy comparable to the non-isothermal model in simulating a series of devolatilization experiments of thermally-thick biomass particles. After the model was validated at particle-scale, it was implemented in the Eulerian multiphase flow model to simulate the biomass devolatilization in a batch bubbling fluidized bed. The results show that the computational efficiency of the heat transfer corrected isothermal model is comparable to the conventional isothermal model, but it predicted a lower heating rate and devolatilization rate, which was in good agreement with the observations in single particle experiments and modelling. Therefore, the corrected isothermal model is applicable to simulate thermally-thick biomass devolatilization in a pilot-scale or large-scale fluidized bed with an acceptable computational cost.
6 A Mass transfer corrected uniform char conversion model

The main objective of this chapter is to develop a simplified char conversion model that can capture the conversion behaviour of the comprehensive char conversion model presented in Chapter 4. The model can be easily implemented in CFD modelling of biomass combustor and gasifier under fluidized bed conditions.

6.1 Introduction

Uniform char conversion models (UCM) and shrinking core models (SCM) have been widely used to describe char conversion in CFD modelling [36–38,43–46]. UCM models consider both external mass transfer and kinetics of reactions, which is reasonable for a case of kinetics controlled or external mass transfer controlled. SCM models is reasonable for char oxidation at high temperatures, which is controlled by mass transfer rate. However, both the UCM and SCM models neglect intra-particle mass and heat transfer, which influence significantly char conversion and gas species concentration distributions inside a char particle [7]. Additionality, UCM models neglect the particle shrinkage during char conversion, which significantly influences the external mass and heat transfer during char conversion. The progressive char conversion models (PCM) consider the char combustion and gasification occurring throughout the particle, including the internal mass and heat transfer, external mass and heat transfer, and particle shrinkage as discussed in section 2.1.3. However, a PCM model is time-consuming when it is directly coupled with CFD, since a biomass particle is required to discrete radially with a large number of mesh grid points (e.g. 50) [193]. Therefore, developing a simplified model that can capture the conversion behaviour of a PCM model, can both save the simulation time and improve the accuracy of CFD simulations.

In this chapter, a mass transfer corrected uniform char conversion (MTC-UCM) has been developed by comparing the difference between a PCM and a UCM model. Three correction coefficients, correction of reaction rate \(H_{R(i)}\), correction of diffusion rate \(H_{m(i)}\), and correction of heat transfer \(H_T\), have been defined. A comparison of the PCM, the UCM, and the MTC-UCM model has been made by modelling single char particle conversion process.

6.2 Model description

The UCM model, PCM model, and MTC-UCM are described in the following section. The general assumptions of the models are listed in Table 6.1.
Table 6.1 General assumptions of the three particle models.

<table>
<thead>
<tr>
<th>Items</th>
<th>Model assumptions</th>
</tr>
</thead>
</table>
| UCM   | (1) Zero-dimensional model  
(2) Internal mass and heat transfer neglected  
(3) The effect of Stefan flow on the external heat transfer neglected  
(4) The effect of Stefan flow on the external mass transfer neglected  
(5) Constant particle size during char conversion  
(6) Pseudo-steady state, with no gas components accumulated inside char particle  
(7) The char only consists of carbon and ash. |
| PCM   | (1) A one-dimensional transient model for spherical wood char particle  
(2) The internal mass and heat transfer are included  
(3) The effect of Stefan flow on the external heat transfer neglected [12,30]  
(4) The effect of Stefan flow on the external mass transfer neglected [308].  
(5) The shrinkage of a char particle is modelled by assuming ash peeling off when the char conversion is over 0.95  
(6) The char only consists of carbon and ash  
(7) The specific surface area for wood chars spreads over a large range as summarized by Haberle et al. [313], and it also changes along with the char conversion [22]. For simplicity, it is assumed to a constant specific surface area of 1.0×10⁶ m²/m³ [12]. |
| MTC-UCM | (1) Zero-dimensional model  
(2) Internal mass and heat transfer neglected  
(3) The effect of Stefan flow on the external heat transfer neglected, but it is corrected by a coefficient of heat transfer rate ($H_T$)  
(4) The effect of Stefan flow on the external mass transfer neglected, but is it corrected by a coefficient of external mass transfer rate ($H_{m,i}$)  
(5) Constant particle size during char conversion  
(6) Pseudo-steady state, with no gas components accumulated inside char particle  
(7) The char only consists of carbon and ash.  
(8) Gasification and oxidation rate are corrected by a correction of reaction rate ($H_{R,i}$) |

6.2.1 Uniform char conversion model

According to the assumption of a pseudo-steady state, the mass transfer rate of a gas species ($i$) from bulk gas to particle equals to its consumption/generation rate inside the char particle. Therefore,
\[
\frac{dm_i}{dt} = \sum_{i=1}^{l} \omega_i r_i \frac{\pi d_{p0}^3}{6} + h_{m,UCM,i} \frac{\rho_g}{M_{w,i}} (Y_{b,i} - Y_i) = 0
\]  

(5.1)

Where \( r_i \) is the reaction rate of reaction \( i \), kg/(m\(^3\)s), which is described in section 4.2.2, \( \omega_i \) is the stoichiometry coefficient of gas species \( i \), \( h_{m,UCM,i} \) is the mass transfer coefficient, m/s, \( \rho_g \) is the gas density inside particle, kg/m\(^3\), \( M_w \) is the molecular weight, kg/mol, \( Y_b \) is mass fraction in the bulk gas, \( Y_i \) is the mass fraction in the particle external surface, \( i = 1,2,3,4,5,6 \) represents O\(_2\), CO\(_2\), H\(_2\)O, CO, H\(_2\), and N\(_2\) respectively. \( i \) is the number of reactions, it is equal to 3 for char conversion.

The gas species concentration at particle can be obtained by solving the above equations. The energy balance equations include convective and radiative heat transfer, and the heat generated or consumed by char oxidation or gasification:

\[
\left( \rho_c C_{pc} + \rho_a C_{pa} + \varepsilon_p \rho_g \sum_{i=1}^{l} Y_i C_{pg,i} \right) \frac{\pi d_{p0}^3}{6} \frac{dT}{dt} = \pi d_{p0}^2 \left( h_{c,UCM} (T_b - T) + \sigma \varepsilon \left( T_b^4 - T^4 \right) \right) + \sum_{i=1}^{l} \Delta H_i r_i
\]  

(5.2)

\( \Delta H_i \) is the enthalpy change of char reaction \( i \), \( i = 1, 2, 3 \), represents char oxidation, char CO\(_2\) gasification, and char H\(_2\)O gasification, respectively. \( C_{pc} \) and \( C_{pa} \) is heat capacity of char and ash, respectively calculated based on Johansen et al. [1] and Jakub et al.[101]. The heat capacity of gas species follows the expression in NIST Chemistry WebBook (https://webbook.nist.gov/). \( \varepsilon_p \) is the particle voidage, \( h_{c,UCM} \) is the convective heat transfer coefficient, W/(m\(^2\)-s), \( T_b \) is the bulk gas temperature, K, \( T \) is the particle temperature, K.

The char conversion rate:

\[
\frac{d \rho_c}{dt} = \sum_{i=1}^{l} r_i
\]  

(5.3)

The mass transfer rate of gas species \( i \) predicted by the UCM model:

\[
J_{UCM,i} = h_{m,UCM,i} \frac{\pi d_{p0}^3}{6} \frac{\rho_g}{M_{w,i}} (Y_{b,i} - Y_i)
\]  

(5.4)

The heat transfer rate predicted by the UCM model:

\[
Q_{UCM} = \pi d_{p0}^2 \left( h_{c,UCM} (T_b - T) + \sigma \varepsilon \left( T_b^4 - T^4 \right) \right)
\]  

(5.5)

The reaction rate of reaction \( i \) predicted by the UCM model:

\[
R_{UCM,i} = \frac{r_i \pi d_{p0}^3}{6}
\]  

(5.6)

### 6.2.2 Progressive char conversion model

The conservation equation of gaseous species \( i \) inside a char particle is,
\[
\frac{\partial \left( \varepsilon_g \rho_g Y_{g,i} \right)}{\partial t} = \frac{\partial \left( \varepsilon_g \rho_g D_{\text{eff},i} \frac{\partial Y_{g,i}}{\partial r} \right)}{r^2 \partial r} + S_i, \quad 0 < r < \frac{d_p}{2} \quad (5.7)
\]

The conservation equation of heat inside a char particle is,
\[
\frac{\partial}{\partial t} \left( \rho_c C_{pc} + \rho_a C_{pa} + \varepsilon_g \rho_g \sum_{i=1}^{l} Y_i C_{pg,i} \right) T = \frac{\partial}{\partial r} \left( \frac{r^2 \lambda_{\text{eff}} \frac{\partial T}{\partial r}}{r^2} \right) + \sum_{i=1}^{l} r \Delta H_i, \quad 0 < r < \frac{d_p}{2} \quad (5.8)
\]

\( S_i \) is the source term of gas species \( i \) in the char particle and the particle boundary layer, respectively, \( \text{kg}/(\text{m}^3 \text{-s}) \), expressed as follows:
\[
S_i = \sum_{i=1}^{l} r \omega_i \quad (5.9)
\]

The sum of all gas species in the gas phase should be unity,
\[
\sum_{i=1}^{l} Y_{g,i} = 1 \quad (5.10)
\]

The mass balance of char and ash inside wood char particle is,
\[
\frac{\partial \rho_c}{\partial t} = -\sum_{i=1}^{l} r_i \quad (5.11)
\]
\[
\frac{\partial \rho_a}{\partial t} = 0 \quad (5.12)
\]

The boundary conditions of Eq. (6.7):
\[
\left. D_{\text{eff},i} \frac{\partial Y_i}{\partial t} \right|_{r=d_p/2} = h_{\text{m,PCM},i} \left( Y_{b,i} - Y_{s,i} \right) \quad (5.13)
\]
\[
\left. \frac{\partial Y_i}{\partial t} \right|_{r=0} = 0
\]

The boundary conditions of Eq. (6.8):
\[
\left. \lambda_{\text{eff}} \frac{\partial T}{\partial t} \right|_{r=d_p/2} = h_{\text{t,PCM}} \left( T_b - T_s \right) + \sigma \xi \left( T_w^4 - T_s^4 \right) \quad (5.14)
\]
\[
\left. \frac{\partial T}{\partial t} \right|_{r=0} = 0
\]

Here, \( T_b \) is the bulk gas temperature, and \( T_s \) is the temperature of the external surface of the particle, and \( T_w \) is the wall temperature of the reactor.

The physical properties, such as effective diffusion coefficients, pore diameter, binary diffusion coefficient of species \( i \) in the gas mixture, the density of gas, particle voidage, effective
conductivity, and heat capacity of char, ash, and gas species, and the external mass and heat transfer coefficients can be calculated based on the correlations given in section 4.2.4.

The average particle conversion is given as:

$$X_{\text{avg}} = \frac{\int_{0}^{R} 4\pi r^2 X_r \, dr}{\int_{0}^{R} 4\pi r^2 \, dr} \quad (5.15)$$

The mass transfer rate of gas species $i$ predicted by the PCM model:

$$J_{\text{PCM},i} = h_{m,\text{PCM},i} A_p \frac{\rho_s}{M_{w,i}} (Y_{b,i} - Y_{s,i}) \quad (5.16)$$

Where $A_p$ is the external particle surface area, m$^2$.

The heat transfer rate predicted by the PCM model:

$$Q_{\text{PCM}} = \pi d_p^2 \left( h_{c,\text{PCM}} \left(T_b - T_s\right) + \sigma \varepsilon \left(T_b^4 - T_s^4\right) \right) \quad (5.17)$$

The reaction rate of reaction $i$ predicted by the PCM model:

$$R_{\text{PCM},i} = \int_{0}^{R} 4\pi r^2 r_i \, dr \quad (5.18)$$

6.2.3 Mass transfer corrected uniform char conversion model

To take account the effect of the internal heat and mass transfer on char conversion, three correction coefficients, $H_T$, $H_{M,i}$, and $H_{R,i}$ are introduced to describe the difference between the UCM model and the PCM model when the same char conversion is predicted by those two models. The assumptions of MTC-UCM model are given in Table 6. 1. According to its definitions, the correction coefficients can be determined as follows:

$$H_{R,i} = \frac{R_{\text{PCM},i}}{R_{\text{UCM},i}} = \frac{\int_{0}^{R} 4\pi r^2 r_i \, dr}{r_i \pi d_{p0}^3} = \frac{24 \int_{0}^{R} r^2 r_i \, dr}{r_i d_{p0}^3} \quad (5.19)$$

$$H_{m,i} = \frac{J_{m,\text{PCM},i}}{J_{m,\text{UCM},i}} = \frac{h_{m,\text{PCM},i} \pi d_p^2 \frac{\rho_s}{M_{w,i}} (Y_{b,i} - Y_{s,i})}{h_{m,\text{UCM},i} \pi d_{p0}^2 \frac{\rho_s}{M_{w,i}} (Y_{b,i} - Y_{s,i})} = \frac{h_{m,\text{PCM},i} \pi d_p^2 (Y_{b,i} - Y_{s,i})}{h_{m,\text{UCM},i} \pi d_{p0}^2 (Y_{b,i} - Y_{s,i})} \quad (5.20)$$

$$H_T = \frac{Q_{\text{PCM}}}{Q_{\text{UCM}}} = \frac{\pi d_p^2 (h_{c,\text{PCM}} \left(T_b - T_s\right) + \sigma \varepsilon \left(T_b^4 - T_s^4\right))}{\pi d_{p0}^2 (h_{c,\text{UCM}} \left(T_b - T\right) + \sigma \varepsilon \left(T_b^4 - T^4\right))} = \frac{d_p^2 (h_{c,\text{PCM}} \left(T_b - T_s\right) + \sigma \varepsilon \left(T_b^4 - T_s^4\right))}{d_{p0}^2 (h_{c,\text{UCM}} \left(T_b - T\right) + \sigma \varepsilon \left(T_b^4 - T^4\right))} \quad (5.21)$$
By using the correction coefficients, the MTC-UCM model can be written as:

\[
\frac{dm}{dt} = \sum_{i=1}^{l} H_{R,i} r_i \left( \frac{\pi d_{p0}^3}{6} + H_{m,i} h_{m,UCM,i} \frac{\rho_s}{M_{w,i}} \right) \left( Y_{b,i} - Y_i \right) = 0
\]  

(5.22)

\[
\left( \rho_{c}, C_{pc} + \rho_{a} C_{d} + \varepsilon_{a} \rho_{b} \sum_{i=1}^{l} Y_{C_{pg,i}} \right) \frac{\pi d_{p0}^3}{6} \frac{dT}{dt} = H_{T} \pi d_{p0}^2 \left( h_{T,UCM} \left( T_{b} - T \right) + \sigma \mu \left( T_{b}^4 - T^4 \right) \right) + H_{R,i} r_i \Delta H_r
\]

(5.23)

\[
\frac{d\rho_c}{dt} = \sum_{i=1}^{l} H_{R,i} r_i
\]

(5.24)

It should be noted that the PCM model is a transient model. The gas species is possible accumulated inside a char particle. Therefore, \(H_{R,i}\) is not equal to \(H_{m,i}\). If the UCM and PCM model is solved under the same conditions, the parameters (e.g. temperature, gas concentration, heat and mass transfer coefficients) at the same degree of char conversion can be obtained to calculate the correction factors. The procedures to obtain the corrected coefficients are shown in Fig. 6. 1:

1. Obtaining the input parameters according to the operating conditions, including the gas and wall temperatures, initial density, diameter, and temperature of char particle, as well as the bulk gas properties and slip velocity between the particle and bulk gas.

2. With the input parameters, the char conversion kinetics, and physical properties, solving the PCM model to obtain the radial profiles (e.g. particle conversion, gas species concentration, particle density, etc.) and mass and heat transfer coefficients. Then the particle average conversion is calculated by Eq. (6.15) and the external mass transfer rate, and heat transfer rate, and reaction rate are calculated by Eq. (6.16), Eq. (6.17), and Eq. (6.18), respectively. A series of data \((X_{av}, J_{m,PCM,i}, Q_{PCM}, R_{PCM})\) are obtained.

3. Using the same input parameters of PCM to solve the UCM model. Then the char particle conversion, temperature, and mass and heat transfer coefficients can be obtained. The external mass transfer rate, and heat transfer rate, and reaction rate of the uniform char conversion model is calculated by Eq.(6.4), Eq.(6.5), and Eq.(6.6), respectively. A series of data \((X, J_{m,UCM,i}, Q_{UCM}, R_{UCM,i})\) are obtained.

4. Based on the data of \((X_{av}, J_{m,PCM,i}, Q_{PCM}, R_{PCM,i})\) from the PCM model, and \((X, J_{m,UCM,i}, Q_{UCM}, R_{UCM,i})\) from the UCM model. Comparing the external mass and heat transfer rate, and reaction rate predicted at the same char conversion predicted by the different models, then calculating the corrected coefficients according to Eq. (6.19)-Eq. (6.21). The corrected coefficients, \(H_{m,i}\), \(H_{R,i}\) and \(H_T\) are dependent on char conversion.

The corrected coefficient can be used in single particle modelling and CFD modelling with the similar operating conditions specified in step (1).
6.2.4. Kinetics of heterogeneous reactions

The kinetics of heterogeneous reactions used in this chapter are the same as the developed char conversion model as shown in Table 4.1. Since the objectives here are to simplify the PCM model to the UCM model and evaluate the MTC-UCM model, only the kinetics of pine wood char are used in the modelling as an example.

6.3 Computational cases

Five different cases are selected with the operating conditions shown in Table 6.2. Significantly different particle size and gas velocity are chosen to investigate its effects on the correction
coefficients. Case 5 is selected to evaluate the effects of the kinetics of char oxidation on the correction coefficients. Since the biomass devolatilization is commonly completed before the particle temperature reaching 873 K [7], the initial char particle temperature is set to this temperature.

Table 6. 2 The operating conditions of five different cases.

<table>
<thead>
<tr>
<th>Items</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
<th>Case 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle diameter (mm)</td>
<td>1.0</td>
<td>1.0</td>
<td>0.5</td>
<td>5.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Slip velocity (m/s)</td>
<td>1.0</td>
<td>0.1</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Char density (kg/m³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>120</td>
</tr>
<tr>
<td>Gas composition (vol%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂: 4%, CO₂: 13%, H₂O: 13%, N₂: 70%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂: 20%, N₂: 80%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactor wall: 1173, Gas: 1173</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash composition (wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.5%</td>
</tr>
<tr>
<td>Particle temperature (K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>873</td>
</tr>
</tbody>
</table>

6.4 Results and Discussion

6.4.1 Comparison with the comprehensive char conversion model

Fig. 6. 2 shows the char conversion profiles predicted by the UCM and PCM models, in comparison with the comprehensive char conversion model (PCM-B) developed in Chapter 4. As we expected, the UCM model, which neglects the internal heat and mass transfer resistance, predicts the shortest char conversion time for both case 3 and case 4. The deviation of predicted char conversion time between UCM model and the PCM-B model is up to 50%. However, char conversion profiles predicted by the PCM model are quite similar to the PCM-B model for a 0.5 mm particle, and the deviation between the PCM and the PCM-B is smaller than 20% for a 5.0 mm particle. Therefore, it is reasonable to reduce the PCM-B model to PCM model by neglecting the homogeneous reactions occurring the particle boundary layer under fluidized bed conditions, which is commonly operated at low temperatures (< 1273 K).

Fig. 6. 2 A comparison of three different models (PCM-B: the char conversion model developed in Chapter 4, both heterogeneous reactions and homogeneous reactions included, PCM: progressive char conversion model, the homogeneous reactions in the particle boundary layer neglected, UCM: uniform char conversion model) with operating conditions of case 3 and case 4.
6.3.2 Correction factors

Fig. 6.3 (a) and (b) shows a comparison of the predicted reaction rate of the UCM and the PCM model and the corresponding correction coefficients, respectively. As expected, the reaction rates of char oxidation and H₂O gasification predicted by the UCM model are higher, as compared to the PCM model. Such phenomena are caused by two aspects. The UCM model neglects the internal mass transfer leading to a higher mass transfer rate than that of the PCM model. In addition, the UCM model assumes a constant particle size, which predicts a higher external mass transfer rate compared to a particle with a shrinking size. Therefore, compared to the PCM model, higher H₂O gasification and char oxidation rates are predicted by the UCM model. The PCM model predicts a higher char CO₂ gasification in a certain range, because CO₂ is transferred from particle to bulk gas. The corrections for reaction rate ($H_{R,i}$) are significantly affected by the char conversion process as shown in Fig. 6.3 (b). For char oxidation, it decreases along with the char conversion. For char CO₂ and H₂O gasification, it is in a range of 0.4-1.5 and does not decrease monotonically, indicating the control mechanism of char oxidation and gasification is different.

Fig. 6.3 (c) and (d) shows a comparison of external mass transfer rate predicted by the UCM and the PCM model and the corresponding correction coefficients, the corrections coefficients also significantly depends on the char conversion as shown in Fig. 6.3 (d).

Fig. 6.3 (e) and (f) shows a comparison of the external heat transfer rate predicted by the UCM and the PCM and the corresponding correction factors. In the beginning, the external heat transfer rate predicted by UCM and PCM model is similar. With the increase of conversion, the heat transfer rate predicted by the PCM model is larger than that of the UCM model and then is smaller with a further increase of char conversion. The correction factor of external heat transfer is in a range of 0.2-1.6.
Fig. 6. 3 Comparison between the UCM and PCM model and the correction factors for reaction rate, external mass transfer, and external heat transfer. Operating conditions: case 1.

6.4.3 Char conversion

Fig. 6. 4 shows the char conversion predicted by using the different models. As compared to the PCM model, the char conversion rate is higher by the UCM model, since the UCM model neglects the particle shrinkage and internal particle mass transfer resistance. To investigate the effects of the correction coefficients on the modelling results of MTC-UCM model, four cases are considered. In the case of MTC-UCM-$H_m$-$H_R$-$H_T$, all correction coefficients derived by Eq. (6.19)-Eq. (6.21) are included, it gives similar results with the PCM model. In the case of MTC-UCM-$H_m$-$H_R$, the correction factor of $H_T$ is neglected and the only $H_{R,i}$ and $H_{m,i}$ are included, the model still gives similar results with the PCM model. Therefore, the correction of external heat transfer is negligible. In the case of MTC-UCM-$H_R$, only the correction of reaction rates is included in the model, the model shows better results than the UCM model, but it still
overestimates the char conversion rate. Therefore, the correction of external mass transfer should be considered in the UCM model. In the case of MTC-UCM-$H_m$, which only corrects the external mass transfer rate, the model gives similar results to the PCM model. Therefore, the mass transfer has the most significant effects on the modelling results among all corrections, and the corrections for the char reaction rate also have certain degree effects on the modelling results. The following discussions will be focused on the effects of some parameters (e.g. particle size, reaction rate, etc.) on correction coefficients.

**Fig. 6.4** The mass conversion profile history predicted by different models. UCM: uniform char conversion model, PCM: progress char conversion model, MTC-UCM-$H_m$-$H_R$-$H_T$: mass transfer corrected uniform char conversion model with $H_m$, $H_R$, $H_T$ corrections, MTC-UCM-$H_m$-$H_R$: mass transfer corrected uniform char conversion model with $H_m$-$H_R$; MTC-UCM-$H_R$: mass transfer corrected uniform char conversion model with $H_R$; mass transfer corrected uniform char conversion model with $H_m$. Operating conditions: case 1.

### 6.4.4 Effects of particle size

Fig. 6.5 (a) and (b) show the effects of particle size on the correction coefficients of char oxidation rate ($H_{R,i}$) and the external mass transfer rate of oxygen. For different particle sizes, the correction degree for char oxidation rate increase along with the increase of char conversion. The probable reason is that the char particle external surface area decreases along with char conversion resulting in a reduction of mass transfer rate. Compared to the case of $d_p = 0.5$ mm, the correction degree of char oxidation is small than that of $d_p = 5.0$ in most of the region.

Fig. 6.5 (c) and (d) show the effects of particle size on the correction factor of the char CO$_2$ gasification rate and the external mass transfer rate of CO$_2$. The correction coefficient of the gasification rate is larger than 1 in most of the region for the small particle, while it is smaller than 1 for the large particle. Since the char oxidation occurs throughout the whole particle for the small particle, the extra intra-particle mass and heat transfer resistance considered in the PCM model may result in a higher CO$_2$ concentration and higher particle temperature inside the char particle. Therefore, a higher CO$_2$ gasification rate observed by the PCM model for the
large particle, the char oxidation only occurs at the external particle surface, the heat generated by char oxidation is quickly transferred to bulk gas, resulting in a lower particle temperature as compared to the UCM model. Therefore, the CO$_2$ gasification rate predicted by the PCM model is smaller than that of the UCM model.

Fig. 6.5 (e) and (f) show the effects of particle size the correction degree of H$_2$O gasification rate and the diffusion rate of H$_2$O. Similar to the case of CO$_2$, the correction degree of both char H$_2$O gasification rate and external mass transfer rate are significantly affected by char particle size.

![Graphs showing the effects of particle size on the correction factors](image)

Fig. 6.5 The effects of particle size on correction factors, operating conditions: $u_v = 1.0$ m/s, $T_w = 1173$ K, $T_g = 1173$ K, gas composition: O$_2$: 4%, CO$_2$: 13%, H$_2$O: 13%, N$_2$: 70%, $T_{p0} = 873$ K.

### 6.4.5 Effects of slip velocity

Since the external mass transfer coefficients are significantly affected by the slip gas velocity, the effects of slip gas velocity on correction factors of reaction rates and diffusion rates are
investigated and shown in Fig. 6. Fig. 6 (a) and (b) show the effect of slip gas velocity on the correction degree of char oxidation and diffusion rate of oxygen from bulk gas to the particle. The results show that the slip velocity has limited effects on the correction degree of both char oxidation rate and the external mass transfer rate, since the char oxidation is dominated by intra-particle mass transfer under the testing case [25].

Fig. 6 (c)-(f) show the effects of slip gas velocity on the CO$_2$ and H$_2$O gasification rate and diffusion rate. Similar to the char oxidation, the correction degree of both the char gasification rate and the external mass transfer rate is insignificantly affected by gas slip velocity.

**Fig. 6.** The effects of gas velocity on correction factors, operating conditions: case 3 and case 4.

Fig. 6. 7 shows the char conversion history predicted by different models with slip velocities of 0.1 m/s and 10 m/s. Even though the corrected coefficients for the MTC-UCM model are
derived from a case with a slip velocity of 1.0 m/s, the MTC-UCM model can give similar modelling results with the PCM model. The reason is that the slip velocity has limited effects on the corrected coefficients as shown in Fig. 6. Therefore, it is possible to calculate the corrected coefficient under a specified condition used in fluidized bed conditions, in which particle slip velocity is dynamically changed.

Fig. 6. The char conversion history predicted by different models with different slip velocity (a) $u_s = 0.1$ m/s, (b) $u_s = 10$ m/s. Operating conditions: $d_p = 1.0$ mm, $T_w = 1173$ K, $T_g = 1173$ K, gas composition: $O_2$: 4%, $CO_2$: 13%, $H_2O$: 13%, $N_2$: 70%, $T_{p0} = 873$ K

6.4.6 Effects of reactions rate

Fig. 6. shows the effects of the reaction rate on the corrected coefficients. To eliminate the effects of $CO_2$ and $H_2O$ gasification, the bulk gas concentration of $CO_2$ and $H_2O$ as well as char gasification rate are set to zero. Therefore, only the correction coefficients of char oxidation and external mass transfer of $O_2$ is shown in Fig. 6. (a) and Fig. 6. (b), respectively. The case of $0.01 r_1$ is that the pine char oxidation kinetic scaled by 0.01 times, which is a representative case of the kinetic control regime. As expected, the corrected coefficient is close 1, which means that similar results can be predicted by the UCM and PCM models. The case of $100R_1$ is a typical mass transfer dominated regime, the correction coefficient decreases along with the char conversion, because a decrease of char particle external surface finally results in a decrease external mass transfer flux of oxygen.
The effects of reaction on correction factors, operating conditions: case 5 with only considering char oxidation, 0.01 $r_1$: the pine char oxidation kinetic scaled by 0.01 times, $r_1$: the original pine char oxidation kinetics.

### 6.5. Summary

A mass transfer corrected uniform char conversion model (MTC-UCM) has been derived by comparing UCM and PCM model. Three correction coefficients: correction of reaction rate ($H_{R,i}$), correction of diffusion rate ($H_{m,i}$), and correction of heat transfer ($H_T$), have been defined. The conventional method to improve the UCM model performance is by introducing an effectiveness factor to correct reactions rate, this model indicates that both reaction rate, diffusion rate and heat transfer rate should be included. It is found that the $H_T$ may be negligible in the test conditions, the UCM model gives similar results with the PCM model by using the correction coefficients of char reaction rate and external mass transfer rate. The sensitivity analysis shows that the particle size and reaction rate have significant effects on the value of correction coefficients, while the gas slip velocity has a limited impact on the correction coefficients. Therefore, it is possible to use the correction coefficient calculated from a specified condition to simulate biomass char particle combustion in fluidized bed reactor. For the biomass char conversion under high temperature case, the gas phase reactions in the boundary layer have significant effects on char conversion process as discussed in Chapter 4, the MTC-UCM model may not be suited for this case.
7 Full-loop CFD simulation of hydrodynamics in a pilot-scale dual fluidized bed system for biomass gasification

The main objective is to investigate the hydrodynamic behaviours in a pilot-scale dual fluidized bed system for biomass gasification. A meso-scale drag model has been evaluated by the experimental data.

7.1 Introduction

Biomass is a renewable fuel, which is considered as an alternative to fossil fuels [331–334]. Gasification is a technology to convert biomass to syngas that can be used for the production of electricity, chemicals and transportation fuels [332]. Fluidized bed [40,332,335] and fixed bed [336] are commonly applied in biomass gasification. Compared to a fixed bed, fluidized bed gasification has the advantages of high fuel flexibility [333], and more importantly, the realization of biomass gasification by a dual fluidized bed system that can obtain high-quality syngas without applying oxygen blown system [332].

In a dual fluidized bed system, gasification, and combustion occur in two separate fluidized beds. The heat for gasification is provided by char combustion in the form of recirculating particles. A dual fluidized bed system may consist of different combinations of fluidized beds. For example, a system with combustion in a fast fluidized bed (FFB) and gasification in a bubbling fluidized bed (BFB) is often applied [9,49,333]. However, the design and scale-up are challenging due to the complex hydrodynamics in the system [171,335].

CFD has been applied to study hydrodynamics in a dual fluidized bed system [9,49,171,337]. The Eulerian-Eulerian (E-E) approach is commonly used [9,32–34], due to it requires lower computational time than the Eulerian-Lagrangian (E-L) approach [338]. Nguyen et al. [9] presented the results of a 2D E-E model validated by cold experimental data from a pilot-scale dual fluidized bed gasification system. Their model was further used to study the effect of the loop-seal valve of the dual-fluidized bed system on solid circulation rate in the recycle loop [32]. Yan et al. [33] developed a 3D model to simulate biomass steam gasification in a dual fluidized bed reactor. CFD modelling of other dual fluidized bed systems, e.g. chemical looping systems, has also been reported [326,339–342].

Most of the existing full-loop CFD models use a single drag model to simulate a dual bed system consisting of a FFB and a BFB [9,32,33,47–49]. For example, the Gidaspow drag model has been used to simulate both FFB and BFB [181]. However, such model usually requires a small grid size (e.g. 20 times of particle size) [174], which is computationally cost for a large-scale system. The model generally overestimates the momentum exchange between gas and solid phase for fast fluidization [174,343,344]. Compared to the Gidaspow drag model and other homogeneous drag models, the heterogeneous EMMS drag model is less grid-size
dependent and thereby more favourable in simulating large-scale systems\cite{174,206,345}. However, due to the different flow regimes of the FFB and the BFB, different EMMS drag models, i.e. the EMMS/matrix model \cite{195,204} for a FFB and the EMMS/bubbling model \cite{205,206,217,346} for a BFB, are required to achieve accurate simulation in the dual bed system. Such a hybrid EMMS drag model applied in a dual bed system has not explored so far. Besides, the solid inventory influences significantly the heat transfer behaviour between sand and fuel particles. However, the effect of solid inventory on the hydrodynamics is rarely investigated in the existing CFD simulations of dual fluidized bed systems.

The main objective of this work is to apply the hybrid EMMS drag models to simulate the hydrodynamics of a full-loop dual fluidized bed system. Experimental results from a pilot-scale dual fluidized bed system for biomass gasification are used to validate the model. The validated model is used to evaluate the effect of solid inventory on the hydrodynamics of the dual fluidized system for biomass gasification.

### 7.2 Experiments

A pilot-scale dual fluidized bed system for biomass gasification is schematically shown in Fig. 7.1. The system was constructed in the Institute of Process Engineering, Chinese Academy of Sciences, which includes a riser (FFB) for char combustion, a cyclone, two loop-seals, and a BFB for biomass gasification. The riser is about 10 m high, and the diameters of the upper and the bottom section are 0.124 m and 0.30 m, respectively. The total height of the BFB is 2.60 m, with an inner diameter of 0.25 m in the bottom cylinder. The origin position marked as “0” in Fig. 7.1, is in the centre of the FFB bottom. Nine pressure transducers are installed along with the height of the riser and that of BFB for measuring the pressure profile in the looping system. The pressures at the bottom of two loop-seals are also monitored.

Biomass particles are fed to the top of BFB by a screw feeder. The full-load of the dual fluidized gasification system is 70 kg (biomass)/h. The pyrolysis and gasification of biomass take place in the BFB. The remaining char is transported together with sand particles through the lower loop-seal to the bottom of FFB, where char combustion takes place. The sand particles are heated by char combustion and recirculated to BFB to provide heat for the biomass pyrolysis and gasification. Both air and steam gasification have been investigated in the experiments, with the conditions shown in Table 7.1. For air gasification, the operating temperatures of the FFB and BFB are 1163 K and 1048 K, with superficial gas velocities of 9.29 m/s and 0.76 m/s, respectively. For steam gasification, the operating temperatures of the FFB and BFB are 1093 K and 963 K, with superficial gas velocities of 9.17 m/s and 0.25 m/s. The sand solid inventory of both cases is 120 kg. The solids circulation rate based on the mass and heat balance calculation is 0.246 kg/s for air gasification and 0.250 kg/s for steam gasification, respectively. The physical properties of the gas in the FFB are estimated by using the gas composition (18%
CO₂, 79% N₂, and 3% O₂) at the outlet of the cyclone. The physical properties of the gas in the BFB is based on the gas composition of the outlet of BFB, which is shown in Appendix D. The particle size distribution of the sand particles is shown in Fig. 7. 2. The Sauter mean diameter of sand particles is 323 µm which belongs to Group B particle based on the classification of Geldart [347].

---

**Fig. 7.** Schematic plot of the pilot-scale dual fluidized bed system for biomass gasification with geometry and mesh. (1): main gas for char combustion, (2) inlet of sand at the start of the setup, (3) outlet of cyclone, (4) fluidization gas for the upper loop-seal, (5) gasification gas for BFB, (6) fluidization gas for the lower loop-seal.
Fig. 7.2 The particle size distribution of the sand particles used in the experiments

Table 7.1 Operating conditions of air and steam gasification

<table>
<thead>
<tr>
<th></th>
<th>Air gasification</th>
<th>Steam gasification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main gas(1), m/s</td>
<td>9.288</td>
<td>9.170</td>
</tr>
<tr>
<td>Gas temperature, K</td>
<td>1163</td>
<td>1093</td>
</tr>
<tr>
<td>Fluidized gas(4,6), m/s</td>
<td>0.088</td>
<td>0.088</td>
</tr>
<tr>
<td>Gasification gas (5), m/s</td>
<td>0.758</td>
<td>0.252</td>
</tr>
<tr>
<td>Gasification gas temperature, K</td>
<td>1048</td>
<td>963</td>
</tr>
<tr>
<td>Temperature of FFB, K</td>
<td>1163</td>
<td>1093</td>
</tr>
<tr>
<td>Temperature of BFB, K</td>
<td>1048</td>
<td>963</td>
</tr>
<tr>
<td>Gauge pressure at cyclone outlet (3), kPa</td>
<td>1.55</td>
<td>2.00</td>
</tr>
<tr>
<td>Gauge pressure at BFB outlet, kPa</td>
<td>4.8</td>
<td>3.30</td>
</tr>
<tr>
<td>Solid inventory, kg</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Particle density, kg/m³</td>
<td>2600</td>
<td>2600</td>
</tr>
<tr>
<td>Mean particle size, µm</td>
<td>323</td>
<td>323</td>
</tr>
</tbody>
</table>

7.3. Model description

The Eulerian multiphase granular model in ANSYS Fluent version 18.0 is employed. Kinetic theory of granular flow (KTGF) is used as a closure correlation of solid stress and viscosity. The algebraic form of the granular temperature model is selected for sand particle instead of the full granular energy balance model, because both models give similar results and the former one has shown a better performance with respect to computational efficiency and numerical convergence [206,327,328]. The no-slip boundary condition is prescribed for both gas and solid
phases, which has been used in the previous studies [348,349] to simulate bubbling fluidized beds with a size of \( \varnothing 154 \times 924 \) mm and \( \varnothing 155 \times 400 \) mm, and the EMMS drag model seems to be insensitive to the wall conditions [174,350]. The solids leaving the cyclone outlets (3) are recirculated to the sand inlet of FFB (2) by using User Defined Functions (UDFs) to maintain the mass balance of incoming and outgoing bed materials. The sand particles are initially patched in the FFB, two loop-seal, and the BFB dense region. The volume averaged solid concentration in FFB and BFB, and the solid flux at different heights of FFB and BFB are monitored to determine when the simulation reaches a quasi-steady state. A time step size of \( 5 \times 10^{-4} \) s and the maximum iteration of 50 is chosen to ensure continuity equations with a convergence of \( 10^{-3} \) and momentum equations with a convergence of \( 10^{-6} \). These parameters are found to reach a quasi-steady after 30 s. Therefore, all simulations of the reactors ran for 50 s and the data of the last 20 s were collected to obtain time-averaged data. All simulations were carried out in the High-Performance Computing system of the Technical University of Denmark, with 16 cores. At such conditions, one simulation takes approximately 2 weeks. The models and parameters used in the simulation are summarized in Table 7.2. The governing equations of the Eulerian multiphase granular model are given in Appendix D.

**Table 7.2 Simulation settings for the dual fluidized bed system**

<table>
<thead>
<tr>
<th>Setting</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsteady formulation</td>
<td>Unsteady, 2nd-order Implicit</td>
</tr>
<tr>
<td>Spatial discretization</td>
<td>Green-Gauss Cell based</td>
</tr>
<tr>
<td>Pressure-velocity coupling</td>
<td>Phase coupled SIMPLE</td>
</tr>
<tr>
<td>Granular viscosity</td>
<td>Gidaspow</td>
</tr>
<tr>
<td>Granular bulk viscosity</td>
<td>Lun et al.</td>
</tr>
<tr>
<td>Frictional viscosity</td>
<td>Schaeffer</td>
</tr>
<tr>
<td>Granular temperature</td>
<td>Algebraic</td>
</tr>
<tr>
<td>Frictional pressure</td>
<td>Based KTGF</td>
</tr>
<tr>
<td>Solid pressure</td>
<td>Lun et al.</td>
</tr>
<tr>
<td>Radial distribution</td>
<td>Lun et al.</td>
</tr>
<tr>
<td>Angle of internal friction</td>
<td>30</td>
</tr>
<tr>
<td>Time-step</td>
<td>0.0005 s</td>
</tr>
</tbody>
</table>

For the dual fluidized bed gasification system, the FFB is operated in the fast fluidization regime, while the BFB is operated in the bubbling fluidization regime. Thus, the EMMS/matrix model which was proposed by Wang and Li [195] and further developed by Lu et al. [174], is applied to simulate the FFB, while the EMMS/bubbling model developed by Hong et al. [205] is chosen for the BFB. For comparison with the hybrid EMMS drag model, the Gidaspow drag model [181] is also used to simulate the same system. Both the Gidaspow drag model and the hybrid EMMS drag model are shown below.

The Gidaspow drag model:
The hybrid EMMS drag model:

\[
\beta = \frac{3}{4} C_{D0} \frac{\varepsilon_g \rho_g (u_g - u_p)}{d_p} \varepsilon_g^{-2.65} \left( \varepsilon_g \geq 0.8 \right) \\
\beta = 150 \left( 1 - \varepsilon_g \right)^2 \mu_g \varepsilon_g d_p^2 + 1.75 \left( 1 - \varepsilon_g \right) \rho_g \frac{u_g - u_t}{d_p} \left( \varepsilon_g < 0.8 \right)
\]

(6.1)

The hybrid EMMS drag model:

\[
\beta = \frac{3}{4} C_{D0} \frac{\varepsilon_g \rho_g (u_g - u_p)}{d_p} \varepsilon_g^{-2.65} H_D
\]

(6.2)

Where,

\[
C_{D0} = \frac{24 (1 + 0.15 \text{Re}_p^{0.687})}{\text{Re}_p} \left( \text{Re}_p < 1000 \right) \\
C_{D0} = 0.44 \left( \text{Re}_p \geq 1000 \right)
\]

(6.3)

Here \( \text{Re}_p \) is Reynolds number, \( u_g \) and \( u_p \) is gas and solid velocity, m/s, respectively, \( \varepsilon_g \) and \( \varepsilon_p \) are gas and solid volume fraction, respectively, \( \rho_g \) is gas density, kg/m\(^3\), and \( d_p \) is particle diameter, m, \( \beta \) is the drag coefficient, kg/(m\(^3\)·s).

In the hybrid EMMS drag model, \( H_D \) is the heterogeneous index defined in Wang and Li [195], which is based on the operating conditions of the dual fluidized bed system. The inputs of the EMMS/matrix drag model are superficial gas velocity, solids circulation rate, and their physical properties (particle diameter and density, gas viscosity and density). The inputs of the EMMS/bubbling drag model are superficial gas velocity, and physical properties of gas and solid. A plot of \( H_D \) coefficients of air and steam gasification conditions is shown in Fig. 7. 3.

For the EMMS/matrix drag model, the \( H_D \) coefficients show a large reduction as compared to the homogeneous Wen-Yu drag model [174], indicating the drag force between gas and solid is significantly affected by heterogeneous flow structure. When the voidage is close to unit, the \( H_D \) is equal to unity due to a transition of the heterogeneous flow structure to homogeneous. For the EMMS/bubbling drag model, the reduction of drag force is much smaller than that of EMMS/matrix drag model, which means the BFB with Group B particle is close to homogeneous flow structure [351]. The formulations of \( H_D \) coefficients for both air and steam gasification are shown in Appendix D.
The hybrid EMMS drag model is implemented in ANSYS Fluent® 18.0 by using UDFs. A plot of mesh is shown in Fig. 7.1 (b). The total grid number used in this study is about 266000, and the average grid size used is about 60 times of the particle size, which is acceptable for the EMMS drag model, because the EMMS drag model was proved to give grid-independent simulation results when the grid size is smaller than 100 times of the particle size [174].

For a dual fluidized bed gasification system, the gas composition and operating conditions of BFB and FFB are significantly different as shown in Table 7.1. The inlet gas temperature is specified as the same as the FFB and BFB temperature, respectively. The other gas properties in the FFB and BFB are estimated based on the temperature and compositions shown in Table 7.1. The mass fraction of the fuel particles is typically less than 5% of the solid materials in fluidized bed [352,353]. Therefore, the hydrodynamic behaviours of the dual fluidized bed are dominated by sand particles. The effect of biomass/char particle is negligible. This assumption has been adopted in many previous studies [9,161,337,354–356] which focus on the hydrodynamic in fluidized bed systems. In this work, we focus on hydrodynamic behaviours. Thus, the effects of biomass/char particles and chemical reactions are not included in the simulations.

Fig. 7.3 A plot of $H_D$ coefficient of air and steam gasification by using the EMMS/matrix model for FFB and the EMMS/bubbling model for BFB.
7.4. Results and discussions

7.4.1 Model validation

7.4.1.1 Solid circulation rate

Table 7.3 shows the solid circulation rates obtained at the outlet of FFB by using the hybrid EMMS drag model and the Gidaspow drag model. The results are compared to those estimated from the experimental data. It is shown that the Gidaspow drag model overpredicts the solid circulation rate, and the results predicted by the EMMS drag model slightly underestimate, but much better than those of the Gidaspow drag model. This tendency is consistent with a previous study [343]. The probable reason of the underestimated the solid circulation rate by the hybrid EMMS drag model is that the heterogeneity index \( H_D \), which is determined by using the operating conditions of the upper region of FFB, is underestimated for the bottom region of the FFB. Developing an operating condition dependent EMMS/matrix drag model may resolve this problem, but it is out of the scope of the current study.

Table 7.3 Solid circulation rate (kg/s) predicted by using the hybrid EMMS drag model and Gidaspow drag model.

<table>
<thead>
<tr>
<th></th>
<th>Gidaspow</th>
<th>EMMS</th>
<th>Mass and heat balance*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0.888</td>
<td>0.214</td>
<td>0.246</td>
</tr>
<tr>
<td>Steam</td>
<td>1.034</td>
<td>0.150</td>
<td>0.250</td>
</tr>
</tbody>
</table>

*The results of mass and heat balance is calculated based on the experimental data.

7.4.1.2 Pressure

Fig. 7.4 shows the axial profiles of pressure in the FFB from the experiments and simulations. Under the air gasification condition, the pressure drop in FFB predicted by the hybrid EMMS drag model is \(~5.0\) kPa, which is comparable with experimental data \(~4.5\) kPa). However, the pressure drop predicted by using the Gidaspow drag model is \(~10.8\) kPa, which is significantly overestimated. Under steam gasification conditions, the pressure drop predicted by the hybrid EMMS drag model is \(~5.0\) kPa which is close to the experimental results of \(~5.1\) kPa, while, the pressure drop predicted by using the Gidaspow model is \(~10.6\) kPa, which is remarkably higher. By looking at the axial pressure profiles in the FFB, it is obvious that the results from the hybrid EMMS drag model are in good agreement with the experimental data. However, the Gidaspow drag generally overestimates the pressure along with the height of FFB.
Fig. 7.4 A comparison of the predicted and measured axial profiles of pressure in the FFB.

Fig. 7.5 compares the simulated and experimental axial profiles of pressure in the BFB. The two drag models give similar results. The reason may be that the drag coefficients from the EMMS/bubbling model and the Gidaspow drag are similar in bubbling fluidization for Group B particles with a low superficial gas velocity [217]. Both the Gidaspow and hybrid EMMS drag model simulated experimental data well under both the air and steam gasification conditions.

Fig. 7.5 A comparison of the simulated and measured axial profiles of pressure in the BFB.
Table 7.4 compares the predicted and measured pressures at the bottom of the loop-seals. For both the air and steam gasification, the Gidaspow drag model overestimates significantly the pressure of the lower loop-seal. However, the hybrid EMMS model gives more reasonable results for both the upper and lower loop-seals. Combining with the results in Fig. 7.4 and Fig. 7.5, it can be concluded that the hybrid EMMS drag model agrees better with experimental data for the FFB, BFB, and recycle loop than the Gidaspow drag model.

Table 7.4 A comparison of the predicted and measured pressure at the bottom of loop-seals

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Predicted pressure (kPa)</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gidaspow</td>
<td>EMMS</td>
</tr>
<tr>
<td>Air</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper loop-seal</td>
<td>11.2</td>
<td>10.01</td>
</tr>
<tr>
<td>Lower loop-seal</td>
<td>10.2</td>
<td>16.66</td>
</tr>
<tr>
<td>Steam</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper loop-seal</td>
<td>10.1</td>
<td>8.51</td>
</tr>
<tr>
<td>Lower loop-seal</td>
<td>11.9</td>
<td>17.03</td>
</tr>
</tbody>
</table>

7.4.1.3 Solid inventory in the FFB and BFB

Table 7.5 shows a comparison of the simulated solid inventory (kg) in the FFB and BFB at air gasification conditions. The experimental solid inventory is estimated by weighting the solid particles remaining in the FFB and BFB after the experiment. In the FFB, the hybrid EMMS drag model shows a higher solid inventory than the Gidaspow drag model and is closer to the experimental data. The results seem to be inconsistent with the results of the pressure drop shown in Fig. 7.4. However, it should be noticed that the FFB outlet has a strong restriction for the solid particles transported from FBB to cyclone when the solid circulation rate is large. As shown in Table 7.3, the solid circulation rate predicted by the Gidaspow drag model is much larger than that of the EMMS drag model. Consequently, a large pressure drop is predicted at the FFB top. In the BFB, the hybrid EMMS drag model gives a lower solid inventory than that of the Gidaspow model. Although both the hybrid EMMS and the Gidaspow drag model overpredict the solid inventory of the BFB, the hybrid EMMS drag model still gives more reasonable results than the Gidaspow drag model.

Table 7.5 Predicted and measured solids inventory (kg) in the FFB and BFB in the case of air gasification

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Solid inventory (kg)</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gidaspow</td>
<td>EMMS</td>
</tr>
<tr>
<td>FFB</td>
<td>25</td>
<td>20.4</td>
</tr>
<tr>
<td>BFB</td>
<td>35</td>
<td>46.2</td>
</tr>
<tr>
<td>Lower loop-seal</td>
<td>-</td>
<td>25.1</td>
</tr>
<tr>
<td>Upper loop-seal</td>
<td>-</td>
<td>24.1</td>
</tr>
<tr>
<td>Other part</td>
<td>-</td>
<td>4.2</td>
</tr>
</tbody>
</table>
7.4.1.4 Solid volume fraction

Fig. 7.6 shows the simulated radial profiles of time averaged solid volume fraction at different height of the FFB. Both models can capture the so-called “core-annulus” structure in the FFB. However, compared to the EMMS drag model, the Gidaspow drag model predicts a higher solid hold up at the outlet of FFB for both air and steam gasification cases. Similar results can be seen in Fig. 7.7, which shows the time averaged axial profiles of the solid volume fraction in the FFB. According to Fig. 7.7, the axial profile of solid volume fraction predicted by the Gidaspow drag model is close to the shape of “C”, indicating that there is a strong restriction at the outlet of FFB. That is why the Gidaspow drag model shows a significant pressure drop at the top of FFB. However, the measured pressure drop is small which implies the restriction at the outlet of FFB is insignificant. The axial profile of the solid volume fraction should be close to an “L” shape according to the discussion of Bi et al. [357]. Therefore, the EMMS drag model gives more reasonable results in solid volume fraction than the Gidaspow drag model.

![Fig. 7.6 The simulated solid concentration distribution by using the Gidaspow and the hybrid EMMS drag models for the case of air (a) and steam (b) gasification.](image_url)
Fig. 7. 7 The simulated solid axial profiles of FFB by using the Gidaspow and the hybrid EMMS drag models for the case of air (a) and steam (b) gasification.

Fig. 7. 8 shows the simulated time averaged solid volume fraction of the BFB by using the Gidaspow and the hybrid EMMS drag model under air and steam gasification conditions. Both models can capture the “core-annulus” flow structure in the BFB at heights of 3.5, 3.7, and 3.9 m. A flat radial profiles of solid volume fraction at a height of 3.3 m are captured due to a uniform inlet gas velocity used in the simulation. In the enlarge and freeboard region of the BFB, both models show a low solid concentration. Fig. 7. 9 shows the simulated axial profile of time averaged solid volume fraction of the BFB. Both models show a dense bubbling phase, a decreasing solid concentration along with the height in the enlarged region, and a low solid concentration in the freeboard. The simulation results of the hybrid EMMS drag model and Gidaspow drag model are similar.

Fig. 7. 8 The simulated solid concentration distribution by using the Gidaspow and the hybrid EMMS drag models for air (a) and steam (b) gasification.
Based on the results and discussions in section 7.4.1.1-7.4.1.4, we can conclude that the hybrid EMMS drag model gives more reasonable results than the Gidaspow drag model.

### 7.4.2 Effects of solid inventory

The hybrid EMMS drag model validated with solid inventory of 120 kg is used to investigate the effects of solid inventory on the hydrodynamics in the dual fluidized bed system. It should be noted that the $H_D$ coefficient may be required to be updated for new operating conditions, since the $H_D$ of the EMMS/matrix model depends not only on voidage but also on the particle Reynolds number. However, the change of solid inventory in this study is not significant (in a range of 100-200 kg), and it has been shown in literature that an EMMS/matrix drag model validated at a specified condition could be used to study the effects of solid inventory on hydrodynamic behaviours [344]. Thus, the $H_D$ coefficient is kept unchanged in our simulations for different solid inventory. For the EMMS/bubbling model, since the solid flux is assumed to be zero in the EMMS/bubbling model, $H_D$ is the same for the case with different solid inventories.

#### 7.4.2.1 Solid circulation rate

Fig. 7. 10 shows the effects of solid inventory on the solid circulation rate in the dual fluidized bed system for biomass gasification. For both cases of air and steam gasification, the solid circulation rate increases slowly with an increase of solid inventory in the range of 100-120 kg, while it increases dramatically in the range of 160-200 kg. The results are consistent with
previous studies [335,344,358], showing that it is possible to convey more heat generated by char combustion from FFB to BFB by increasing the solid inventory. The solid circulation rates predicted for air and steam gasification are very similar. The minor difference is caused by the slightly different operating conditions in the FFB and BFB.

Fig. 7. 10 A plot of solid inventory versus the time averaged solid circulation rate (kg/s) for the case of air and steam gasification

Fig. 7. 11 shows the transient solid circulation rate for the cases of air (a) and steam (b) gasification with different solid inventory (100, 120, 160, 200 kg). The standard deviation \( \sigma = \sqrt{\frac{(x_i - \bar{x})^2}{N-1}} \) is averaged value of the variable \( x \), \( N \) is the total number of variable \( x \) of the solid circulation rate (determined by using the data from 30-50 s) is also shown in Fig. 7. 11. The fluctuation of the solid circulation rate increases with an increase of solid inventory for both air (The standard deviation changes from 0.1 to 2.28) and steam gasification (The standard deviation changes 0.01 to 1.94) conditions. The probable reason is that the choking occurs in the recycle loop for the case \( I = 200 \) kg, which is typical type B “choking” [359]. The solid circulation rate is over the maximum value that the recycle loop can be conveyed. It should be noted that the large fluctuation of solid circulation rate may influence significantly on the operation of the upper loop-seal and the heat balance in the BFB. Therefore, it may challenge a stable condition on the dual fluidized bed gasification system [335].
7.4.2.2 Solid volume fraction

Fig. 7. 12 shows the transient volume averaged solid volume fraction of the upper loop-seal for the case of air (a) and steam (b) gasification with different solid inventory (100, 120, 160, 200 kg). For both cases of air (a) and steam (b) gasification, the fluctuation of solid volume fraction increases with an increase of solid inventory. Therefore, the operations of the upper loop-seal may become more unstable with increasing solid inventory. The solid inventory of the operating condition is recommended to be in a range of 100-160 kg.

Fig. 7. 13 (a) shows the time averaged axial profiles of solid volume fraction in the FFB. For the cases of solid inventory of 100 kg and 120 kg, the restriction at the outlet of FFB is relatively weak due to the low solid circulation rate (0.186 kg/s, and 0.214 kg/s) and the time averaged axial profile of solid volume fraction is close to a “L” curve. With the increase of solid inventory, a dramatical increase of solid circulation rate leads to accumulation of solid in the top outlet of FFB. Therefore, the curve is close to a “C” curve as reported by Bai et al. [357]. Fig. 7. 13 (b) shows the time averaged axial profiles of solid volume fraction of FFB for the case of steam gasification.

Fig. 7. 11 The transient solid circulation rate (kg/s) for the case of air (a) and steam (b) gasification with different solid inventory (100, 120, 160, 200 kg).
gasification with the different solid inventories. The results show the similar phenomena of steam gasification to those of air gasification.

Fig. 7.13 The time averaged axial profiles of solid volume fraction of FFB for the case of air (a) and steam (b) gasification with different solid inventory (100, 120, 160, 200 kg).

Fig. 7.14 shows the time averaged axial profiles of solid volume fraction of the BFB for the case of air and steam gasification with different solid inventories. The solid volume fraction in the BFB bottom is similar. However, the height of bed expansion increases with increasing solid inventory, meaning that the solid inventory in the BFB is increased to keep the pressure balance between the FFB and BFB. In the enlarged region of BFB, the solid volume fraction decreases with an increase of height of BFB, due to the decrement of superficial gas velocity. In the freeboard region of BFB, the solid concentration is very small, because the superficial gas velocity at this part is not high enough to support the entrainment of a large amount of solid.
7.5. Summary

A three dimensional full-loop CFD simulation of the hydrodynamics of a dual fluidized bed system for biomass gasification has been conducted by using a Eulerian multiphase granular model. A hybrid EMMS drag model (the EMMS/matrix model for FFB and the EMMS/bubbling drag model for BFB) is proposed to simulate the system. The Gidaspow drag model is also applied for comparison. The pressure distributions predicted by the hybrid EMMS drag model are in good agreement with the measurement in the FFB, BFB, and the whole loop. However, the Gidapow drag model overestimates the solid concentration in the top FFB as well as at the bottom of the lower loop-seal, because of an overestimation of momentum exchange between gas and solid. The results suggest that the hybrid EMMS drag model performs better than the Gidaspow drag model. The effects of solid inventory on the hydrodynamics of the dual fluidized bed system have been evaluated by the hybrid EMMS drag model. The results show that the solid circulation rate increases with an increase of solid inventory. But it leads to the operation condition in an unstable regime. In the simulation, a solid inventory of 100-160 kg gives adequate heat carrier capability and stable operation of the dual fluidized bed system.
8 Conclusions and future work

8.1 Summary of conclusions

Based on the single particle devolatilization experiments and the comprehensive devolatilization model presented in Chapter 3, the following conclusions can be made:

- The developed comprehensive model can well-simulate biomass devolatilization under a wide range of gas temperature (1473-1723 K), particle moisture contents (0.0-50 ar%), particle size (3-4 mm), and particle dry density (50-1200 kg/m$^3$).
- Under the investigated conditions, the devolatilization kinetics have limited effects on the devolatilization of large wood particles (> 1 mm), suggesting that the devolatilization process is mainly heat transfer controlled.
- Under the investigated conditions, the particle density, size, gas temperature, and particle moisture content have significant effects on the devolatilization time, while the other parameters, such as volatile content, gas velocity, only have a small influence on the devolatilization time.
- Both modelling and experimental studies show that the devolatilization time increases linearly with the increase of particle dry density, suggesting the importance of obtaining particle dry density to predict/evaluate biomass devolatilization behaviours.
- Under the conditions of particle size (1-10 mm) and gas temperature (1273-1873 K), the devolatilization time of wood particles can be predicted by a simple correlation based on the comprehensive biomass devolatilization model with an accuracy of ±25%.

Based on the single char particle conversion experiments and the comprehensive char conversion model presented in Chapter 4, the following conclusion can be made:

- The developed comprehensive char conversion model has been validated by single char conversion experiments under the conditions of gas temperature (1473-1723 K), O$_2$ concentration (0.0-10.5%), and H$_2$O concentration (25-42%).
- Under the investigated conditions, the char gasification kinetics have significant effects on the modelling results, while the oxidation kinetics have limited effects on the modelling results, indicating that the char gasification process is dominated by both mass transfer and chemical kinetics, and the char oxidation is controlled by external mass transfer under experimental conditions.
- Under the investigated conditions, the char conversion time decrease with the increase of gas temperature as well as oxygen and steam content.
- The CO oxidation in the boundary layer results in a reduced char conversion rate. However, water-gas shift reaction and H$_2$ oxidation has insignificantly influences on the modelling results.
The char reactions contribution is significantly affected by temperature, slip velocity, and particle size. The char gasification reactions are negligible in the modelling of char combustion and gasification under the following conditions: low temperature (< 1273 K), small particle (< 1 mm), or large slip velocities (e.g. 9 m/s). They should be considered in the following conditions: low temperature (> 1273 K), small particle (> 1 mm), or small slip velocities (e.g. 0.1 m/s).

A heat transfer corrected model for CFD simulation of devolatilization of thermal-thick biomass in fluidized beds was presented in Chapter 5, the following conclusion can be made based on the investigations:

- The heat transfer corrected isothermal model can give similar devolatilization rate as compared to the comprehensive biomass devolatilization model developed in Chapter 3 and validated by a series of devolatilization experiments with a particle size range of (0.079-10.5 mm)
- The model is implementable in CFD method (e.g. Eulerian multiphase flow method) with a computational cost similar to a conventional isothermal model for biomass devolatilization.

A mass transfer corrected uniform char conversion model was presented in Chapter 6, the main conclusions are:

- The mass transfer corrected uniform char conversion model can give a similar char conversion rate as compared to the progressive char conversion model.
- The homogeneous reactions in the particle boundary layer are negligible at low temperature conditions.
- The mass transfer corrected char conversion model points out that both the reaction rate and external mass transfer of the uniform char conversion model are needed corrections, while the external heat transfer is negligible.

In Chapter 7, a three dimensional full-loop CFD simulation of the hydrodynamics of a dual fluidized bed system for biomass gasification has been conducted by using a Eulerian multiphase flow model, the following conclusions are made:

- The pressure distributions predicted by the hybrid EMMS drag model are in good agreement with the measurement in the FFB, BFB, and the whole loop. However, the Gidapow drag model overestimates the solid concentration in the top FFB as well as at the bottom of the lower loop-seal.
- The solid circulation rate increases with an increase of solid inventory. But it leads to the operation condition in an unstable regime when the solid inventory is larger than 160 kg for the studied dual fluidized bed system.
8.2 Suggestions for future work

Particle-scale model

- Investigating particle shrinkage mechanism: In our model presented in Chapter 4, the particle shrinkage during char conversion is based on the assumption that ash peels off immediately when char conversion reaches 0.95. It gives a good prediction of the char size evolution during combustion. However, the particle size cannot be well predicted under gasification conditions, indicating a different particle shrinkage mechanism between char gasification and oxidation. The mechanism should be further studied by both experiments and modelling.
- The char gasification kinetics are significantly affected by ash content and composition. A lot of experimental work of the effects of ash species on char reactivity has been reported. It is might be to develop a tool by deep learning method, with a large database collected from the published literature to determine char reactivity based on a number of input parameters.
- In our model presented in Chapter 4, the global lumped kinetics of homogeneous reactions used. A detailed chemical kinetics model can be applied in the particle boundary layer.
- The correction method presented in this work for biomass devolatilization and char conversion can be extended to other similar processes (e.g. coal combustion and gasification, cement calcination, etc.).

Implementing the sub-model in CFD simulations

- The mass transfer corrected char conversion model has been developed at particle-scale, it needs further validation in CFD software.
- The heat transfer corrected is only implemented in Eulerian multi-fluid methods, the model could be further implemented and tested in E-L methods.

CFD modelling biomass combustion and gasification

- The results presented in Chapter 7 focuses on the hydrodynamic behaviours in fluidized bed reactors, a further simulation and validation including both hydrodynamic and reactions are required.
- The CFD modelling biomass combustion and gasification is time-consuming for large-scale fluidized bed reactor, developing a strategy to combine the CFD modelling and chemical reaction engineering model may significantly improve the modelling efficiency.
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Appendix A

Bulk gas physical properties

In this work, the physical properties of the gas mixture are mole averaged of N\textsubscript{2}, O\textsubscript{2}, and H\textsubscript{2}O as shown in Eq. (A.1).

\[ \varphi_{g} = \sum_{i=1}^{3} x_i \varphi_i \]  

(A.1)

Where \( x_i \) is the mole fraction, \( \varphi \) is the physical properties, \( i=1,2,3 \) is N\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}O, respectively.

Heat capacity

The heat capacity of gas species can be found in https://webbook.nist.gov/chemistry/. It can be expressed as follows:

\[ C_{p1} = 19.5058 + 19.8871 \frac{T}{1000} - 8.5985 \left( \frac{T}{1000} \right)^2 \]

\[ + 1.3698 \left( \frac{T}{1000} \right)^3 + 0.5276 \left( \frac{1000}{T} \right)^2 \]  

(500 < \( T \) < 2000)  

(A.2)

\[ C_{p2} = 30.0324 + 8.7729 \frac{T}{1000} - 3.9881 \left( \frac{T}{1000} \right)^2 \]

\[ + 0.7883 \left( \frac{T}{1000} \right)^3 + 0.7416 \left( \frac{1000}{T} \right)^2 \]  

(700 < \( T \) < 2000)  

(A.3)

\[ C_{p3} = 30.0920 + 6.8325 \frac{T}{1000} + 6.7934 \left( \frac{T}{1000} \right)^2 \]

\[ - 2.5345 \left( \frac{T}{1000} \right)^3 + 0.0821 \left( \frac{1000}{T} \right)^4 \]  

(500 < \( T \) < 1700)  

(A.4)

Where \( C_{pi} \) is the heat capacity of gas species, J/mol/K, \( T \) is the gas temperature, K.

Viscosity

The Viscosity of gases species \( i \) is fitted from data of reference [360]. For H\textsubscript{2}O, the data for DIPPR system used (https://dippr.aiche.org/SampleDb). It can be expressed as below:

\[ \mu_1 \times 10^6 = 2.4448 + 0.0608T - 3.333 \times 10^{-5}T^2 \]

\[ + 1.3722 \times 10^{-8}T^3 + 2.1908 \times 10^{-12}T^4 \]  

(100 < \( T \) < 2000)  

(A.5)

\[ \mu_2 \times 10^6 = 1.9101 + 0.0738T - 3.9165 \times 10^{-5}T^2 \]

\[ + 1.5459 \times 10^{-8}T^3 + 2.4262 \times 10^{-12}T^4 \]  

(100 < \( T \) < 2000)  

(A.6)

\[ \mu_3 = 1.7096 \times 10^{-8}T^{1.1146} \]  

(273.16 < \( T \) < 1073.15)  

(A.7)

Where \( \mu \) is the viscosity gas species, Pa.s, \( T \) is the gas temperature, K.

Thermal Conductivity
The heat conductivity of gas species $N_2$ and $O_2$ is fitted data from reference[361] and [362]. For H2O, the data for DIPPR system used (https://dippr.aiche.org/SampleDb), it can be expressed as below:

$$\lambda_1 = -2.7043 \times 10^{-4} + 1.0642 \times 10^{-3}T - 7.7347 \times 10^{-9}T^2$$
$$+ 4.8613 \times 10^{-11}T^3 - 1.0883 \times 10^{-14}T^4 \quad (100 < T < 2000)$$

$$\lambda_2 \times 10^4 = -47.4178 + 1.3456T - 0.0013T^2$$
$$+ 9.9727 \times 10^{-7}T^3 - 2.8351 \times 10^{-10}T^4 \quad (300 < T < 1000)$$

$$k_3 = 6.0241 \times 10^{-6}T_g^{3.3973} \quad (273.16 < T < 1073.15)$$

Where $k_i$ is the thermal conductivity of gas species, W/m/K, $T$ is the gas temperature, K.
Appendix B

Source term of governing equations

The source terms of the governing equations of Eq. (4.4) and Eq. (4.5) are listed as below:

For $O_2$:

\[
S_{11} = -\frac{\eta + 2}{2\eta + 2} r_i \\
S_{12} = 0.5r_4 + 0.5r_6
\]

(B.1)

(B.2)

For $CO_2$:

\[
S_{s2} = \frac{1}{\eta + 1} r_1 - r_2 \\
S_{s2} = r_1 + r_2
\]

(B.3)

(B.4)

For $H_2O$:

\[
S_{s3} = r_3 \\
S_{s3} = -r_3 + r_6
\]

(B.5)

(B.6)

For $H_2$:

\[
S_{s4} = r_3 \\
S_{s4} = r_5 - r_6
\]

(B.7)

(B.8)

For CO

\[
S_{s5} = \frac{\eta}{\eta + 1} r_1 + 2r_2 + r_3 \\
S_{s5} = -r_4 - r_3
\]

(B.9)

(B.10)

Grid and time-step size independent studies of the model

The grid and time-step size independent studies of the comprehensive char combustion model had been carried out under following conditions: pine wood, $d_p = 3.2$ mm, $T_g = 1483$ K, $T_w = 1283$ K, $\rho_{v0} = 120$ kg/m$^3$, $u_g = 2.86$ m/s, 4.4 vol% $O_2$, 25.7 vol% $H_2O$. Figure. A.1 shows the conversion time predicted by the comprehensive char combustion with different grid numbers inside the particle. The coarsest grid predicts the fastest conversion of the pine wood char particle, as compared to the finest grid, $N_p = 1900$. The convergent modelling results can be obtained with $N_p = 900$, because the modelling results predicted by using $N_p = 900$ is almost the same as that of $N_p = 1900$. 
Fig. B. 1 The conversion time predicted by the comprehensive char conversion model with different grid numbers inside the particle, the grid number in the boundary layer is $N_g = 100$ and time-step size is $\Delta t = 0.001s$.

Fig. B. 2 shows the conversion time predicted by the comprehensive char conversion model with different grid numbers in the particle boundary layer. The difference between the results predicted by the coarsest and the finest grid is small, therefore, it is reasonable to use $N_g = 100$ in the particle modelling.

Fig. B. 2 The conversion time predicted by the comprehensive char combustion model with different grid numbers in the particle boundary layer, the grid number inside particle is $N_p = 900$ and time-step size is $\Delta t = 0.001s$.

Fig. B. 3 shows the conversion time predicted by the comprehensive char combustion with different time-step size. The largest time-step size, $\Delta t = 0.1s$, show the lowest char conversion rate, and the difference of predicted char conversion by using $\Delta t = 0.01s$ and $\Delta t = 0.001s$ is
small. Therefore, it is reasonable to use a time-step size of 0.001s in the modeling of char conversion.

![Graph showing char conversion over time with different time-step sizes](image)

*Fig. B. 3 The conversion time predicted by the comprehensive char conversion model with different time-step size, the grid number of the particle is \( N_p = 900 \) and the boundary layer is \( N_g = 100 \).*

**Image post-processing method to determine particle size**

The image post-processing method to determine the particle size is illustrated in Fig. B. 4. The char combustion process is firstly recorded by a high-resolution (1920×1080) camera with a frequency of 70 Hz. Then the recorded video is processed by an imaging method as follows:

**Step 1:** The recorded video is imported into MATLAB by using the function “VideoReader”, with each frame being saved. The original frame when the flame of volatile combustion distinguished is defined as the initial image \( (t = 0) \) of char combustion. There are also several other images shown in Fig. B. 4 (a), which corresponds to the char conversion time of 10, 20, and 25 s.

**Step 2:** Converting the original frame to a binary image by using the function “im2bw”. The image center is determined by using the function “regionprops” and then the averaged particle diameter is calculated. To remove the background, such as the Tungsten wire used to support the char combusted in the single particle combustor, the data outside the particle boundary is set to zero, corresponding to the gray figure as shown in Fig. B. 4 (b). After several iterations, the optimized particle region can be captured, which is highlighted as blue in Fig. B. 4 (b).

**Step 3:** Calculating the corresponding area by summing of the pixels of the blue region, then the dimensionless particle size of the corresponding frame can be calculated as Eq. (B.11) by assuming a circle captured area:
\[
\frac{d_p}{d_{p0}} = \sqrt{\frac{A_p}{A_{p0}}}
\]  \hspace{1cm} (B.11)

Here, \( \frac{d_p}{d_{p0}} \) is that the char particle simulated diameter at any time divided by the initial char particle determined diameter, which is corresponding to the frame at \( t = 0 \), \( A_p \) is the area of the particle region at any time, and \( A_{p0} \) is the area of the particle region at \( t = 0 \).

**Fig. B. 4** The image post-processing method to determine the particle size, (a) the origin frame extracted from the recorded video, (b) converting the original frame to a binary image, with the blue region shown in the figure being the captured particle, (c) sum of the pixels of the blue region and the calculated dimensionless particle size evolution.
Appendix C

A demonstration of how to calculate $H_T$ and $H_{R,i}$

A specific case (Gas: $N_2$, spherical particle, $d_p = 10$ mm, $\rho_{DB} = 580$ kg/m$^3$, Vol = 90 db%, moisture = 6.38 db%, $T_g = T_w = 1173$ K) with convective heat transfer coefficient $h_c = 100$ W/m$^2$/K is selected here to show how to obtain $H_T$ and $H_{R,i}$ by following Fig. 5.1.

Step 1: Defining a trial value, $h_c = 100$ W/(m$^2$·K)

Step 2: The temperature, and water and volatile conversion distribution inside the particle, and particle surface temperature of all-time $t$ can be obtained by solving the non-isothermal model. Based on the above data, the average particle temperature ($T_{aver}$), and the average conversion of water and volatile ($X_{aver,i}$), and dimensionless temperature ($\theta$) can be calculated by Eq. (5.6), Eq. (5.7), and Eq. (5.12), respectively. The heat flux ($q_{non-iso}$), and reaction rate ($R_{non-iso,i}$) of the non-isothermal model are calculated by Eq. (5.5) and (5.4), respectively. In this way, a series of data ($\theta$, $q_{non-iso}$, $R_{non-iso,i}$) can be obtained. A plot of ($\theta$, $q_{non-iso}$, $R_{non-iso,i}$) is shown in Fig. C.1.

![Figure C.1](image)

Fig. C. 1 A plot of heat flux (W/m$^2$/s) and devolatilization rate (kg/s) predicted by non-isothermal model versus dimensionless temperature ($\theta$).

Step 3: Assuming an isothermal particle with the same average particle temperature ($T_{aver}$) or dimensionless temperature ($\theta$), and average conversion of water and volatile ($X_{aver,i}$) obtained from Step 2, the heat flux and reaction rate of the conventional isothermal model are calculated by Eq. (5.3) and Eq. (5.2), respectively. A series of ($\theta$, $q_{iso}$, $R_{iso,i}$) of the conventional isothermal model are obtained and shown in Fig. C. 2. Obviously, there is a significant difference when compared with Fig. C. 1 and Fig. C. 2.
Step 4: Using $q_{noniso}$, $R_{noniso}$, $q_{iso}$, $R_{iso}$ obtained from Step 2 and Step 3, calculate $H_T$ and $H_R$ based on Eq. (5.8) and Eq. (5.9). A plot of $H_T$ and $H_R$ versus dimensionless temperature ($\theta$) is shown in Fig. C. 3. To avoid numerical problem, $H_T$ is set to 1 when $\theta < 0.001$ or $\theta > 0.999$, and $H_R$ is set to 1 when $X_1 < 0.001$ or $X_1 > 0.999$. After obtaining $H_T$ and $H_R$ under a specified $h_c$, we repeat Step 1 ~ Step 4 to obtain the heat transfer corrected coefficient with other $h_c$ values.
Step 5: After calculating $H_T$ and $H_R$ with trial values of $h_c$, from $h_{c_{\text{min}}}$ and $h_{c_{\text{max}}}$, then we can save and output $h_c$, $H_T$, $H_R$, and $\theta$. The $h_c$ starts with a minimum $h_{c_{\text{min}}}$ and ends with a maximum $h_{c_{\text{max}}}$ value. The range of $h_{c_{\text{min}}}$ and $h_{c_{\text{max}}}$ covers the possible value of the convective heat transfer coefficient under a specified operating condition. For this specific case with $h_c$ from 10 to 1000 W/(m$^2$·K). The two heat transfer corrected coefficients $H_T$ and $H_R,i$ are shown in Fig. 5. 2.

Step 6: For using the save data ($\theta$, $h_c$, $H_T$, $H_R,i$) in single particle modelling or CFD simulations, a two-dimensional linear interpolation method is used to calculate $H_T$ and $H_R,i$ [324].

Particle proximate analysis of experimental data

Following Tables are particle proximate analysis of different cases, the mass fraction is expressed on a dry basis.

Table C. 1 Proximate analysis of small-size particles [1]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>%</td>
<td>0.0</td>
</tr>
<tr>
<td>Volatile</td>
<td>%</td>
<td>91.9</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>%</td>
<td>7.90</td>
</tr>
<tr>
<td>Ash</td>
<td>%</td>
<td>0.2</td>
</tr>
<tr>
<td>Density</td>
<td>kg/m$^3$</td>
<td>1180</td>
</tr>
</tbody>
</table>

Table C. 2 Proximate analysis of raw and torrefied fuels of middle-size particles of Lu et al. [278]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>raw</th>
<th>230C1h</th>
<th>260C1h</th>
<th>290C1h</th>
<th>290C4h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>%</td>
<td>3.2</td>
<td>1.0</td>
<td>1.7</td>
<td>1.6</td>
<td>4.0</td>
</tr>
<tr>
<td>Volatile</td>
<td>%</td>
<td>81</td>
<td>78.4</td>
<td>78.3</td>
<td>76.3</td>
<td>70</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>%</td>
<td>16.1</td>
<td>17.8</td>
<td>20.4</td>
<td>22.4</td>
<td>28.8</td>
</tr>
<tr>
<td>Ash</td>
<td>%</td>
<td>2.9</td>
<td>2.8</td>
<td>1.3</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Density</td>
<td>kg/m$^3$</td>
<td>3 mm: 702.3</td>
<td>3 mm: 592.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 mm: 615.5</td>
<td>4 mm: 536.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 mm: 628.6</td>
<td>5 mm: 541.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The particle size after torrefied has certain degree reduction, they are: 5.5% for sample 230C1h, 10.6% for 260C1h, 15.7% for 290C1h and 26% for 290C4h. The particle size in Table C. 2 is raw material.

Table C. 3 Proximate analysis of middle-size particles of Momeni et al.[275]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>dwt%</td>
<td>10.3</td>
</tr>
<tr>
<td>Volatile</td>
<td>wt%</td>
<td>85.3</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>wt%</td>
<td>14.3</td>
</tr>
<tr>
<td>Ash</td>
<td>wt%</td>
<td>0.4</td>
</tr>
<tr>
<td>Density</td>
<td>kg/m$^3$</td>
<td>780</td>
</tr>
</tbody>
</table>
Table C. 4 Proximate analysis of large-size particles of Lu et al.[12]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>dwr%</td>
<td>6.38/66.7</td>
</tr>
<tr>
<td>Volatile*</td>
<td>wt%</td>
<td>90</td>
</tr>
<tr>
<td>Fixed carbon *</td>
<td>wt%</td>
<td>9.5</td>
</tr>
<tr>
<td>Ash*</td>
<td>wt%</td>
<td>0.5</td>
</tr>
<tr>
<td>Density</td>
<td>kg/m³</td>
<td>580</td>
</tr>
</tbody>
</table>

*Estimated from Lu et al.[12]

Devolatilization model used in CFD modelling

The devolatilization model described in section 3.2 is used. With the assumption of constant particle size, for the isothermal model, the net devolatilization rate is given as:

$$ R_g = k_1 \varepsilon_{s1} (\rho_{s1} - \rho_c) $$  (C.1)

The net consumption of particle mass:

$$ R_{s1} = -k_1 \varepsilon_{s1} (\rho_{s1} - \rho_c) $$  (C.2)

The char generation rate is given as Eq. (10), which is assumed to be proportional to the devolatilization rate,

$$ R_c = \frac{1-Y_{10}}{Y_{10}} k_1 \varepsilon_{s1} (\rho_{s1} - \rho_c) $$  (C.3)

And the net consumption of raw wood:

$$ R_{bio} = -R_g - R_c $$  (C.4)

For the isothermal model, Eq. (C.1)-(C.4) can be directly coupled with CFD software by using User Defined Functions (UDFs) in ANSYS Fluent® 18.0. For the corrected isothermal model, Eq. (C.1)-(C.4) are scaled by heat transfer corrected coefficients for reactions, $H_R$, which is obtained from the heat transfer corrected isothermal model.

$H_T$ and $H_R$ used in CFD modelling

Fig. C. 4-Fig. C. 7 shows the raw data of $H_T$ and $H_R$ predicted by the heat transfer corrected isothermal model for different particle sizes ($d_p = 1/3/6/10$ mm). According to the value of $H_T$ and $H_R$, the modification degree for isothermal model increase with the increase of particle size, implying that the internal heat transfer has more significant effects on biomass devolatilization in fluidized bed. The raw data of $H_T$ and $H_R$ showed in Fig. C. 4-Fig. C. 7 can be stored in Ansys Fluent® by using User Defined Functions (UDFs). The two-dimensional linear interpolation method [324] is used to calculate $H_T$ and $H_R$ in each cell by using UDFs.
Fig. C. 4 The heat transfer corrected coefficients ($H_T$ and $H_R$) for the case of $d_p = 1$ mm (Gas: $N_2$, spherical particle, $\rho_{DB} = 580$ kg/m$^3$, Vol=90%, $M_c = 0$%, $T_g = T_w = 1173$ K, $h_c = 100$-1500 (W/(m$^2$ K))).

Fig. C. 5 The heat transfer corrected coefficients ($H_T$ and $H_R$) for the case of $d_p = 3$ mm (Gas: $N_2$, spherical particle, $\rho_{DB} = 580$ kg/m$^3$, Vol=90%, $M_c = 0$%, $T_g = T_w = 1173$ K, $h_c = 30$-1000 (W/(m$^2$ K))).

Fig. C. 6 The heat transfer corrected coefficients ($H_T$ and $H_R$) for the case of $d_p = 6$ mm (Gas: $N_2$, spherical particle, $\rho_{DB} = 580$ kg/m$^3$, Vol=90%, $M_c = 0$%, $T_g = T_w = 1173$ K, $h_c = 20$-1000 (W/(m$^2$ K))).
Fig. C. 7 The heat transfer corrected coefficients ($H_T$ and $H_R$) for the case of $d_p = 10$ mm (Gas: $N_2$, spherical particle, $\rho_{DB} = 580$ kg/m$^3$, Vol= 90%, $M_e = 0\%$, $T_g = T_w = 1173$ K, $h_e = 10-500$ (W/(m$^2$·K))).
Appendix D

The gas composition at the outlet of BFB

Table D. 1 The gas composition (vol%) at the outlet of BFB

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Air gasification</th>
<th>Steam gasification</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>16.67</td>
<td>16.59</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>1.88</td>
<td>2.80</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.36</td>
<td>0.84</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>N.A</td>
<td>0.71</td>
</tr>
<tr>
<td>H₂</td>
<td>9.41</td>
<td>11.39</td>
</tr>
<tr>
<td>O₂</td>
<td>0.46</td>
<td>0.79</td>
</tr>
<tr>
<td>N₂</td>
<td>47.18</td>
<td>27.80</td>
</tr>
<tr>
<td>CH₄</td>
<td>5.85</td>
<td>11.83</td>
</tr>
<tr>
<td>CO</td>
<td>18.20</td>
<td>27.25</td>
</tr>
</tbody>
</table>

Governing equations and constitutive relatives of Eulerian multiphase granular model

Continuity equations of gas and solids phase:

\[
\frac{\partial (\varepsilon \rho u_g)}{\partial t} + \nabla \cdot (\varepsilon \rho u_g) = 0 \quad (D.1)
\]

\[
\frac{\partial (\varepsilon \rho_p u_p)}{\partial t} + \nabla \cdot (\varepsilon \rho_p u_p) = 0 \quad (D.2)
\]

Momentum equations of gas and solids phase:

\[
\frac{\partial (\varepsilon \rho u_g)}{\partial t} + \nabla \cdot (\varepsilon \rho u_g u_g) = -\varepsilon \nabla p + \nabla \cdot \tau_g + \varepsilon \rho g - \beta (u_g - u_s) \quad (D.3)
\]

\[
\frac{\partial (\varepsilon \rho_p u_p)}{\partial t} + \nabla \cdot (\varepsilon \rho_p u_p u_p) = -\varepsilon \nabla p - \nabla \cdot \tau_p + \varepsilon \rho_p g + \beta (u_p - u_s) \quad (D.4)
\]

The stress-strain tensor of gas and solid phase:

\[
\tau_g = \varepsilon_g \mu_g (\nabla u_g + \nabla u_g^T) - \frac{2}{3} \mu_g \nabla \cdot u_g I \quad (D.5)
\]

\[
\tau_p = \varepsilon_p \mu_p (\nabla u_p + \nabla u_p^T) + \varepsilon_p (\lambda_p - \frac{2}{3} \mu_p) \nabla \cdot u_p I \quad (D.6)
\]

Granular temperature equation:

\[
\frac{3}{2} \frac{\partial}{\partial t} (\varepsilon \rho_p T_p) + \nabla \cdot (\varepsilon \rho_p T_p u_p) = \left(-P_p I + \tau_p\right) : \nabla u_p + \nabla \cdot \left(\kappa_p \cdot \nabla T_p\right) - \gamma_p - 3 \beta T_p \quad (D.7)
\]

Solid shear viscosity:

\[
\mu_p = \mu_{p, col} + \mu_{p, kin} + \mu_{p, fr} \quad (D.8)
\]
Where,

\[ \mu_{p,\text{col}} = \frac{4}{5} \varepsilon_p \rho_p d_p g_0 \left(1 + e_p\right) \sqrt{\Theta_p / \pi} \]  
(D.9)

\[ \mu_{p,\text{lin}} = \frac{1}{960} \varepsilon_p \rho_p \sqrt{\Theta_p / \pi} \left(1 + \frac{4}{5} g_0 \varepsilon_p \left(1 + e_p\right)\right)^2 \]  
(D.10)

\[ \mu_{p,fr} = \frac{p_p \sin \Phi}{2 \sqrt{I_{2D}}} \]  
(D.11)

Solid bulk viscosity:

\[ \lambda_p = \frac{4}{3} \varepsilon_p \rho_p d_p g_0 \left(1 + e_p\right) \sqrt{\Theta_p / \pi} \]  
(D.12)

Solid pressure:

\[ P_p = \varepsilon_p \rho_p \Theta_p \left[1 + 2 \left(1 + e_p\right) \varepsilon_p g_0\right] \]  
(D.13)

Radial distribution function:

\[ g_0 = \left[1 - \left(\frac{e_p}{e_{\text{max}}}\right)^{1/3}\right]^{-1} \]  
(D.14)

Diffusion coefficient for granular energy:

\[ \kappa_p = \frac{150 \varepsilon_p \rho_p d_p \sqrt{\Theta_p / \pi}}{384 \left(1 + e_p\right) g_0} \left[1 + \frac{6}{5} e_p g_0 \left(1 + e_p\right)\right]^2 + 2 \rho_p \varepsilon_p^2 d_p g_0 \left(1 + e_p\right) \sqrt{\Theta_p / \pi} \]  
(D.15)

Collisional dissipation of energy:

\[ \gamma_p = \frac{12 \left(1 - e_p^2\right) g_0^2 \rho_p P_p \Theta_p^{1/2}}{d_p \sqrt{\pi}} \]  
(D.16)
The formulations of $H_D$ coefficient for both air and steam gasification

Table D. 2 Fitting correlations of $H_D$ for the FFB and BFB of air gasification.

| FFB ($H_D = \alpha \text{Re}_p$) | $a = \left( \frac{\text{1.0}}{-190.8865 - 0.8849 e_g + 194.2217 / e_g} \right) + 0.0585 e_g$ | $b = 0.0726$ | $0.667 \leq e_g < 0.98$ |
| | $b = -0.0340 e_g^{5.1846}$ | | |
| | $a = 0.0157 e_g^{5.9296} \left( 1.0 - e_g \right)^{-0.6396}$ | $b = 0.1230 e_g^{-1291.1610} + 0.0396 e_g^{-4.1562}$ | $0.98 \leq e_g < 0.9997$ |
| | $a = 1$ | $b = 0$ | $0.9997 \leq e_g \leq 1$ |

| BFB ($H_D$) | $H_D = 0.5168 + \frac{0.7980}{1.0 + (e_g / 0.4781)^{0.0170}}$ | $0.455 \leq e_g < 0.562$ |

$H_D = 2.1188 - 2.0826 \exp \left(-1.5825 e_g^{2.5006} \right)$ | $0.562 \leq e_g < 0.695$ |

$H_D = 1$ | $0.695 \leq e_g \leq 1$ or $0.4 \leq e_g < 0.455$ |
Table D. 3 Fitting correlations of $H_D$ for the FFB and BFB of steam gasification.

<table>
<thead>
<tr>
<th></th>
<th>FFB ($H_D = a , \text{Re}^b_p$)</th>
<th>BFB ($H_D$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$-0.0239 + 0.3099$</td>
<td>$-3.0166 + 2.5579 \exp\left(\varepsilon_g\right) + \frac{0.2497}{\log\left(\varepsilon_g\right)}$</td>
</tr>
<tr>
<td>$b$</td>
<td>$\left(1.0 + \left(1.0 + (\varepsilon_g - 0.5483)/0.0846\right)^{1.0}\right)$</td>
<td>$0.5 \leq \varepsilon_g &lt; 0.551$</td>
</tr>
<tr>
<td></td>
<td>$\frac{(-0.0132 + 0.0822 \varepsilon_g - 0.1689 \varepsilon_g^2 + 0.1146 \varepsilon_g^3)}{\left(1.0 - 4.6464 \varepsilon_g + 5.3485 \varepsilon_g^2 + 2.7716 \varepsilon_g^3 - 5.7125 \varepsilon_g^4\right)}$</td>
<td>$0.551 \leq \varepsilon_g \leq 1.0 \alpha$</td>
</tr>
<tr>
<td></td>
<td>$\left(0.0640 - 0.2010 \varepsilon_g + 0.1626 \varepsilon_g^2\right)$</td>
<td>$0.4 \leq \varepsilon_g &lt; 0.541$</td>
</tr>
<tr>
<td></td>
<td>$\left(0.0779 - 0.5298 \varepsilon_g + 0.9005 \varepsilon_g^3\right)$</td>
<td>$0.541 \leq \varepsilon_g &lt; 0.663$</td>
</tr>
<tr>
<td></td>
<td>$\left(1.0 - 5.8498 \varepsilon_g^2 + 8.9932 \varepsilon_g^4\right)$</td>
<td>$0.663 \leq \varepsilon_g &lt; 0.98$</td>
</tr>
<tr>
<td></td>
<td>$\left(0.0150 \varepsilon_g^{0.4000} \left(1.0 - \varepsilon_g\right)^{0.6477}\right)$</td>
<td>$0.98 \leq \varepsilon_g &lt; 0.9997$</td>
</tr>
<tr>
<td></td>
<td>$0.0211 \varepsilon_g^{4.13122} + 0.0432 \varepsilon_g^{5.8200}$</td>
<td>$0.9997 \leq \varepsilon_g \leq 1.0$</td>
</tr>
<tr>
<td></td>
<td>$\left(a = 1\right)$</td>
<td>$H_D = 1$</td>
</tr>
<tr>
<td></td>
<td>$\left(b = 0\right)$</td>
<td>$0.4 \leq \varepsilon_g &lt; 0.458$</td>
</tr>
<tr>
<td></td>
<td>$\left(0.2497/\log\left(\varepsilon_g\right)\right)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\left(0.5 \leq \varepsilon_g &lt; 0.551\right)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\left(0.551 \leq \varepsilon_g \leq 1.0 \alpha\right)$</td>
<td></td>
</tr>
</tbody>
</table>