Effect of Chemical and Physical Properties on Combustion of Biomass Particle

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EFFECT OF CHEMICAL AND PHYSICAL PROPERTIES ON COMBUSTION OF BIOMASS PARTICLE

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Abstract

Biomass combustion is an interesting alternative to fossil fuel. Modeling and simulation is used for design optimization of biomass boilers and furnace. It is difficult to develop a sufficiently accurate and computationally efficient model because the combustion system is highly complicated multi-scale, multi-phase and multi-physics problem. The study of biomass combustion in different scales allows engineers to understand the combustion process and to choose necessary simplification to develop a computationally efficient model.

The chemical and physical properties of fuels are altered during different fuel preparation methods (i.e. pretreatment and pelletization), and as a result the fuel conversion is also affected. The aim of this thesis is to understand thermal conversion of those chemically or physically altered fuels. Both experimental and modeling techniques were chosen to address the aim. Experiments were performed in thermogravimetric analysers, isothermal macro thermogravimeters (iTG), and a pot furnace to account fuel conversion in micro-, meso- and macro scale. In addition, three different types of mathematical model were developed. They are (i) a simplified particle pyrolysis model, (ii) two detailed numerical models that simulate particle pyrolysis and char oxidation and (iii) finally a computational fluid dynamic (CFD) model of combustion of biomass particles in a bed.

The results indicate that both the intrinsic and the apparent conversion of the fuel was influenced by the process conditions of fuel preparation methods. Intrinsic pyrolysis reactivity was reduced due to mild pretreatment; however, it was increased with further increase in pretreatment severity. In contrary, severity of pelletization tends to reduce the apparent reactivity of pellets combustion.

It was also investigated that how each physical and chemical parameter should be modelled for a untreated biomass (i.e. wood logs) and a densified biomass (i.e. pellets) through parametric studies with a detailed particle simulation. The result shows that a model for wood logs should exclude convective heat transfer by volatiles if the fibers align to longitude direction while it is important part in the models for pellets. Devolatilization of wood logs was expressed as endothermic reactions while the model results showed best agreement with experimental data of wood pellets when the heat of reaction was assumed to be zero, possibly due to the secondary reactions. Then, it was demonstrated that a constitutive equation, i.e. analytical solution of the shrinking core model, is sufficient to express devolatilization rate of thermally-thick particles at the temperature of 1173 K.

While studying apparent oxidation of wood pellet char, it was found that change in intrinsic char oxidation reactivity due to different pyrolysis conditions does not influences the model prediction at high temperature. In addition, at high temperature, the reaction front became thin and reaction rate was hardly affected by temperature.

It was also found by the simulation of pellet bed combustion that the apparent density of the particle significantly affected the flame velocity.
This thesis is a summary of the following publications

**Paper I**


**Paper II**


**Paper III**


**Paper IV**

A. K. Biswas, M. Broström, and K. Umeki, “Apparent combustion rate of large wood char particles,” *Manuscript*

**Paper V**

A. K. Biswas, M. Risberg, E. Nikola, and K. Umeki, “Effect of the bed compaction on fixed bed combustion” *Manuscript*
Co-author statement

**Paper I** was planned and written by the author of the thesis, while other co-authors contributed with discussion and comments. The author of this thesis has done all experiments.

**Paper II** was planned and written by the author of this thesis. Experiments were done in collaboration with Magnus Rudolfsson and Markus Broström. Kentaro umeki contributed through discussion and comments.

**Paper III** was planned and written in joint co-operation with Kentaro Umeki. The author developed the detailed model and performed all experiments.

**Paper IV** was planned and written by the author of this thesis. Experiments were done in collaboration with Markus Brostöm while model was developed by the author of this thesis. All authors contribute through discussion.

**Paper V** was planned and written by the author of this thesis. Experiments were done in collaboration with Nikola Evic while model was developed by the author. The other authors contribute through discussion.
Acknowledgement

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## Terminology

### Reaction rate

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent</td>
<td>Rate of heterogeneous reactions observed under the influence of mass and heat transfer</td>
</tr>
<tr>
<td>Intrinsic</td>
<td>Rate of heterogeneous reaction without the influence of mass and heat transfer (i.e. controlled by only chemical kinetics)</td>
</tr>
</tbody>
</table>

### Devolatilization

Volatile release from biomass due to heat-driven thermal decomposition and phase changes for certain heavy molecules such as tar. It may undergo under both oxidizing and inert atmosphere. It is also called pyrolysis in paper 1.

### Scale

<table>
<thead>
<tr>
<th>Scale</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro</td>
<td>Small enough to ignore the mass and heat transfer at the scale of interest. Typically smaller than 100 μm.</td>
</tr>
<tr>
<td>Meso</td>
<td>Large enough to be affected by mass and heat transfer. Typical example is thermally thick wood particles such as a pellet.</td>
</tr>
<tr>
<td>Macro</td>
<td>Largest scale of interests where both intra and inter particle mass and heat transfer is important (i.e. reactor scale).</td>
</tr>
</tbody>
</table>

### Solid-gas fractions

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>A fraction of homogeneous phase inside a particle</td>
</tr>
<tr>
<td>Void fraction</td>
<td>A fraction of homogeneous phase between particles, usually in macro scale.</td>
</tr>
</tbody>
</table>

### Density

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>Density at macro-scale. The total mass of particles is divided by the volume of the reactor (i.e. container).</td>
</tr>
<tr>
<td>Particle</td>
<td>Density at meso-scale. Mass of a single particle is divided by the total volume of solid and internal pores.</td>
</tr>
<tr>
<td>True</td>
<td>Actual density of the solid. Solid mass is divided by the actual volume occupied by solid.</td>
</tr>
</tbody>
</table>
Nomenclature

A
Pre-exponential factor, s⁻¹

Bi
Biotnumber, -

Cp
specific heat, J kg⁻¹ K⁻¹

C₂
turbulence model constant

D
particle diameter, m

D_{AB}
molecular diffusivity, m²s⁻¹

D_{eff}
mass diffusivity, m² s⁻¹

d_{pore}
pore diameter, m

E
activation energy, J mol⁻¹

h
specific enthalpy, J kg⁻¹

h_{eff}
effective heat transfer coefficient, W m⁻² K⁻¹

h_{conv}
convective heat transfer coefficient, W m⁻² K⁻¹

Δh°
heat of reaction, J kg⁻¹

I
Irradiation, W m⁻²

k
rate constant, s⁻¹

K
heterogeneous rate constant, m s⁻¹

L
length of cylindrical particle, m

M
Molecular weight, kg kmol⁻¹

m
mass of the sample, g

Nu
Nusselt number, -

P
pressure, Pa

P_{O₂}
Partial pressure of oxygen, kpa

P(L/D)
shape correlation factor, -

Pr
Prandtl number, -

Q
rate of heat flow or accumulation, W

R
particle radius, m

r
particle radius, m

R_g
ideal gas constant, J K⁻¹ mol⁻¹

Re
Reynolds number, -
radial position, m

position of reaction front, m

source term in the k equation, N/m²s

source term in the ε equation, N/m²s

molecular weight

temperature, K

environmental temperature, K

solid temperature, K

time, s

gas velocity, m s⁻¹

volume of control volume, m³

molecular mass, kg mol⁻¹

Conversion, -

residual mass, -

volume fraction, -

char mass fraction, -

thermal diffusivity, m² s⁻¹

absorption coefficient, m⁻¹

heating rate, K s⁻¹

emissivity, -

solid fraction, -

turbulence model constant, (m²s⁻³)

tortuosity, -

thermal conductivity, W m⁻¹ K⁻¹

viscosity, Pa s

bridge factor, -

density, kg m⁻³

Stefan-Boltzmann constant, W m⁻² K⁻⁴

Scattering coefficient, m⁻¹

permeability, m²
\( \phi \) void fraction, -
\( \omega \) rate of reaction, kg m\(^{-3}\) s\(^{-1}\)

**Subscript**
- \( a \) accumulation
- \( \text{ash} \) ash
- \( \text{ave} \) average value
- \( C \) char
- \( c \) conduction
- \( \text{conv} \) convection
- \( \text{dev} \) devolatilization
- \( e \) environment
- \( \text{eff} \) effective value
- \( f \) final
- \( \text{finite} \) value for the finite length
- \( G \) gas
- \( I \) inert gas
- \( i \) specie \( i \)
- \( j \) reaction \( j \)
- \( \text{max} \) at maximum rate of reaction
- \( \text{moist} \) moisture
- \( p \) particle
- \( \text{por} \) pore
- \( \text{rad} \) radiation
- \( S \) source
- \( \text{S} \) surface
- \( \text{solid} \) solid
- \( \text{SCM} \) special value for the shrinking core model
- \( \text{SE} \) Steam explosion
- \( T \) tar
- \( W \) wood
- \( 0 \) initial
Chapter 1

Introduction

The total energy consumption and pollutant emissions of the world have doubled in the last 40 years [1]. The share of abundant non-edible biomass feedstock in the world energy consumption is around 11%, although only a third of those resources are used efficiently in industrialized countries [2]. Combustion of biomass is the main technology route that globally contributes to 90% of the bioenergy used [3]. Biomass can be efficiently burned to produce electricity and heat in combined heat and power plants (CHP). The International Energy Agency (IEA) predicts that biomass usage in power generation will grow from the current level of 54 GW to 82 GW by the end of 2020 [4].

The principal technologies used in biomass fuelled CHP plants are fixed and fluidized bed combustion. Computational fluid dynamic (CFD) simulation has become an important tool for the design optimization of biomass combustors. CFD modelling provides an opportunity to simulate reacting multiphase flows.

Biomass fuels used in the combustor are inhomogeneous in their chemical and physical properties (e.g. particle shape and size). As a consequence, designing the combustion system is a highly complicated multi-scale, multi-phase and multi-physics problem. One of such complexities appears when relatively large biomass particles such as wood chips, logs, pellets, and briquettes are used as fuel. Several sub-processes are involved during thermal conversion of large fuel particles, such as chemical reaction, intra-particle diffusion and convection, particle shrinkage, porosity development, fragmentation etc. It is usually a big challenge to develop simulation models that are sufficiently accurate and computationally efficient [5]. Studying biomass combustion at micro-, meso- and macro levels can provide information about the nature of the process and allow researchers to select the most important phenomena when modelling full scale combustion systems.

Chemical and physical properties of the fuel determine heat and mass transfer rates, reaction pathways and kinetics during fuel conversion [6–9]. Biomass pre-treatment and pelletizing affects both the chemical and physical properties of the fuel (i.e. density, thermal conductivity, permeability). The aim of this thesis is to understand thermal conversion of those chemically or physically altered fuels. The main emphases are (i) to study how fuel preparation (i.e. pre-treatment and pelletizing) processes influence the thermal conversion behaviour, and (ii) to examine the relative importance of different physical and chemical processes during thermal conversion of pelletized wood.
Chapter 2

Phenomenological overview and motivation

Biomass is mainly composed of hemicellulose, cellulose, lignin and extractives where their proportions can vary depending on the type and origin of the plant. Additionally, mineral matter is also found in biomass which varies from 0.1-2% in wood to 15%-25% in herbaceous biomass. When a biomass particle is exposed to reacting atmosphere, it can experience either subsequent or simultaneous, drying, devolatilization and char oxidation. This chapter discusses about thermochemical conversion of biomass at particle and reactor scales. The terminologies used are described at the beginning of the thesis.

2.1 Particle scale

2.1.1 Particle devolatilization

Several processes, i.e. chemical kinetics, transport phenomena and fuel morphology change, determine the devolatilization of a particle. Figure 2.1 shows a schematic of a particle during devolatilization.

![Figure 2.1: Schematic of fuel particle devolatilization](image)

When particles are exposed to a high temperature environment inside a boiler, the particle surface is heated by radiation and convection. Heat is transferred towards the centre of the particle by conduction. Water starts to evaporate when the local particle temperature reaches a certain temperature. After water evaporation, gases are produced due to local thermal degradation (i.e. devolatilization) of the biomass. As the devolatilization proceeds, gases produced inside a fuel particle travel towards the hot surface and leave the particle. However,
in the case of large fuel particles, the evolving gases may also migrate towards the colder part of the fuel which can result in condensation. The transport behaviour of gases in the fuel can be determined by fuel structure such as the development of network of cracks, surface regression, internal shrinkage or swelling and, primary fragmentation.

Although thousands of gas, liquid, and solid species are generated during devolatilization, they can be lumped primarily to three main components; permanent gases, char and liquid products. Permanent gases include CO, CO2, H2, CH4 and C2 hydrocarbons. Liquid products consist of water, oxygenates (primary vapour, acids, ketones, phenols, guaiacols and furans), light aromatic hydrocarbons (benzene, toluene, etc.) and poly-cyclic aromatic hydrocarbons (PAHs). Secondary decomposition of tars (i.e. liquid product of devolatilization) can play an important role at high temperatures and long residence times [10]. Secondary reaction takes place both heterogeneously and homogeneously [11]. Secondary reaction includes intra-particle cracking of tar on char surfaces [10]. Janse et al. observed that intra-particle tar cracking is likely to be significant for particles larger than 1 mm diameter at temperature above 900 K [12].

The heat of devolatilization reaction varies largely in literature [13–16]. Experimental observations at chemically controlled conditions (i.e. with TGA and DSC) showed that heating rate and char yield have strong correlation with heat of reaction [13,15]. Milosavljevic et al. [13] observed that high heating rate favoured endothermic volatile formation over exothermic char formation. Devolatilization heat of a thermally thick particle is difficult to comprehend. Bilbao et al. [17] showed that overall devolatilization of thick particles was endothermic up to 60 % conversion before turning exothermic. Lee et al. [18] observed that the devolatilization heat in the inner core of a particle was initially endothermic and later turned to exothermic. These observations imply that there are more than two steps of reactions in solid-phase inside the thick particle that allows reaction heat to shift from endothermic to exothermic reaction.

Among all chemical and transport processes, heat transfer is the most important transport process during particle devolatilization. The Biot (Bi) number is frequently used to characterize particle devolatilization. Bi represents the relative importance of external and internal heat transfer. Bi<< 1 means that the characteristic time of external heat transfer is much longer than that of heat transport through conduction. Such processes are controlled by external heat transfer and the temperature inside the particle is rather uniform. Such particles are usually called thermally fine (or thin) particles. In contrast, Bi>> 1 means faster external heat transfer than internal heat transfer through the particle. Such particles tend to have significant intra-particle temperature gradients during devolatilization and are therefore called thermally thick particles.
2.1.2 Char oxidation

The solid residue from devolatilization, so-called char, is further oxidized by $O_2$, $CO_2$, and $H_2O$ in the reactor. Figure 2.2 shows a schematic of char oxidation. The reaction rate of a char particle can be controlled by external and internal mass diffusions as well as by chemical reaction kinetics.

![Figure 2.2: Schematic of char of oxidation](image)

The relative importance of mass diffusion and chemical reaction rates during char oxidation can be characterized by two dimensionless numbers. They are the Thiele modulus and the effectiveness factor. The Thiele modulus is the ratio between the times for internal mass diffusion to that of reactions. The effectiveness factor is the ratio of the apparent reaction rate to the intrinsic reaction rate (i.e. reaction rate in a condition when all available reaction surfaces are exposed to the surrounding reaction atmosphere) [7]. Based on those dimensional numbers, three different regimes can be identified. The first regime is the chemically controlled regime (regime I), where the Thiele modulus is small and the effectiveness factor is unity. In this regime, the diffusion rate is much faster than the chemical kinetics. As a result, the char particles experience conversion throughout the particles. This regime typically appears for small char particles at low reaction temperature [19]. When the particle size or reaction temperature increases, the Thiele modulus becomes much greater than unity and the effectiveness factor becomes less than unity. The time scale of mass diffusion becomes comparable to the chemical kinetics, and therefore affecting the conversion process. This regime is called Regime II, or the internal diffusion regime, although it is not necessary controlled only by internal mass diffusion. The apparent reaction rate in regime III is controlled by external mass transfer from the bulk gas to the external surface of the particle[7]. In all the regimes, heat transfer and heat of reactions, in addition to mass transfer and chemical kinetics, may play a vital role for char conversion by oxygen. The temperature gradient inside the particle can vary significantly due to exothermicity of the combustion reactions.

Intrinsic char reactivity is decided mainly by how the char morphological structure is shaped during devolatilization and also by the composition of inorganic matters in the char. Therefore, the devolatilization conditions and the type of biomass are the key factors that
decide char reactivity. Several devolatilization conditions such as heating rate, residence time and pressure have been identified as key contributors to the char reactivity [7]. High heating rates during devolatilization initiate higher intra-particle pressure and fast release of volatiles. This breaks and merges small pores to produce large internal cavities. As a consequence, the char produced is more reactive. The presence of macro and mesopores is a good indicator of high reactivity of char[7]. On the other hand, long residence times of tar vapour inside the particle can initiate condensation that reduces reactivity of char. In addition to devolatilization condition, inorganic matters can act as catalyst during thermal conversion of char. For instance, alkali metals such as Na and K are known to promote catalytic oxidation of the char[20].

2.2 Reactor dynamics

Grate combustion of biomass is the most widely used among different available combustion technologies due to its ability to handle wide range of fuels [21]. However, its application is mostly confined to small and medium scale wood pellet or chips fired boilers and grates. Figure 2.3 shows a schematic of a grate furnace. A well designed grate furnace ensures uniform distribution of the reacting fuels over the bed. Uneven fuel distribution may cause operational problems and efficiency losses. Technologies that are applied to reduce operational problems are continuously moving grates, frequency controlled primary air supply at various section of the grate etc. The combustion chamber may be separated in two parts, namely the freeboard and the fuel bed. In the fuel bed, solid and gas phases interact through transfer of mass, momentum and energy. In the freeboard, the gas phase reacts and interactions with the fuel bed occur mainly through radiative and convective heat transfer.

![Combustion process in a grate combustor](image)

Biomass fuel is generally inhomogeneous in its chemical, physical and morphological properties. This leads to inhomogeneous combustion of the bed and possibly increases of
pollutant emission and decrease of process efficiency. It is usually difficult to obtain detailed information inside a fuel bed due to measurement difficulties; therefore, only a limited number of studies on bed combustion is available. Several studies at laboratory scale have been conducted in order to understand the dynamics of the grate combustion [22–24]. Influencing parameters are fuel composition, operating conditions and fuel morphology [22]. Although attempts have been made to correlate reaction front speed with fuel composition (e.g. moisture content and lower heating value)[23,25], operating condition (i.e. primary air supply) was found to be the most influential [26]. Little information is available on the effect of pellet bed packing on combustion.

2.3 Pre-treatment and pelletizing of biomass

Biomass handling is usually inefficient and expensive due to its low bulk density. The bulk density of raw biomass can vary in the range of 40 to 200 kg/m³. Pelletizing can improve the bulk density to 700 kg/m³, reducing the transport cost [27,28]. Pelletized fuels are also more consistent in their structure which is beneficial for the automated fuel system in the boilers. The wood pellet industry is an important part of current bioenergy industry. The annual production of wood pellets worldwide was 14 million tons in 2010 and the wood pellet market has been growing steadily worldwide, driven by both industrial and residential consumers.

Small biomass particles are subjected to mechanical pressure inside a pelletizing die during pelletizing. The particle temperature is increased due to friction between the biomass and the pelletizing die during the forced passage through press channel. As a result, the temperature increases and this activates natural binders inside the particles to physically bond with neighbouring particles. Several key process parameters that affect the pellet properties are biomass type, moisture, temperature, particle size, and pelletizing pressures. For example, a high pelletizing temperature and a low moisture content in biomass have shown to enhance the pellet strength and density, while also reducing the energy consumption during pelletization[27]. Biomass pre-treatment prior to pelletization can further improve the fuel properties of biomass pellet as well as the handling efficiency [29]. It is a promising method to pre-process low quality biomass into high energy density feedstock with consistent and uniform physical and chemical characteristics. Two main pre-treatment technologies emerging are torrefaction and steam explosion [29]. In this thesis, only steam explosion of biomass is discussed.

The steam explosion (SE) process involves hydrolysis of biomass with high pressure saturated steam for wide variety of residence time. In the SE process, hydrolysis is followed by a rapid decompression. Woody biomass consists of cell wall mainly with polysaccharides (cellulose and hemicelluloses) and aromatic polymers named lignin. SE pre-treatment is known to bring adequate disruption of carbohydrate structure by releasing parts of hemicelluloses into the water solution [30]. Additionally, both cellulose and lignin are also altered depending on the severity of the process [31,32]. Parameters that affect SE is pre-treatment time, temperature, chip size, moisture content and type of wood.
2.4 Motivation of this study

As summarized previously, fuel conversion of large wood particles may be affected by chemical reactions, intra-particle physical phenomena, and inter-particle physical phenomena (see Figure 2.4). To provide reliable CFD models for bed combustion, it is important to understand the relative importance of each phenomenon during fuel conversion for both conventional and pre-treated biomass fuels. This thesis elaborates on the complicated fuel conversion process from various angles: (i) the effect of pre-treatment, (ii) the effect of pelletizing, (iii) dynamic conversion behaviour in large particles, and (iv) conversion dynamics of the bed. The research gaps from the literature, used as motivation for the different studies of this thesis, are summarized below.

Pre-treatment: A limited number of studies have discussed how different fuel preparation methods affect thermal conversion of biomass. For instance, few studies have discussed about the effect of steam explosion pre-treatment on devolatilization of biomass. Xu et al observed an increase in char yield after devolatilization for steam pre-treated wool fibre residue [33]. Deepa et al. observed a slight change in degradation temperature of hemicellulose in SE pre-treated banana fibre residue [34]. Negro et al. observed a shift in lignin peak towards lower temperature for a severely pre-treated residue in comparison with the mildest condition [30].

No study was available that systematically studied the effect of SE pre-treatment on devolatilization of biomass.

Pelletizing: Several process conditions affect the pelletizing as discussed previously, but the effect of pelletizing conditions on combustion of wood pellet has rarely been investigated. Previous studies showed that the combustion time of a single pellet was significantly affected...
by biomass composition while the role of particle size distribution in the combustion time of a single particle was insignificant [35–37]. The effect of other pelletizing conditions, such as pelletizing temperature and biomass moisture content, on combustion of a single pellet has not been investigated previously.

**Large wood particles:** In most industry relevant conditions, relatively large biomass particles (5–20 mm) are fed to reactors such as grate boilers and fluidized-bed reactors. Large particle conversion is affected by several factors as discussed previously. Therefore, it is important to have a deep understanding of the reaction process to accurately model the conversion process. Devolatilization models of single particles have been developed by many researchers, and a substantial volume of studies have been published [38–41]. Some previous studies showed that it is important to consider not only intra-particle mass and heat transfer, but also the gas flow surrounding the particle [42], particle shrinkage [43,44], particle shape [45], and internal microstructure during particle devolatilization modelling. On the other hand, some studies demonstrated that the detailed particle model such as internal mass transport phenomena [12] or temperature dependent physical properties are unnecessary to acquire the accurate predictions. There are very limited numbers of studies that discussed about the modelling strategies for densified biomass particle e.g. pellets (1000-1300 kg/m³).

Char oxidation/gasification of large particles occurs under the influence of intrinsic reaction kinetics, mass diffusion and non-uniform temperatures inside the particles. While a number of studies have investigated char reactivity under chemically controlled regime, e.g. [46–48], few studies have discussed the fundamentals of large particle oxidation or gasification [45,49–54]. It is well known that devolatilization conditions affect the intrinsic reactivity of char. Identified important parameters include heating rate, holding time (annealing or the loss of ash forming elements), temperature, cooling rate, reaction atmosphere, and the presence of volatile-char interactions [7]. In large particles, local conditions of these parameters change dependent on the type of particles (log or pellet), particle size, and devolatilization conditions. However, the effect of overall reaction conditions on intrinsic char reactivity of large particles has not been studied thoroughly despite its possible importance for the overall char oxidation/gasification time.

**Fuel conversion in a fixed bed combustion chamber:** The effect of bed compaction on grate combustion has rarely been investigated. Bed compaction is strongly dependent on several fuel morphological parameters (i.e. particle size, shape, density) but available studies have used different fuels and undefined/arbitrary particle shapes and size [55–57]. Therefore, the true effect of the bed compaction (i.e. bulk density) on the reaction front is still unaddressed.

**Scope of the thesis:** As shown in Figure 2.4, the specific research questions are

i. to investigate the effect of SE pre-treatment conditions on the intrinsic reactivity of woody biomass during devolatilization,

ii. to investigate the effect of pelletizing conditions on the apparent combustion rate of wood pellet,

iii. to examine the relative importance of different physical and chemical processes during devolatilization and oxidation of wood pellets, and

iv. to investigate the importance of bed packing during combustion of wood pellet.
Both experimental and modelling approaches were chosen to address these questions. Experiments were performed in thermogravimetric analysers, an isothermal macro thermogravimetric analyser (iTGs), and a pot furnace. In addition to experimental work, three different types of mathematical model were developed. They are (i) a simplified particle devolatilization model, (ii) two detailed numerical model that simulate particle devolatilization and char oxidation, and (iii) a computational fluid dynamic (CFD) model of combustion of biomass particles in a bed.
Chapter 3

Experimental methods

3.1. Samples

Several types of biomass samples were used in this study. Short rotation willow (Salix) was used as a raw material for SE pre-treatment experiment (Paper I). Salix was pre-treated in a laboratory scale reactor by varying two main process parameters, saturated steam temperature ($T_p$) and time ($t$). Three pre-treatment temperatures were chosen: 478, 493 and 501 K. For pre-treatment temperatures of 478 K and 493 K, pre-treatment time was chosen to 6 min, 9 min and 12 min. For 501 K, pre-treatment time was set to 6 min and 12 min. The detailed description of the test facility and experimental procedure is explained elsewhere [58]. Solid hydrolysed residues were dried and grounded to particle size less than 0.125 mm for thermogravimetric analysis.

Ground pine samples were used to make wood pellets in a laboratory scale pelletizer setup (Paper II). A cylindrical die with a diameter of 8 mm was used to produce pellets in a piston press at die temperatures of 20, 100, 150 and 200 °C. Moisture contents of raw biomass were 1 wt.% and 12 wt.%. To compare single die pellets with pellet from semi-industrial scale plants, the same raw biomass was used to produce pellets in a semi-industrial roll die type pelletizer. The detailed descriptions of the pelletizing equipment and processes can be found elsewhere [59].

Wood pellets from a mixture of woods (90 wt.% pine and 10 wt.% spruce, Bioenergi i Luleå AB) were used in rest of the three studies (Paper III–V). Pellet diameters were 6 and 8 mm with length-to-diameter (L/D) ratios of 3.5 for Papers III and IV and between 1-2.5 for paper V. The mean apparent density of the wood pellets was around 1100 kg m$^{-3}$.

Paper III and IV were complimented with an additional sample to represent untreated biomass. It was a cylindrical-shaped wood log of Cercidiphyllum japonicum (Katsura tree). The particle diameters of wood logs were 9.5 and 14.5 mm with various length-to-diameter (L/D) ratios. The mean apparent density of the wood logs was around 500 kg m$^{-3}$. Table 3.1 summarizes the fuel analysis of the samples used in this study.
Table 3.1: fuel analysis of the samples

<table>
<thead>
<tr>
<th>Paper</th>
<th>I</th>
<th>II</th>
<th>III-V</th>
<th>III-IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
<td>Salix</td>
<td>Pine</td>
<td>Pine (90 wt%) and Spruce (10 wt%)</td>
<td>Cercidiphyllum japonicum</td>
</tr>
<tr>
<td>C, wt.%</td>
<td>49.40</td>
<td>n.a.</td>
<td>50.6</td>
<td>46.66</td>
</tr>
<tr>
<td>H, wt.%</td>
<td>6.10</td>
<td>n.a.</td>
<td>6.2</td>
<td>5.50</td>
</tr>
<tr>
<td>N, wt.%</td>
<td>0.29</td>
<td>n.a.</td>
<td>&lt;0.1</td>
<td>0.29</td>
</tr>
<tr>
<td>O, wt.%</td>
<td>41.80</td>
<td>n.a.</td>
<td>42.69</td>
<td>45.78</td>
</tr>
<tr>
<td>S, wt.%</td>
<td>0.043</td>
<td>n.a.</td>
<td>[-]</td>
<td>[-]</td>
</tr>
<tr>
<td>Ash, wt.%</td>
<td>2.367</td>
<td>n.a.</td>
<td>0.50</td>
<td>1.77</td>
</tr>
</tbody>
</table>

3.2. Experimental facilities

Three types of experimental facilities were used in this study. They are Thermogravimetric analyzer (TGA), Isothermal macro thermogravimetric analyzer (iTG) and a laboratory scale batch reactor mimicking grate combustion.

A TGA was used to measure intrinsic reaction rate of devolatilization and char oxidation. A sample weight of around 0.5 mg was used in every occasion and placed in a crucible. Initially, the biomass was heated to 378 K and kept for at least half an hour under the nitrogen atmosphere to remove moisture from the biomass. The information about heating rate, final reaction temperature and composition of the reactant for those is listed in Table 3.2.

Two types of iTGs were used in this study (Paper II-IV). Figure 3.1 shows a schematic of iTG. It is essentially a laboratory scale reactor that can be heated electrically to a desired reaction temperature (973, 1073 and 1173 K). The reaction atmosphere can be filled by a continuous supply of desired gas. The reactors are also equipped with an analytical balance enabling it to be used as a macro-TGA. Detailed description of these iTGs can be found in refs [60,61]. The sample was hung in a basket (Pt/Ni-Cr) connected to an analytical balance with a steel wire and kept in a cooling chamber with nitrogen flow before the experiment. Experiments started when the sample was inserted into the furnace from the cooling chamber. The experimental conditions in iTGs are listed in Table 3.2.

Table 3.2 Description of the experimental conditions

<table>
<thead>
<tr>
<th>Paper</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment</td>
<td>TGA</td>
<td>iTG</td>
<td>iTG</td>
<td>TGA</td>
<td>iTG</td>
</tr>
<tr>
<td>Sample weight, g</td>
<td>0.005</td>
<td>0.6</td>
<td>1–2</td>
<td>0.0005</td>
<td>0.3–0.5</td>
</tr>
<tr>
<td>Particle size, mm</td>
<td>0.125</td>
<td>8</td>
<td>6/8/9.5/14.5</td>
<td>0.075</td>
<td>6/8/9.5/14.5</td>
</tr>
<tr>
<td>Heating rate, K/min</td>
<td>10</td>
<td>n.a.</td>
<td>n.a.</td>
<td>5/10/15</td>
<td>n.a.</td>
</tr>
<tr>
<td>Temperature, K**</td>
<td>1023</td>
<td>1073</td>
<td>973/1073/1173</td>
<td>923</td>
<td>973/1073/1173</td>
</tr>
<tr>
<td>Gas flow rate, L min^-1</td>
<td>0.3</td>
<td>9</td>
<td>7</td>
<td>0.5</td>
<td>7</td>
</tr>
<tr>
<td>Nitrogen (N2), vol%</td>
<td>100</td>
<td>79</td>
<td>100</td>
<td>85/90/95</td>
<td>90</td>
</tr>
<tr>
<td>Oxygen (O2), vol%</td>
<td>0</td>
<td>21</td>
<td>0</td>
<td>5/10/15</td>
<td>10</td>
</tr>
</tbody>
</table>

*Sieve size and diameter **Final temperature for TGA, wall temperature for fixed bed
A laboratory scale pot furnace was used to examine the effect of packing of fixed bed on combustion rate of wood pellet (paper V). Figure 3.2 shows a schematic of the bed combustor. It consists of a cylindrical retort with 335 mm height and an internal diameter of 120 mm. It was electrically heated by PID controllers. The biomass was placed inside a cylindrical holder and placed inside the retort. Air was introduced from the bottom of the reactor. The retort was surrounded by thick wall of firebricks and was sealed properly to avoid unwanted admission of air inside the reactor. A detailed description of the laboratory furnace was published previously [62,63]. The lower part of the reactor was heated to 723 K and upper part was heated to 1073 K. The biomass samples were placed inside the cylindrical pot that was subsequently place inside the cylindrical retort with the help of a mechanical lift. The cylindrical pot was place on a scale and the fuel conversion data was logged. Air was introduced through a perforated plate at the bottom of the fuel bed. Four thermocouples were placed inside the fuel bed to measure bed temperature.

To ensure consistency in measurement, each experiment was repeated and good agreement between different experimental cases was found.
Figure 3.2: A schematic of the experimental setup for bed combustion [62]
4.1 Particle models

4.1.1 Simplified particle model

Figure 4.1 shows a schematic description of biomass particles during devolatilization under the assumptions of the Shrinking core model (SCM) [61]. The formulation of SCM is based on the assumption that an infinitely thin reaction zone, which travels from the particle surface to centre during devolatilization, divides the particles into a char layer and a biomass core. At the particle surface, char surface receives heat from the surrounding environment. Then, heat conducts through the char layer from the surface to the centre while accumulation of heat in the char layer is considered as negligible. The biomass core is assumed to remain as the initial temperature and rise to devolatilization temperature at the reaction front, where devolatilization occurs. Volatiles formed during devolatilization are assumed to leave the particle instantly as it is formed (i.e. to longitude direction). Biomass particles were assumed to be infinitely long cylindrical particles and not shrink by devolatilization. It is also assumed that physical properties remain constant against the change in temperature.

\[
Q_e = 2\pi RL h_{\text{eff}}(T_e - T_s)
\]  

Where the effective heat transfer coefficient takes into account both convective and radiative heat transfers, i.e. \( h_{\text{eff}} = h_{\text{conv}} + \varepsilon \sigma (T_e + T_s)(T_e^2 + T_s^2) \).
\[ Q_c = 2\pi r L \lambda_\alpha \frac{dT}{dr} \]  

(2)

The rate of heat accumulation by the raw biomass and the heat of reaction of devolatilization at the reaction front is

\[ Q_a = -2\pi r_{dev} L \rho \nu \left[ C_p \nu (T_{dev} - T_0) + \Delta h_{dev} \right] \frac{dr_{dev}}{dt}. \]  

(3)

The heat accumulation in the char layer is comparably small in comparison to the heat flow itself, so it is assumed that \( Q_e, Q_c \) and \( Q_a \) can be approximated to be equal and following equation can be derived

\[ 1 - \frac{t}{t_{dev}} = \left( \frac{r_{dev}}{R} \right)^2 - \frac{2B_{SCM}}{B_{SCM} + 2} \left( \frac{r_{dev}}{R} \right)^2 \ln \left( \frac{r_{dev}}{R} \right) \]  

(4)

Where \( B_{SCM} = \frac{h_{mg} r_{c} \lambda_{c}}{h_{mg} r_{c} \lambda_{c}} \) is the dimensionless number with the same form as the Biot number, which expresses the ratio of the internal to external heat transfer resistance.

\[ \frac{dX}{dt} = \frac{B_{SCM}}{B_{SCM} + 2} \]  

(5)

\[ t_{dev} = \frac{R^2}{2B_{SCM}} \frac{T_{dev} - T_0}{B_{SCM} + 2} \]  

(6)

4.1.2 Detailed particle model

Detailed particle simulation was carried out as a numerical solution of the set of transport equations inside the particle with sub-models for chemical reactions and physical parameters. It is a one-dimensional model under the assumption of local thermal equilibrium between gas and solid phase. In the current model, two solid species (wood and char) were considered during particle devolatilization. An additional solid phase (ash) was considered for char oxidation modelling. The mass conservation of wood, char and ash can be described as

\[ \frac{\partial (\rho_\nu V)}{\partial t} = S_\nu V \]  

(7)

\[ \frac{\partial (\rho V)}{\partial t} = S_c V \]  

(8)

\[ \frac{\partial (\rho_{ash} V)}{\partial t} = 0 \]  

(9)

Product gases of devolatilization were volatiles, tar and nitrogen while for char oxidation they were inert gas (N\(_2\)), Oxygen (O\(_2\)), and carbon dioxide (CO\(_2\)). Since we considered both convective and diffusive mass transfer, mass and species transport equations can be written as:

\[ \frac{\partial (\phi \rho_c)}{\partial t} + \frac{1}{r} \frac{\partial (r \rho_c U)}{\partial r} = S_B \]  

(10)

\[ \frac{\partial (\phi \rho_c Y_i)}{\partial t} + \frac{1}{r} \frac{\partial (r \rho_c U Y_i)}{\partial r} = \frac{1}{r} \frac{\partial}{\partial r} \left( \rho_c D_{eff} \frac{\partial Y_i}{\partial r} \right) + S_i \]  

(11)
The particle can be considered as porous medium and Darcy’s law can express the flow field inside the particle. In addition, we approximated the behaviour of total gas in the particle by the ideal gas law.

$$U = -\frac{\phi_{por}}{\mu} \frac{\partial P}{\partial r}$$  \hspace{1cm} (12)

$$p = \frac{\rho_g R_g T}{W_g}$$  \hspace{1cm} (13)

A local thermal equilibrium between the solid and gas phases was assumed in the energy equation.

$$\frac{\partial [\rho_{solid} h_{solid} + \phi (\rho_i h_i)]}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \lambda_{eff} \frac{\partial T}{\partial r} \right) + \Delta h S_g = \frac{\rho_{solid} h_{solid} + \phi (\rho_i h_i)}{V} \frac{\partial V}{\partial t}$$  \hspace{1cm} (14)

Different types of models are available to express biomass devolatilization under chemically controlled atmosphere [64–66]. Some of them are detailed and still under development. The most classic and widely used model is the one component reaction model where biomass decomposes to primary gas, tar and char. Secondary reactions play significant roles for product yields as discussed previously. Primary devolatilization reaction models are often complimented with secondary reactions, where primary tar decomposes to secondary gas and char. Kinetic parameters were taken from Di Blasi and Branca[67] after the assessment of several kinetic parameters by comparison with experimental data in the same manner as Haseli et al. [68]. All the reactions were assumed to be first order with respect to the mass of the reactants, and rate coefficients were expressed by Arrhenius-type expression.

Modelling the heat of reaction in particle models is highly complex because devolatilization can be either endothermic to exothermic while it is important part of chemical-physical interaction inside the particle. Two different approaches for heat of reactions were examined in this study. In the first approach, devolatilization was assumed to be endothermic. Second approach set heat of reactions of devolatilization as zero. The kinetic parameters and reaction heat of devolatilization are presented in Table 4.1

### Table 4.1: kinetic parameter for devolatilization and char oxidation

<table>
<thead>
<tr>
<th>Devolatilization and drying</th>
<th>Kinetic parameters</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry wood → Gas</td>
<td>$4.38 \times 10^6 \exp(-152 \times 10^3/R_gT)$</td>
<td>[67]</td>
</tr>
<tr>
<td>Dry wood → tar</td>
<td>$1.08 \times 10^{15} \exp(-148 \times 10^3/R_gT)$</td>
<td>[67]</td>
</tr>
<tr>
<td>Dry wood → Char</td>
<td>$3.27 \times 10^6 \exp(-111 \times 10^3/R_gT)$</td>
<td>[67]</td>
</tr>
<tr>
<td>Heterogeneous char reaction</td>
<td>$K_{log} = 7.48 \times 10^7 \exp \left( -\frac{218 \times 10^3}{RT} \right) Y_l^{1.49} P_o^2$</td>
<td>TGA</td>
</tr>
<tr>
<td></td>
<td>$K_{pellet} = 1.16 \times 10^{11} \exp \left( -\frac{258 \times 10^{11}}{RT} \right) Y_l^{1.95} P_o^2$</td>
<td>TGA</td>
</tr>
</tbody>
</table>

The char combustion was modelled as a one-step global reaction. A one-step global reaction was chosen due to its simplicity and the presence of only one distinguishable peak in
the derivative of thermogravimetric analysis (not shown here). The absence of other peaks or shoulders indicated that there were likely no intermediate devolatilization stages and that the only prominent reaction was the oxidation of char.

The char combustion rate is related to the partial pressure of oxygen and pore surface area\[^{[47]}\]. Eq. 15 is the reaction rate equation. Evolution of the pore surface area during combustion was described by a simple power law expression of the solid mass fraction\[^{[69]}\]. Since the reaction order with respect to oxygen is in the range of 0.8 to 1 for wood char, the value of the exponent m was taken equal to 1. The kinetic parameters of char oxidation are presented in Table 4.1.

$$R = A \exp(-E/R_oT) P_o^{m} Y_c^n$$ \hspace{1cm} (15)

Several models are available for the overall thermal conductivity inside the particle\[^{[70–72]}\]. It is important to take into account for the effect of macroscopic (1–10 \(\mu\)m) pore structure on thermal conductivity due to the differences in fiber orientation in different wood. A model developed by Kollmann and Cote\[^{[71,72]}\], which attributes the contribution of gas-phase, solid-phase, and radiation across the pore on the overall thermal conductivity by porosity, was used in this study. The weighting bridge-factor was used to account for the macroscopic pore structure, which can be expressed as the mixture of the direction parallel to and perpendicular to fibers. Thermal conductivities in the ideal directions (parallel/perpendicular) can be expressed in the same way as the electrical conductance of parallel and series circuits. The bridge factor for wood pellets was 0.33 \[^{[73]}\], and for wood logs 0.68 \[^{[74]}\].

Different methods are available to incorporate particle shrinkage in the particle model\[^{[38,39,44]}\]. It was assumed that the radial direction of shrinkage occurs uniformly over the particle during conversion. The temporary radius of the particle was simply calculated as the product of initial radius, final shrinkage ratio, and the temporary overall conversion. The final shrinkage ratio, defined as the ratio of the particle radius before and after the devolatilization, was experimentally determined in this study, which was around 0.75 for wood pellets and 0.8 for wood logs for devolatilization.

The effective diffusivity of gas species in the particle was calculated by considering parallel pore model \[^{[45]}\]. An identical diffusivity for all species was chosen to avoid more formal multicomponent diffusion calculation. The values and correlation of physical properties are listed in Table 4.2.
Table 4.2: Values and correlations for physical properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Correlation/value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular mass of gases, kg kmol^{-1}</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Reaction rate, kg m^{-3} s^{-1}</td>
<td>( \omega_j = A_j \exp(-E_j/RT)\rho_i )</td>
<td>-</td>
</tr>
<tr>
<td>Effective thermal conductivity, W m^{-1} K^{-1}</td>
<td>( \lambda_{\text{eff}} = \xi \lambda_1 + (1 - \xi) \lambda_\perp )</td>
<td>[75]</td>
</tr>
<tr>
<td>Effective thermal conductivity parallel to the fibre, W m^{-1} K^{-1}</td>
<td>( \lambda_{\parallel} = (1 - \phi) \lambda_{\text{gas}} + \phi (\lambda_\text{g} + \lambda_{\text{rad}}) )</td>
<td>[75]</td>
</tr>
<tr>
<td>Effective thermal conductivity perpendicular to the fibre, W m^{-1} K^{-1}</td>
<td>( \lambda_{\perp} = \left( \frac{1 - \phi}{\lambda_{\text{gas}} + \phi} \right)^{-1} \lambda_\text{g} )</td>
<td>[75]</td>
</tr>
<tr>
<td>Thermal conductivity of biomass parallel to the fibre, W m^{-1} K^{-1}</td>
<td>( \lambda_{\text{b,\parallel}} = 0.87 )</td>
<td>[76]</td>
</tr>
<tr>
<td>Thermal conductivity of biomass perpendicular to the fibre, W m^{-1} K^{-1}</td>
<td>( \lambda_{\text{b,\perp}} = 0.43 )</td>
<td>[76]</td>
</tr>
<tr>
<td>Thermal conductivity of char, W m^{-1} K^{-1}</td>
<td>( \lambda_{\text{c,\parallel}} = 1.47 + 0.00117 T )</td>
<td>[77]</td>
</tr>
<tr>
<td>Radiative heat transfer through the pore, W m^{-1} K^{-1}</td>
<td>( \lambda_{\text{rad}} = 13.5 \sigma d_{\text{por}} T^3 / \varepsilon )</td>
<td>[78]</td>
</tr>
<tr>
<td>Effective pore diameter, m</td>
<td>( d_{\text{por}} = \eta d_{\text{por},w} + (1 - \eta) d_{\text{por},c} )</td>
<td>[41]</td>
</tr>
<tr>
<td>Wood pore diameter, m</td>
<td>( d_{\text{por},w} = 5 \times 10^{-5} )</td>
<td>[41]</td>
</tr>
<tr>
<td>Char pore diameter, m</td>
<td>( d_{\text{por},c} = 1 \times 10^{-4} )</td>
<td>[41]</td>
</tr>
<tr>
<td>Emissivity, –</td>
<td>( \varepsilon = 0.90 )</td>
<td>[41]</td>
</tr>
<tr>
<td>Thermal conductivity of gas, W m^{-1} K^{-1}</td>
<td>( \lambda_\text{g} = 25.77 \times 10^{-3} )</td>
<td>[78]</td>
</tr>
<tr>
<td>Void fraction of solid, –</td>
<td>( \phi = 1 - \frac{\rho_\text{w}}{\rho_\text{c}} = \rho_\text{c} )</td>
<td>[75]</td>
</tr>
<tr>
<td>Intrinsic density of wood, kg m^{-3}</td>
<td>( \rho_\text{c} = 1450 )</td>
<td>[77]</td>
</tr>
<tr>
<td>Intrinsic density of char, kg m^{-3}</td>
<td>( \rho_\text{w} = 1950 )</td>
<td>[77]</td>
</tr>
<tr>
<td>Specific heat of wood, J kg^{-1} K^{-1}</td>
<td>( C_{\text{p}_\text{c}} = 1500 + T \times 10^{2} T^{-2} )</td>
<td>[44]</td>
</tr>
<tr>
<td>Specific heat of char, J kg^{-1} K^{-1}</td>
<td>( C_{\text{p}_\text{c}} = 1430 + 0.355 T - 7.32 \times 10^{2} T^{-2} )</td>
<td>[75]</td>
</tr>
<tr>
<td>Specific heat of tar, J kg^{-1} K^{-1}</td>
<td>( C_{\text{p}_\text{t}} = 1800 - 800 \exp(-0.0055 T) )</td>
<td>[75]</td>
</tr>
<tr>
<td>Specific heat of gases, J kg^{-1} K^{-1}</td>
<td>( C_{\text{p}_\text{g}} = 770 + 0.629 T + 0.000191 T^2 )</td>
<td>[75]</td>
</tr>
<tr>
<td>Effective permeability of solid, Darcy</td>
<td>( \phi_{\text{por}} = \eta \phi_\text{w} + (1 - \eta) \phi_\text{c} )</td>
<td>[68]</td>
</tr>
<tr>
<td>Permeability of wood, Darcy</td>
<td>( \phi_\text{w} = 1 )</td>
<td>[45]</td>
</tr>
<tr>
<td>Permeability of char, Darcy</td>
<td>( \phi_\text{c} = 100 )</td>
<td>[45]</td>
</tr>
<tr>
<td>Mass diffusivity m^{-2} s^{-1}</td>
<td>( D = D_{\text{AB}} (T/298)^{1.75} )</td>
<td>[45]</td>
</tr>
<tr>
<td>Molecular diffusivity of gases, m^{-2} s^{-1}</td>
<td>( D_{\text{eff}} = \phi D_\text{c} T (D_{\text{AB}} = 3 \times 10^{-5}) )</td>
<td>[45]</td>
</tr>
<tr>
<td>Dynamic Viscosity of gases, kg m^{-1} s^{-1}</td>
<td>( \mu = 4.847 \times 10^{-7} \eta^{0.64487} )</td>
<td>[39]</td>
</tr>
<tr>
<td>Nusselt number, –</td>
<td>( \text{Nu} = (0.376 \Re^{1/2} + 0.057 \Re^{2/3}) \Pr^{1/3} )</td>
<td>[79]</td>
</tr>
<tr>
<td></td>
<td>( + 0.92 \left[ \ln \left( \frac{7.4055}{\Re} \right) \right]^{-1/3} \Re^{1/3} \Pr^{1/3} )</td>
<td></td>
</tr>
</tbody>
</table>

A set of partial differential equations (PDEs), which consists of the conservation equations for solid, gas, momentum and energy inside the particles, was discretized on a staggered grid by the finite volume method. The particles were discretized into 200 control
volumes with constant radial distances, and time steps were chosen to satisfy the Courant-Friedrichs-Lewy condition for implicit method dependent on the particle size. A fully implicit scheme was applied for transient terms in the PDEs and diffusion/convection terms were discretized by the power law scheme. Discretized form of each differential equation was solved by using the TDMA (tri-diagonal matrix algorithm) method. Pressure-velocity coupled system of equations were solved by the SIMPLE (Semi-Implicit Method for Pressure Linked Equations) algorithm. The program was written in Matlab. Initial and boundary conditions are shown in Table 4.3.

Table 4.3: Initial and boundary conditions

<table>
<thead>
<tr>
<th>Initial conditions</th>
<th>Boundary conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r=0; ) ( r=0; )</td>
<td>( r=R; )</td>
</tr>
<tr>
<td>( \rho_w(r,0) = \rho_{wa} )</td>
<td>( \lambda_{eff} \frac{\partial T}{\partial r} = h_{eff}(T_e - T_s) )</td>
</tr>
<tr>
<td>( \rho_e(r,0) = 0 )</td>
<td>( D_{eff} \frac{\partial \rho}{\partial r} = h_m(A(Y_e - Y_s)) )</td>
</tr>
<tr>
<td>( T(r,0) = T_e )</td>
<td>( P_s = P_{atm} )</td>
</tr>
<tr>
<td>( P(r,0) = P_{atm} )</td>
<td>( U_e(r,0) = 0 )</td>
</tr>
<tr>
<td>( Y_i(r,0) = 1 )</td>
<td>( \ast h_{eff} = h_{conv} + \varepsilon \sigma (T_e + T_s)(T_e^4 + T_s^4) )</td>
</tr>
</tbody>
</table>

4.2 Reactor scale modelling

A fixed-bed combustion model by Gomez et al [80] was modified and used to study combustion of wood pellet in a packed bed. The model was two dimensional with the assumption of porous zone of the bed. Standard porous media CFD (computational fluid dynamics) code in ANSYS fluent was modified with different sub-models by using the user defined function (UDF) platform to account for solid phases. The main assumptions of the model are:

- Porous bed is a disperse media.
- Thermally thin spherical-equivalent particles are assumed in the bed.
- The particle density decreases during drying and devolatilization while the particle diameter shrinks during char oxidation.
- The rate of drying changes with temperature according to the Arrhenius law.
- Devolatilization can be approximated by three lumped reactions.
- The solid and gas phases exchange heat by both convection and radiation. The gases released by the solids are introduced in the gas phase at the same temperature as the solid phase.
- The gas mixture is incompressible and follows the ideal gas law.

The presence of solid phase in the packed bed influences the flow and, hence, the development of the flame. Commercially available CFD code for porous zone does not have the necessary sub-models to represent packed bed combustion in solid phase (e.g. solid
conversion, effect intra-particle mass and heat transfer on conversion, void fraction development). Hence, such sub-models were implemented to the CFD code through user defined functions, UDF, written in C++. The combustion chamber was divided into two separate zones. The first zone describes the bed where both solid and gas phases exist and their interaction was considered by the model described below. The second zone describes the freeboard, where only gas phase was modelled. In this model, six variables were externally defined to describe the properties of the solid phase: 1) temperature 2) the solid fraction 3) the moisture density 4) the dry biomass density 5) the char density 6) the particle characteristic volume. Table 4.4 shows governing equations for solid phase variables and their source terms are listed in Table 4.5.

### Table 4.4: Governing equations of solid phase variables

| Solid temperature | $\frac{\partial (\rho_s \rho_p T_s)}{\partial t} = \nabla(k_{s,eff} \nabla T_s) + S_s$ | (16) |
| Solid fraction | $\frac{\partial \varepsilon}{\partial t} = \frac{\omega_{c, char}}{\rho_p} \varepsilon_s$ | (17) |
| Third power of particle diameter | $\frac{\partial \rho_p}{\partial t} = \omega_{c, char} \frac{\partial \rho_p}{\partial t}$ | (18) |
| Moisture density | $\frac{\partial (\varepsilon_p \rho_{w, dry})}{\partial t} = -\omega_{m, char} \varepsilon_s$ | (19) |
| Dry wood density | $\frac{\partial (\varepsilon_p \rho_{w, dry})}{\partial t} = -\omega_{c, char} \varepsilon_s$ | (20) |
| Char density | $\frac{\partial (\varepsilon_p \rho_{c, char})}{\partial t} = (\omega_{c, char} - \omega_{c, char}) \varepsilon_s$ | (21) |
| Particle total density | $\rho_p = \rho_{m, char} + \rho_{w, dry} + \rho_{c, char}$ | (22) |
| Energy equation source | $S_s = S_{\text{react}} + S_{\text{conv}} + S_{\text{rad}} + S_{\text{loss}}$ | (23) |

### Table 4.5: Source terms for the solid phase governing equations

| Drying rate | $\omega_{m, char} = \rho_{m, char} A \exp \left(\frac{-E}{R T}\right)$ | (24) |
| Devolatilization rate | $\omega_{w, dry} = \rho_{w, dry} \sum_{i=1}^{N} \frac{A_i}{T_i} \exp \left(\frac{-E_i}{R T}\right)$ | (25) |
| Char consumption rate | $\omega_{c, char} = K_{g, glob} \alpha [O]_{M} + K_{g, glob} \alpha [CO]_{M} + K_{g, glob} \alpha [H_2O]_{M}$ | (27) |
| Global char constants | $K_{g, glob} = \frac{1}{1 - \frac{T_s}{T_{ref}}} K_{g, glob}^{\alpha_2} = \frac{1}{1 - \frac{T_s}{T_{ref}}} K_{g, glob}^{\alpha_2}$ | (28) |
| Char oxidation parameter | $\psi = \frac{2 + 4.3 \exp(-3390/ T_s)}{T_s}$ | (29) |
| Total reaction heat | $S_{\text{react}} = -\omega_{m, char} \varepsilon_s L_H \rho_{m, char} - \omega_{w, dry} \varepsilon_s L_H \rho_{w, dry} + S_{\text{char}} \varepsilon_s$ | (30) |
| Char reaction heat | $S_{\text{react}} = K_{g, glob} \alpha [O]_{M} [2(\psi - 1) \Delta H_{CO2} + 2(\psi - 1) \Delta H_{CO}] + K_{g, glob} \alpha [CO]_{M} \Delta H_{CO} + K_{g, glob} \alpha [H_2O]_{M} \Delta H_{CO}$ | (31) |
| Loss of energy from solid phase | $S_{\text{rxn}} = (\omega_{m, char} + \omega_{w, dry} \varepsilon_s + \omega_{c, char}) \varepsilon_s (C_p, T_s) t^{-\Delta t}$ | (32) |
The heat and mass exchange between phases was modelled in a formulation analogous to the experimental correlation of Wakao and Kaguei for the Nusselt and Sherwood number [86]. Equivalent diameter, a function of particle length and diameter, was considered as the characteristic length of the particle. As a result, mass and heat exchange between phases is
influenced by the particle shape and size. Detailed description about thermal conductivity, diffusivity and other model parameters can be found in Gomez et al., [80].

The radiative heat transfer was modelled with the discrete ordinate model (DOM) and was modified to account for the presence of solid phase in the model[80,87]. Standard CFD code solves a transport equation for radiation (RTE) and adds a source term in the gas phase. The effect of solid phases on RTE was included by modification of the solid phase absorption and scattering coefficients and adds one addition source term in the solid phase energy equation. The detailed description of this method is found in ref [80,87]. Eq. 37 shows the modified RTE considering both gas and solid phases. Eq. 38 and 39 shows the source terms for gas and solid phases energy equations, respectively.

\[
\begin{align*}
\nabla l(r,s) + \left(\alpha_{bs} + \alpha_{bd} + \sigma_{\text{stat}}^{\text{gas}} + \sigma_{\text{stat}}^{\text{sólida}}\right)l(r,s) \\
= \frac{a_{bs}n^2\sigma T_s^4}{\pi} + \frac{a_{bd}n^2\sigma T_s^4}{\pi} + \frac{\sigma_{\text{stat}}^{\text{gas}} + \sigma_{\text{stat}}^{\text{sólida}}}{4\pi} \int_{0}^{4\pi} l(r,s),\Phi(r,s)d\Omega \\
S_{\text{rad}}^{\text{gas}} = \int_{0}^{4\pi} \left(\alpha_{bs}l(r,s) - \frac{a_{bs}n^2\sigma T_s^4}{\pi}\right)d\Omega \\
S_{\text{rad}}^{\text{sólida}} = \int_{0}^{4\pi} \left(\alpha_{bd}l(r,s) - \frac{a_{bs}n^2\sigma T_s^4}{\pi}\right)d\Omega
\end{align*}
\]
Chapter 5

Results and discussion

5.1 Intrinsic reaction rate

Change in intrinsic reaction rate due to various factors is discussed in this section: (i) the effect of steam explosion (SE) on devolatilization rate; (ii) the effect of pelletizing on devolatilization rate; and (iii) the effect of devolatilization conditions on char oxidation rate.

Devolatilization experiments were carried out on grounded SE residue under chemically controlled condition in a TGA. To have a comprehensive view of change in reactivity due to pre-treatment of biomass, devolatilization temperatures at 90% of conversion ratio ($T_{90}$) was examined. It is an indicator of overall conversion of devolatilization process as listed in Table 5.1. Pre-treatment at 478 K made the biomass more resistant to thermal decomposition. However, increases in pre-treatment temperature to 493 K and 501 K showed reduction of the devolatilization temperature ($T_{90}$) of pre-treated biomass compared to untreated biomass.

### Table 5.1: Devolatilization temperature and DTG at 90% conversion

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<tr>
<td>Untreated Biomass</td>
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<td>762</td>
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<td>478</td>
<td>6</td>
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<td>501</td>
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Biomass consists of three major components which are cellulose, hemicellulose, and lignin. Due to inherent differences in structure of these components, it is possible to qualitatively identify characteristics of those components from their intensity and location in Derivative of thermogravimetric (DTG) [9]. The DTG distribution of pre-treated biomass at 478 K is shown as a function of temperature in Figure 5.1 with that of untreated biomass. Pre-treatment times were 6, 9 and 12 min. In every occasion, the highest peak was identified at around 643 K. This peak stands for decomposition of celluloses. A relatively broad region with some small shoulders was observed before the cellulose peak (645 K) in comparison with untreated biomass. This broadened region represents decomposition of transformed hemicelluloses.
Figure 5.1: Change of DTG distributions due to steam explosion (478 K; 6, 9 and 12 min), adopted from paper I.

The region before cellulose peak showed overall higher intensity of decomposition comparing to untreated biomass in every occasion. In addition, this region for pre-treated biomass shifted to lower temperature zone than that of untreated biomass. In general, hardwood hemicelluloses are mostly comprised of xylan (4-O-methylglucuronoxylans). Hemicellulose goes through depolymerization reaction during pre-treatment and reduces hemicelluloses to smaller molecular weight components which in turn exhibit sensitivity to low temperature of devolatilization.

The cellulose maximum peak intensity varied incoherently with increase of pre-treatment temperature. The peak intensities were found to be around 0.9 wt.%/K for the raw biomass, 0.5–0.56 wt.%/K for pre-treated biomass at 478 K, and 0.94–0.96 wt.%/K for pre-treated biomass at 501 K. Previous studies showed that cellulose decomposition of biomass was related to alkali metal content and crystallinity of biomass[32,89]. In this study, no relation was found between the cellulose decomposition rate and alkali metal or crystallinity of biomass (see paper I for more detail).

Significant alteration in the region beyond the cellulose peak was also observed in pre-treated residue. Peak intensity was observed to be higher than untreated biomass. When the pre-treatment temperature was further increased (not shown here), the region beyond cellulose peak showed a slight shift towards lower temperature. This shift in peak may suggest the formation of thermolabile chemical bond due to the increase of the severity of the process.
Next, thermogravimetric analyses were performed under chemically controlled atmosphere to examine if there was any chemical change in biomass during pelletization. Figure 5.2 shows DTG of wood powder from raw biomass, single die pellets and semi-industrial pellet. In every occasion, the highest peak was observed at around 360 °C, corresponding to cellulose decomposition. Peak intensities of ground pellets were slightly higher than that of raw biomass. Difference in DTG curves between ground pellets and raw biomass was negligible in the hemicellulose decomposition region (temperature range of 150 °C and 300 °C) and in the lignin decomposition region (temperature range of 350 °C to beyond 500 °C). These observations in the hemicellulose, cellulose and lignin decomposition region of DTG indicated that there were insignificant chemical changes in biomass due to pelletization.

Finally, it was investigated how devolatilization conditions affect intrinsic oxidation reactivity of char particles from wood pellet. Chars were prepared at different reactor temperatures (i.e. 973, 1073 and 1173 K) in an iTG, and intrinsic reactivity tests were performed with grounded char particles in a TGA at 10 K min⁻¹ with 10 vol % of O₂.

Figure 5.3a shows char conversion versus temperature for pellet chars at various reactor temperatures during char preparation. For the devolatilization temperature between 973 and 1073 K, char reactivity was not significantly affected. However, char produced at 1173 K was much less reactive than other pellet chars. The possible reasons are the secondary char formation from volatiles inside the particle or polymerization of char structure (annealing) during devolatilization, both of which decrease active sites of the particle. Figure 5.3b shows how particle size during devolatilization affects the intrinsic char reactivity. The intrinsic reaction rate was affected by the change of pellet diameter but the effect was small. In summary, the intrinsic reactivity of wood char was affected by both devolatilization temperature and particle diameter.
Figure 5.3 Comparison of intrinsic char oxidation a) produced at different reactor temperature during devolatilization, b) produced from different diameter of the pellets at reactor temperature of 1073 K, adopted from paper IV.
5.2 Apparent reaction rate of pelletized biomass

Two different approaches were used to understand the effect of pelletization on apparent reaction rate of a particle (i.e. pellet). The first approach was to experimentally investigate how pelletization conditions affect the combustion of a single wood pellet. In the second approach, a detailed numerical model was used to understand fuel conversion of wood pellet.

5.2.1 Effect of pelletizing conditions on single particle combustion

The effect of pelletizing conditions (i.e. temperature and moisture) upon combustion of a single wood pellet is shown in Figure 5.4. Pellets were produced at various die temperatures (i.e. 20, 100, 150 and 200 °C) with initial biomass moisture content of 12%. Time needed for char oxidation varied more significantly than that of flaming devolatilization. Char oxidation time significantly increased when pelletizing temperature was raised from 20 °C to 100 °C and from 150 °C to 200 °C. However, char oxidation time of pellets produced at the die temperature of 100 and 150 °C had negligible differences.

The combustion behaviour of thermally thick particle is controlled both by chemical and physical properties of fuel. DTG of wood powder from raw biomass, single die pellets and semi-industrial pellet showed insignificant changes in chemical composition of biomass section 5.1). Hence, difference in chemical property cannot account for the difference in char oxidation time. Density (one of the physical properties) is an important factor for fuel conversion [37]. Figure 5.5a shows char oxidation time standardized by the density of pellet (standardized char conversion time) vs. apparent density of pellet. Apparent density is calculated as the mass per unit volume of the pellet. The standardized char combustion time remained almost constant until the pellet density reach around 1200 kg/m$^3$. At the density of around 1200 kg/m$^3$, on the other hand, standardized char conversion time scattered between

![Figure 5.4: Comparison of the flaming devolatilization and char oxidation time for pellets with different pelletizing temperatures (i.e. 20, 100, 150 and 200 °C) where pellet were produced with 12 wt.% moisture in biomass, adopted from paper II.](image-url)
79 and 109 cm³/s/g. Figure 5.5b shows the relationship between pelletizing temperature and apparent density of pellets for different moistures in raw biomass (i.e. 1% and 12%). Apparent density of pellets increased with pelletizing temperature in the range 20–150 °C, but density hardly changed with further increase in temperature. Pelletizing temperature plays an important role in increase of pellet density through inter-particle bonding by allowing softening and flow of lignin. After reaching certain compaction level, an increase in pelletizing temperature did not affect pellet density significantly although char conversion time increased. At this compaction level, fuel conversion was affected by other physical properties than density.

![Figure 5.5: (a) Standardized char conversion time (cm³ s/g) vs. apparent pellet density and (b) apparent pellet density vs. pelletizing temperature, adopted from paper II.](image)

Three distinctions were observed when comparing the combustion behaviours of semi-industrial pellet with that of single die pellet. First, when standardized char conversion time of semi-industrial pellet was plotted along with single die pellet in Figure 5.5, they were in the region where the char combustion time was independent from the apparent density of single die pellets. Second, char conversion time of semi-industrial pellet was significantly longer than any single die pellets. Finally, semi-industrial pellets shrunk during devolatilization with flame while single die pellets swelled.
To examine the difference in particle bonding between semi-industrial and single die pellet (below density 1200 kg/m³), SEM images of semi-industrial pellet and single die pellet (pelletizing temperature at 100 °C with 12% moisture in biomass) were taken in cross section as shown in Figure 5.6. Particles in semi-industrial pellet were severely distorted and there was surface adhesion and fibre interlocking in tracheid. In addition to that, inter-particle bonding in radial direction of pellet was evident in semi-industrial pellet (see Figure 5.6a). On the other hand, particles in single die pellet lacked both surface adhesion in tracheid of a particle and inter-particle connectivity (see Figure 5.6b).

Biomass densification process can be separated into two different stages, i.e. particle arrangement and, deformation (elastic/plastic)[27,90–92]. The particle bonding nature observed from SEM images (Figure. 5.6) shows that both semi-industrial and single die pellets experienced plastic deformation. However, the degree of plastic deformation was higher in the semi-industrial than in single die pellet. The high degree of plastic deformation in the semi-industrial pellet was probably due to high pressure in industrial scale pelletizer as the aspect ratio of the industrial press is extremely high compared with single die pellet press [27]. Moreover, the lack of fibre adhesion and radial direction inter-particle connectivity in single die pellet is probably due to differences in biomass flow pattern. In a single die pelletizer, biomass particles flow along the direction of the piston. In contrary, in industrial scale pelletizer, biomass is compressed in layers and those layers of biomass travels gradually through a narrow neck of the die. This facilitates particles to bond to each other in radial
direction [93]. Therefore, due to the difference in pressure magnitude and biomass flow inter-particle bonding was weaker in single die pellet than semi-industrial pellet.

### 5.2.2 Effect of intra-particle transport phenomena on devolatilization of single wood pellet

A detailed model was used to investigate devolatilization and char oxidation characteristics of wood pellet. Conversion of wood log was also considered to illustrate difference in conversion behaviour between untreated biomass and wood pellet.

The results from the detailed particle model were compared to the experimental data to identify necessities of intra-particle convective heat transfer, heat of reaction, and shrinkage in devolatilization of wood pellet. Other forms of physical changes such as particle cracking and fragmentation were not considered due to its absence in experiments during devolatilization of wood pellet. Then, the thickness of the reaction zone was examined to identify if the assumption of a simplified model (i.e. shrinking core model assumption) is valid for wood pellet.

Figure 5.7 shows the comparison of experimental data to particle simulation with and without the consideration of convective transport of heat by the outflow gases inside the particle. The model results for wood pellet showed reasonable agreement with experiments with convective heat transfer while significant error was observed without convective heat transfer. In contrast, the intra-particle convective heat transfer was not an essential part of the particle model for wood logs. The difference between wood logs and pellets would be their anisotropic and isotropic natures. It can be speculated that volatile gases left wood logs only in the longitudinal direction while volatiles in wood pellets flowed in both radial and longitudinal directions. Therefore, relatively cold volatile gases cool down relatively hot char while they travel through the char layer to the particle surface in wood pellets.

A comparison of the model to experimental data with and without heat of reaction was made. Devolatilization of wood logs was represented well with endothermic reactions while devolatilization of wood pellets showed closest agreement with the thermal neutral approach. In our experiments, wood pellets showed slightly higher char yield both in experiments and simulations. Hence, it is highly likely that exothermic secondary reactions were responsible for the differences in char yield and heat of reactions between wood logs and pellets. It is reasonable because volatiles from wood logs leave particles in the longitudinal direction while volatiles from wood pellets diffuse in all directions.

Figure 5.8 shows the local reaction rate at various overall conversions for both wood logs and pellets. It can be observed that the progress of the reaction zone from the surface to the centre is thin in the early stage of conversion. This means that the SCM (as described in subsection 4.1.1) assumption would be a reasonable assumption to simplify the particle model. However, the reaction zone became relatively thick at the late stage of the conversion. For 14.5 mm wood logs, local reaction rate at the centre of the particle stayed below 25% of that at the reaction front when the overall conversion was 90%, while the number was 46% for 8 mm wood pellets. This implies that the SCM assumption may cause more significant error to wood pellets than it does to wood logs.
Figure 5.7: The effect of convective heat transfer by outflow of volatiles on time vs. residual mass curves at \( Tr = 1073 \) K. (a) Wood logs with the diameter of 14.5 mm, and (b) wood pellets with the diameter of 8 mm, adopted from paper III.
Figure 5.8: Profiles of local reaction rate of devolatilization within the particle at various overall conversions at \( Tr = 1173 \) K. (a) Wood log with the diameter of 14.5 mm, and (b) wood pellets with the diameter of 8 mm, adopted from paper III.

The results of the shrinking core model (SCM) were compared to the experimental results for validation. Figure 5.9 shows the residual mass of wood logs and pellets plotted over the reaction time of the particle. The SCM results agreed with the experimental data well at high reactor temperature with respect to the overall devolatilization time for all the examined samples. It is reasonable considering that high reactor temperature is favourable for the assumption of infinitely thin reaction zone. The shape of time to residual mass curve by the SCM was deviated from the experimental data although it is acceptable difference considering the degree of simplification. The model might improve its performance if the effect of initial heating period is considered. Comparing the particle types, the SCM results of wood logs agreed with the experimental data better than those for wood pellets.
Figure 5.9: The reaction time vs. residual mass curves during devolatilization as a comparison of the shrinking core model with experimental data. (a) wood logs, and (b) wood pellet, adopted from paper III.

5.2.3 Oxidation behaviour of a single wood pellet

Global devolatilization conditions may affect overall char reactivity of large wood particles not only by mass diffusion inside char particles but also by changing chemical property of char. Chars were produced at different reactor temperatures (i.e. 973, 1073 and 1173 K) at iTG and intrinsic reactivity test was performed on grounded char particles in a TGA at 10 K min⁻¹ with 10 kPa of O₂. The results showed that the intrinsic reactivity of wood char was affected by both devolatilization temperature and particle diameter. A particle model for char combustion was used to investigate how this change in intrinsic reaction rate...
impacts the prediction of apparent reaction rate of large wood particles. The particle model was validated using TGA data of time vs. residual mass at 1073 K (shown in appended paper). The model matched very well with the experimental data of wood pellets. About 99% of the pellet conversion was estimated properly by the particle model.

Figure 5.10 shows comparison of experiments and particle simulation for time vs. conversion, using original kinetic parameters and tortuosity. Original kinetic parameters were estimated on 8 mm wood pellet char pyrolyzed at 1073 K. The particle model showed reasonable agreement with experiments when the reactor temperature was 1173 K without modifying kinetic parameters or tortuosity. In other words, although the intrinsic reaction rate was influenced by the reactor temperatures, their effect on overall conversion of a large particle was limited when oxidation temperature is high. An additional parameter (i.e. tortuosity), rather than kinetic constants, was adjusted in order to fit the experimental data of char conversion with simulation result for the 6 mm particle (see Figure 5.10b). The tortuosity value was 1.5 for 8mm pellet while it was 1.35 for 6 mm pellet. It implies that the diffusional resistance was small in smaller pellet. This result implies that it is valid to use constant kinetic parameters for particle simulation of char combustion at different conditions although the difference in devolatilization conditions may vary resulting kinetic parameters.

Figure 5.11 shows the local char conversion and partial pressure of oxygen within the particle at various overall conversions. The data is shown for an 8mm wood pellet exposed at 973 and 1173 K. The char combustion was taking place throughout the particle at different overall conversions when the reactor temperature was 973 K. In fact, local char conversion increased nearly uniformly throughout the particle as the overall conversion increased. At the temperature of 1173 K, on the other hand, the reaction took place at the surface of the particle and progressed toward the particle centre as the local conversion shows. Local partial pressures of O2 showed that the oxygen could not reach the centre of particles at 1173 K while oxygen was present at the particle centre throughout the reaction at 973 K. It means that the reaction progressed in the manner of regime 2 (intra-particle diffusion control) phenomenologically.
Figure 5.10: Residual mass with time of wood a) at reactor temperature of 973 and 1173 K. b) 6 mm wood pellet at 1073 K, adopted from paper IV.
Figure 5.11: Profiles of (left) local conversion and (right) mass fraction of oxygen within the particle at various overall conversions at. (a) 973 K, (b) 1173 K, adopted from paper IV.
5.3 Combustion of wood pellet in reactor scale

Figure 5.12: Experimentally measured a) flame velocity b) conversion mass flux with bulk density of the bed, adopted from paper V.

Figure 5.12a shows relation between flame velocity and bulk densities of the bed at two different air flows. The flame velocity was experimentally measured as a correlation between two thermocouples and the time elapsed since the first one reaches 800 K until the second one is at the same temperature[80]. Flame velocity was increased with increase of the bulk density from 625 to 635 kg m\(^{-3}\) but flame velocity was less influenced by the bulk densities when it varied between 635 to 670 kg m\(^{-3}\).

The flame velocity was significantly affected by the increase of air flow rate between 635 to 670 kg/m\(^3\) of bulk densities. However, it was little affected by air flow rates when bed density was 625 kg/m\(^3\).
Figure 5.12b shows conversion mass flux as a function of bulk density of the bed. The conversion mass flux was estimated only between 10 to 90% of conversion. There was no systematic change in conversion mass flux when the bulk bed density varies. Air flow rate, on the other hand, affected the conversion mass flux significantly. It is likely due to the increase of mass transfer rate at high flow rate.

\[
\rho_{\text{bulk}} = 300 \text{ kg/m}^3 \quad \rho_{\text{bulk}} = 585 \text{ kg/m}^3 \quad \rho_{\text{bulk}} = 650 \text{ kg/m}^3
\]

Figure 5.13: Wood density contour in fuel bed at three different bulk densities. Simulation time was 1000 sec, adopted from paper V.

To investigate the effect of bed bulk density due to the change by particle density, numerical simulation was carried out at void fraction. Figure 5.13 shows the particle density in the bed at simulation time of 1000 seconds. It shows that the devolatilization front moves faster in low density fuel (e.g. \(\rho_{\text{bulk}} = 300 \text{ kg/m}^3\)) than in high density fuel (e.g. \(\rho_{\text{bulk}} = 585 \text{ kg/m}^3\)). It is likely due to enhanced heat transfer inside the bed from hot to cold part. In contrary, devolatilization front moves in an identical manner inside the bed in high density fuels (i.e. \(\rho_{\text{bulk}} = 585\) and \(650 \text{ kg/m}^3\)). There is more mass available in a cell-volume for high density than low density fuels. Energy required for heating up, drying and devolatilization is also higher in high density than low density fuels. As a consequence, the local temperature increase was delayed in high density. It reduces the heat transfer rate inside the bed from hot to cold part. Relatively large amount of gas, produced during drying and devolatilization, also makes the local gas mixture to be fuel rich. Therefore, lack of sufficient energy and inadequate air-fuel mixture delays the ignition of the volatiles from devolatilization.

There are some limitations in the present model that can introduce major uncertainties. The limitations are two dimensional representation of the reactor, no shrinkage of the bed, no movement of mass and energy in solid phase, no influence of particle movement on turbulence, incomprehensive devolatilization kinetic model and absence of proper definition of porosity distribution close to the wall. The effect of those limitations was obviously reflected on the estimation by the model. For instance, the CFD model underestimated the flame velocity. However, it managed to show a flame velocity and bulk density relationship which is similar to the previously published experimental data. This implies that the model can provide better qualitative than quantitative information. Further improvement on above mentioned limitations may also make the model quantitatively accurate.
Chapter 6

Conclusions

The chemical and physical properties of fuels are altered during different fuel preparation methods (i.e. pre-treatment and pelletizing). The objective of this thesis is to understand in what extent various chemical and physical properties of large wood particles affect the overall fuel conversion under the reaction condition similar to grate boilers and fluidized bed reactors. The findings are concluded in the following list.

- Implementation of steam explosion significantly altered the structure and devolatilization characteristics of biomass. The hemicellulose decomposition region shifted to the low temperature range due to the depolymerization caused by SE pre-treatment. The peak intensities of cellulose decreased at mild pre-treatment condition while they increased at severe conditions. Lignin reactivity also increased due to SE pre-treatment. However, severe pre-treatment condition resulted in reduction of lignin reactivity due to condensation and re-polymerization reactions. In summary, a higher pre-treatment temperature provided a more active biomass compared with milder pre-treatment conditions. Pelletization, on the other hand, does not affect either the chemical composition or intrinsic devolatilization reactivity of biomass.

- The influences of devolatilization conditions (devolatilization temperature and particle diameter) on both intrinsic and apparent reaction rates were investigated. The intrinsic char oxidation rate was influenced by both devolatilization temperature and particle diameter, but this change of intrinsic reaction rate had a limited effect on the apparent reaction rate estimation of a particle model.

- Pelletizing conditions affect the combustion time of a wood particle. Time required for single pellet combustion generally increased with both increase of pelletizing temperature and moisture content of the biomass. In addition, combustion behavior of single die pellets was significantly different than those produced in a pilot scale pelletizing plant (semi-industrial scale pellet). That difference was due to variation in physical properties of pellets (e.g. density, morphology).

- Detailed modeling of particle devolatilization indicates that different modeling strategies are required to model naturally formed (i.e. wood logs) biomass and pelletized biomass. The model for wood logs should exclude convective heat transfer by volatiles if the fibers align to longitude direction, while it is an important part in the models for pellets. Devolatilization of wood logs was expressed as endothermic reactions while the model results showed best agreement with experimental data of wood pellets when the heat of reaction was assumed to be zero, possibly due to the secondary reactions. At the examined reaction conditions, devolatilization of both wood pellets and logs occurred at a very thin reaction zone.

- A simplified model for devolatilization in thermally thick particles was developed based on the observations from the detailed modeling study with assumptions of so-
called the shrinking core model (SCM). It was found that the SCM results agreed better with the experimental data of wood logs than wood pellets at a high reactor temperature.

- The experimental observations suggested that conversion time did not change significantly by increasing temperature when the reactor temperature is above 1073 K. The reaction front became thinner at reactor temperatures above 1073 K.
- The experimental results at reactor scale indicated that the void fraction had a small effect on the conversion of a wood pellet bed. In contrary, the simulation results indicated that the apparent particle density significantly affected the flame velocity. It implies that apparent density of particles is an important parameter of bed combustion. On the other hand, the effect of air flow rate on the conversion of the wood pellet in a bed was equally important as the apparent particle density.

This thesis gave insight on how the change of chemical and physical properties in biomass fuel, due to pretreatment and pelletizing, affected the fuel conversion behavior. It also highlighted the importance of fuel conversion at particle scale. Special attention was required while modeling conversion for those chemically and physically altered fuels at particle scale. Future studies on these fuels should improve understanding about
- Pathways of intrinsic devolatilization reaction and its relation with reaction heat
- Fuel structural effect on apparent reaction rate (e.g. pore development) and
- Importance of meso-scale on conversion at macro-scale of fuel conversion
Chapter 7

References


Paper 1
1. Introduction

In recent time, wood pellet industry has experienced dramatic expansion in energy market at annual production of 73 million ton in 2009 [1]. The main barometers of the physical quality of wood pellets are hardness, specific weight, sensitivity to moisture and heating value [2–4]. Different approaches have been considered to improve the quality of the wood pellet, for example, torrefaction and fast pyrolysis. Those technologies are mostly in research and development phase and require further efforts on development and commercialization [5,6]. Recently steam explosion (SE) pretreatment, previously devoted to ethanol production and binderless panel production [7–9], has been brought into attention for improvement of wood pellet. SE pretreatment has been implemented for the production of wood pellet. This paper investigated changes in biomass structure due to implication of steam explosion process by its pyrolysis behavior/characteristics. Salix wood chip was treated by SE at different pretreatment conditions, and then pyrolysis characteristic was examined by thermogravimetric analyzer (TGA) at heating rate of 10 K/min. Both pyrolysis characteristics and structure of biomass were altered due to SE pretreatment. Hemichellulose decomposition region shifted to low temperature range due to the depolymerization caused by SE pretreatment. The peak intensities of cellulose decreased at mild pretreatment condition while they increased at severe conditions. Lignin reactivity also increased due to SE pretreatment. However, severity of pretreatment condition resulted in reduction of lignin reactivity due to condensation and re-polymerization reaction. In summary, higher pretreatment temperature provided more active biomass compared with milder pretreatment conditions.

Change of pyrolysis characteristics and structure of woody biomass due to steam explosion pretreatment

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Steam explosion (SE) pretreatment has been implemented for the production of wood pellet. This paper investigated changes in biomass structure due to implication of steam explosion process by its pyrolysis behavior/characteristics. Salix wood chip was treated by SE at different pretreatment conditions, and then pyrolysis characteristic was examined by thermogravimetric analyzer (TGA) at heating rate of 10 K/min. Both pyrolysis characteristics and structure of biomass were altered due to SE pretreatment. Hemichellulose decomposition region shifted to low temperature range due to the depolymerization caused by SE pretreatment. The peak intensities of cellulose decreased at mild pretreatment condition while they increased at severe conditions. Lignin reactivity also increased due to SE pretreatment. However, severity of pretreatment condition resulted in reduction of lignin reactivity due to condensation and re-polymerization reaction. In summary, higher pretreatment temperature provided more active biomass compared with milder pretreatment conditions.

Celluloses into solution [11]. Additionally, both cellulose and lignin are also altered depending on the severity of the process [12,13].

Pyrolysis is one of the major conversion steps during thermochemical conversion of solid fuels. Therefore, it is important to focus on the pyrolysis characteristics of SE treated biomass since variation in main components of biomass has significant effect on its reaction behavior. Despite a number of studies on thermochemical behavior of steam pretreated biomass has been conducted, most of them were performed on the residue which had gone through simultaneous saccharification and fermentation (SSF) [14–16]. In such studies, lignocelluloses structure was further modified due to SSF. A limited number of studies have been previously reported considering pyrolysis of SE residue [11,17,18]. Xu et al. [17] observed increase in char yield after pyrolysis for steam pretreated wool fiber residue. They associated this observation with removal of loose substances of biomass during steam explosion. Deepa et al. [18] observed slight change in degradation temperature of hemichellulose in SE pretreated banana fiber residue which was attributed to the presence of trace quantity of hemichellulose. Negro et al. [11] observed shift in lignin peak towards lower temperature for severe pretreated residue in comparison with the mildest condition. They suggested development of thermolabile chemical bonds in lignin when severity of pretreatment was high. Although those studies provide pyrolysis behavior of SE residue, no study was found which investigated detailed effect of process parameters of steam explosion (i.e. pretreatment temperature and time) on the pyrolysis characteristics of SE residue.

The aim of this research is to observe the effect of SE conditions on the reactivity of woody biomass during pyrolysis process. Structural
changes of biomass were examined to address the reason why reactivity changed due to SE. Salix chips were used as samples for SE pretreatment. Thereafter, thermogravimetric analysis with raw sample and pretreated residues was performed under pure nitrogen atmosphere.

2. Experimental

Short rotation willow (Salix) of chip size 2–10 mm was used for pretreatment experiment. The ultimate and proximate analysis of untreated biomass sample is shown in Table 1. The moisture content of fresh biomass was 46%. Wood was collected and chopped and stored in a plastic bag at 277 K prior to experiment. Eight SE experiments were performed on Salix wood chips using a laboratory scale reactor by varying two process parameters, temperature (Tp) and time (t). Three pretreatment temperatures were chosen: 478, 493 and 501 K. For pretreatment temperature of 478 K and 493 K, pretreatment time was chosen as 6 min, 9 min and 12 min. For 501 K, pretreatment time was set as 6 min and 12 min. The detailed description of test facility and experimental procedure is explained elsewhere [5,7]. The steam was used in saturated condition. After pretreatment, biomass was separated from liquid and dried in air to reduce moisture content.

Pyrolysis of SE residue was performed in a thermogravimetric analyzer (TG, PerkinElmer) under nitrogen atmosphere. The nitrogen flow rate was kept at around 300 ml min\(^{-1}\) at standard state. Prior to the experiments, samples were ground and size less than 0.125 mm was used to minimize intra-particle heat and mass transfer effect on the pyrolysis behavior. A sample weight of around 5 mg was used in every occasion and placed in a crucible. Initially, the biomass was heated to 373 K and kept for at least half an hour under the nitrogen atmosphere to remove all the moisture content from biomass. Afterwards, biomass sample was heated from 373 K to 1023 K at a heating rate of 10 K/min. The residual mass and sample temperature were recorded every 4 s. Residual mass ratio, derivation of thermogravimetry (DTG) and conversion ratio are represented by following equation:

\[
\text{Residual mass ratio} \, \alpha = \frac{m_f}{m_i} \tag{1}
\]

Derivation of thermogravimetry DTG = \(\frac{da}{dT}\)

Conversion ratio \(X = \frac{m_f-m_t}{m_i-m_m}\) \tag{3}

X-Ray diffraction (XRD) of both untreated and pretreated biomass was carried out using a diffractometer (Siemens, D 5000), with monochromatic Cu K\(_\alpha\) radiation (\(\lambda = 0.154180 \text{ nm}\)), generated at 35 kV and 40 mA. The diffracted intensity was measured in a 2\(\theta\) range between 10\(^\circ\) and 30\(^\circ\) for every 0.02\(^\circ\).

To confirm the repeatability in experimental measurement, experiments of both TGA and XRD were performed repeatedly.

3. Results and discussions

3.1. Effect of SE condition on the reactivity of residue

To have comprehensive view of change in reactivity by pretreatment of biomass, pyrolysis temperatures at different conversion ratios were examined. In previous studies [19], temperature at 50% \(T_{50}\) of conversion ratio was used to describe pyrolysis reactivity where lower \(T_{50}\) temperature indicates faster decomposition of the biomass. In this study, pyrolysis temperatures at three different conversion ratios, 10%, 50%, and 90%, were used as listed in Table 2 with their corresponding weight loss rate.

Pretreatment lowered initial decomposition temperature \(T_{50}\) that is attributed to modified structure and breakdown of hemicelluloses from biomass as discussed later. However, almost no change in reaction intensity (wt.%/K) was observed at 100% of conversion ratio for pretreated materials. It indicates the increased reactivity of pretreated biomass since the equivalent reaction intensity was observed at lower temperature. No significant alteration in \(T_{90}\) was observed in pretreated residue although pretreatment decreased the corresponding reaction intensity (wt.%/K) when pretreatment temperature was 478 K. When pretreatment temperature was further increased to 493 K and 501 K, reaction intensity was observed to increase significantly. Temperature at 90% of conversion ratio \(T_{90}\), which is an indication of overall conversion of pyrolysis process, showed that pretreatment at 478 K made the biomass more resistance to thermal decomposition. However, further increase in pretreatment temperature to 493 K and 501 K showed the equivalent temperature \(T_{90}\) of pretreated biomass compared to untreated biomass.

3.2. Pyrolysis characteristics of untreated biomass

Biomass consists of three major components which are cellulose, hemicellulose, and lignin. It has been recognized that those components can be characterized by means of derivative thermogravimetry (DTG) [19,20]. In other terms, due to inherent difference in structure of those components, it is possible to qualitatively identify characteristics of those components from their intensity and location in DTG. In general, hemicellulose decomposition occurs within the range of 423 to 623 K, cellulose decomposes within the range of 623 to 773 K, and lignin decomposition ranges from 623 K to beyond 773 K [20].

Residual mass ratio and DTG of untreated biomass against temperature are shown in Fig. 1. DTG distribution showed different

### Table 1
Proximate and ultimate analysis of untreated biomass, dry basis.

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
<th>Ultimate analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Carbon</td>
<td>10.4</td>
<td>Carbon (C) 40.40</td>
</tr>
<tr>
<td>Volatile</td>
<td>81.20</td>
<td>Hydrogen (H) 0.10</td>
</tr>
<tr>
<td>Ash</td>
<td>2.40</td>
<td>Oxygen (O) 41.80</td>
</tr>
<tr>
<td>Nitrogen (N)</td>
<td>0.29</td>
<td>Sulfur (S) 0.043</td>
</tr>
</tbody>
</table>

### Table 2
Pyrolysis temperature and weight loss at three different conversion ratios, 10%, 50%, and 90%.

<table>
<thead>
<tr>
<th>Pretreatment conditions</th>
<th>Conversion ratio (%)</th>
<th>Temperature (K)</th>
<th>Time (min)</th>
<th>T10 (%)</th>
<th>T50 (%)</th>
<th>T90 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Biomass</td>
<td></td>
<td>478</td>
<td>6</td>
<td>530</td>
<td>0.12</td>
<td>639</td>
</tr>
<tr>
<td></td>
<td></td>
<td>493</td>
<td>6</td>
<td>514</td>
<td>0.10</td>
<td>641</td>
</tr>
<tr>
<td></td>
<td></td>
<td>501</td>
<td>6</td>
<td>514</td>
<td>0.13</td>
<td>634</td>
</tr>
</tbody>
</table>
peaks at different temperatures. The main peak appeared at around 657 K that corresponds to decomposition of cellulose. Before cellulose peak (657 K), no definite peak was observed. Moreover, cellulose peak was appeared unsymmetrical. According to Bridgeman [21], hemicellulose content in willow is around 14%. Therefore, it can be interpreted that low amount of hemicelluloses in Salix makes hemicelluloses decomposition to merge with cellulose decomposition, hence, attributed to the unsymmetrical shape at that region. Beyond 657 K, several broaden shoulders appeared at different temperatures. Those shoulders can be attributed to deformation of lignin components. This reflects that lignin of Salix decomposed in different steps during pyrolysis rather than having uniform decomposition over temperature. Upon observation, it should be pointed out that DTG of untreated Salix revealed a different zone of decomposition for different biomass components. Therefore, it is possible to qualitatively justify changes in lignocelluloses’ structure and their corresponding pyrolysis characteristics.

3.3. Change of biomass structure and pyrolysis characteristics by pretreatment

DTG distribution against temperature for pretreated biomass at 478 K is shown in Fig. 2 with that of untreated biomass. Pretreatment times were 6, 9 and 12 min. In every occasion, the highest peak was identified at around 643 K. This peak stands for decomposition of celluloses. When pretreatment time was 6 min, a relatively broad region with some small shoulders was observed before the cellulose peak (645 K) in comparison with untreated biomass. That broadened region represents decomposition of transformed hemicelluloses. When pretreated residue produced at 478 K and 9 min was tested, several peaks were observed before cellulose peak with a notable peak at 425 K. Further increase of pretreatment time to 12 min showed only one peak at 426 K.

Fig. 3 provides DTG distribution against temperature of pretreated residue when pretreatment temperature was 493 K for residence time 6, 9 and 12 min with that of untreated material. Similar to previous case (Fig. 2), a peak at around 423 K was observed for pretreatment time 6 and 9 min before cellulose peak (643 K). However, further increment of pretreatment time to 12 min did not show any definite peak before cellulose peak. When pretreatment temperature was further increased to 501 K (Fig. 4), peak at around 423 K was observed for the case where pretreatment time was 6 min. However, no such peak in that region was observed when pretreatment time was 12 min.

The region before cellulose peak in every occasion showed overall higher intensity of decomposition comparing to untreated biomass. In addition, this region for pretreated biomass shifted to lower
temperature zone than that of untreated biomass. In general, hardwood hemicelluloses are mostly comprised of xylan (4-O-methylglucuronoxylans) [12]. This component goes through depolymerization reaction and reduces hemicelluloses to smaller molecular weight components which in turn exhibit sensitivity to low temperature zone of pyrolysis. The observed peak at around 423 K (Figs. 2, 3 and 4) can be attributed to the cross-linking reactions of liquefied D-xylose. D-xylose is the major monosaccharide of xylan and its melting point varies from 417 K to 424 K [22,23]. With the increment of pretreatment conditions, pretreatment temperature and time, hemicellulose can be hydrolyzed to monosaccharide. It can be thought that D-xylose molecules that had been distributed to the wood structure came into contact with other molecules after melting, and the cross-linking reactions occurred. Further increment of both pretreatment temperature and time (i.e. 493 K and 12 min) resulted in the disappearance of peak around 423 K, which indicates the destruction of monomerized xylose to smaller molecules.

Cellulose maximum peak intensity varied incoherently with increase of pretreatment temperature. The peak intensities were found to be around 0.9 wt.%/K for the raw biomass, 0.5–0.56 wt.%/K for pretreated biomass at 478 K, 0.95–1.03 wt.%/K for pretreated biomass at 493 K, and 0.94–0.96 wt.%/K for pretreated biomass at 501 K. Previous studies showed that cellulose decomposition of biomass was related to alkali metal content and crystallinity of biomass [20,24]. Higher alkali metal content tends to reduce cellulose content with increase of pretreatment temperature. Therefore, no certain dependency of alkali metal on cellulose decomposition rate and temperature can be correlated.

To examine the effect of crystallinity on cellulose decomposition, X-ray diffraction (XRD) analysis was performed on three samples including untreated biomass. Fig. 5 represents diffraction pattern with 2θ values at around 15° and 22° for untreated biomass, which represents 101 and 002 lattice spacing in cellulose of wood [25]. Those peaks became narrow when biomass was pretreated at 478 K for 12 min. XRD pattern of pretreated residue produced at 501 K and 12 min exhibited similar narrow and intense peak at those positions. These observations suggest increase of crystallinity in pretreated biomass. Similar observation was made by Yamashiki and coworkers [26] for steam exploded residue. They explained that high temperature water penetrated to the Paracrystalline and amorphous part of cellulose, and recrystallised the Paracrystalline by releasing free water molecule of wood cell. However, increased crystallinity does not show any dependency on cellulose decomposition. Ye and coworkers [27] observed increase in crystallinity in steam exploded biomass while they also observed reduction in mean hydrogen bond strength and degree of polymerization in steam pretreated biomass. Hence, nature of cellulose peak intensity in DTG might be also related to the strength of hydrogen bond and degree of polymerization. However, further detailed research is required to explain this nature of cellulose decomposition of pretreated biomass. Although both pretreatment parameters, temperature and time, played significant roles in alteration of hemicelluloses, the effect of pretreatment temperature was more transparent on the thermal decomposition of cellulose under the examined conditions.

Significant alteration in the region beyond cellulose peak was also observed in pretreated residue. For pretreatment temperature of 478 K and 6 min (Fig. 2), lignin decomposed gradually after cellulose peak. In every occasion, peak intensity was observed to be higher than untreated biomass. In addition, a definite shoulder was observed at around 943 K for each pretreated samples. When pretreatment temperature was further increased (i.e. 493 K and 501 K), in Figs. 3 and 4, the region beyond cellulose peak showed a slight shift towards lower temperature. This shift in peak can be suggested to the

![Fig. 5. XRD patterns of raw biomass and steam exploded biomass (478 K and 501 K; 12 min).](image)

![Fig. 6. Repeatability of DTG curves: (a) 478 K; 12 min and (b) 501 K; 12 min.](image)
formation of thermobond. The chemical bond due to increase of the severity of the process. However, intensity of those peaks reduced with the increase of pretreatment temperature from 478 K to 501 K.

Reduction in intensity of the lignin peak during increase of pretreatment temperature can be attributed to the increase of Kason lignin in the biomass due to condensation and depolymerization reaction between decomposition product of hemicellulose and lignin. According to Chau and Wayman [28], at drastic pretreatment condition, some reactive components from hemicellulose such as furfural may react with lignin and increase fraction of acid insoluble lignin in biomass. Ramons et al. [12] mentioned that at severe condition, lignin structure can be severely modified and it can increase the apparent yield of lignin. Hence, during thermochemical conversion, higher lignin content can lower the reactivity of biomass due to softening, melting and carbonization of lignin and partial blocking of the pores of the char [29].

3.4. Reproducibility of experiments

To observe consistency in measurement, the experiments of both TG and XRD were repeated. Fig. 6 shows the example of reproducibility tests for TG. It shows less than 5 K of temperature error and less than 0.05 wt.%/K of error in the peak intensity. Table 3 shows the reproducibility of XRD experiments. Since the peak shape is affected by relative magnitude, crystallinity was calculated based on Eq. (4).

\[
\alpha = \frac{I_{002} - I_{002i}}{I_{002i}} \quad (4)
\]

where \(I_{002}\) and \(I_{002i}\) Represents intensity at 002 lattice spacing in cellulose and amorphous region at 2θ = 16°. It shows good agreement between different experimental cases.

4. Conclusions

Implementation of steam explosion significantly altered the structure and pyrolysis characteristics of biomass. At pretreatment temperature of 478 K, biomass became more resistant to thermal decomposition. While hemicellulose decomposition rate was increased, cellulose decomposition peak intensity was reduced significantly in pretreated residue in comparison with untreated biomass. Likewise, pretreatment also enhanced thermal stability of lignin at this pretreatment condition. Increment in pretreatment temperature to 493 K resulted in the increase of cellulose decomposition peak intensity. On the other hand, lignin decomposition rate reduced at severe conditions due to apparent increase of lignin. However, lignin content of pretreated biomass under severe conditions decomposed earlier than that of pretreated biomass under mild conditions. Hence, severe pretreatment condition seems to produce more reactive biomass compared with mild pretreatment conditions.

In addition, increase in cellulose crystallinity was observed in pretreated residue. However, no clear dependency of cellulose peak intensity on either crystallinity or alkali metal of biomass was observed. Therefore, further detailed research is required to explain this nature of cellulose peak intensity.


Paper II
Effect of pelletizing conditions on combustion behaviour of single wood pellet

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Highlights

Effect of pelletizing conditions on combustion of single wood pellet was investigated.
- Time required for single pellet combustion was affected by pelletizing conditions.
- Combustion behaviour of single die pellets was different than those from pilot scale pelletizer.

Abstract

This paper presents how pelletizing die temperature and moisture content affect combustion behaviour of single wood pellet. Pine wood particles with two different moisture contents (i.e. 1 wt.% and 12 wt.%) were pelletized in a laboratory-scale single pelletizer (single die pellets) at die temperature of 20, 100, 150 and 200 °C. The pellets were combusted in a laboratory scale furnace at 800 °C. Time required for single pellet combustion generally increased with both increase of pelletizing temperature and moisture content of biomass. In addition, combustion behaviour of single die pellets was significantly different than those produced in a pilot scale pelletizing plant (semi-industrial scale pellet). That difference was due to variation in physical properties of pellets (e.g. density, and morphology).

1. Introduction

Wood pellet industry is an important part of bioenergy industry at annual production of 14 million tons in 2010. The production capacity of pellet varies among the largest producers, North America and Scandinavia, and emerging producing countries for example Australia, South Africa and South America [1]. The wood pellet market has been growing steadily worldwide driven by industrial and residential consumers for heat and power production [2]. The performance of conversion units for heat and power production depends on the optimal design of the chemical reactors (e.g. combustors and gasifiers) [3]. Understanding fundamentals of fuel particle conversion is of great importance in the optimization of reactor performances.

Phenomena that occur during biomass pellet production are complex. Biomass particles are compacted under pressure to form densified pellet. Under mechanical pressure, biomass particles first rearrange in a pelletizing die to remove air in the gaps among particles, and then deform to remove air in intra-particle pores. At the same time, the temperature of the biomass particles increases due to the friction between biomass and the pellet die during the forced passage through press channel. Elevated temperature in wet biomass activates the natural binders in particles and makes physical bonds with neighbour particles to form a pellet. Several pelletizing conditions for biomass densification process have important roles on both process efficiency and the quality of product. For example, high pelletizing temperature and low moisture content in biomass have shown to enhance the pellet strength and density, and also reduced the pelletizing energy consumption [4].

Fig. 1 shows the schematic presentation of different factors affecting fuel conversion of pellets. We defined operational parameters as the parameters pellet producers can control directly (drying temperature etc.). Pelletizing conditions, which are the local conditions of biomass particles at the moment of pelletization and not able to be observed directly, are largely affected by these operation parameters. Chemical and physical properties of biomass...
pellet are affected both by these factors (see Fig. 1). Chemical properties (e.g. organic and inorganic composition) are determined mainly by the choice of feedstock, but they might change during and after pelletization process as well [5,6]. On the other hand, physical properties (density, thermal conductivity, permeability) are affected by pelletizing conditions. For instance, pelletizing conditions (i.e. pressure, temperature and moisture) significantly affect pellet density and thermal conductivity due to compression of vacuole in wood particles as well as improved solid–solid contacts.

Combustion behaviour of pellets is significantly affected both by chemical and physical properties (Fig. 1). Chemical and physical properties of the fuel determine heat and mass transfer rate, reaction path and kinetics [7]. Effect of chemical property (i.e. raw material composition) and particle size distribution of biomass sample on single fuel pellet combustion was investigated by Erlich et al., Bergström et al. and Rhén et al. [8–10] although the results have not been validated with full scale pellets. Combustion time of single pellet was significantly affected by biomass composition while the role of particle size distribution in pellets was insignificant. No study was found on the effect of pelletizing temperature and biomass moisture content on single pellet combustion.

Modeling of detailed reactor scale combustion is computationally expensive process due to presence of multiple particles. Simplification of particle conversion model is often practiced to overcome problem associated to the time of computation. Study of single particle combustion can provide information to modelers to choose most important phenomena to take into consideration and to discard least important one while modeling combustion process. The aim of this study is to investigate the effect of pelletizing conditions (i.e. pelletizing die temperature and moisture content) on fuel conversion behaviour of single wood pellet combustion.

2. Experimental

2.1. Sample preparation

Pine sample was ground for pellet production. The particle size distribution of the ground sample from sieve analyses is presented in Table 1. A cylindrical die with diameter of 8 mm was used to produce pellet in a piston press at the die temperatures of 20, 100, 150 and 200°C. Moisture contents of raw biomass were 12 wt.% and 1 wt.%. A cylindrical die was heated to desired temperature. When the temperature of the die reached target temperature, around 600 mg of biomass was placed in the die and compressed at 0.5 mm/s to 398 MPa with a computer controlled hydraulic press. When pressure reached 398 MPa, the sample was held for 10 s and then released. Later on, pellet was pressed out of the die. To compare single die pellets with pellet from semi-industrial scale plants, the same raw biomass was used to produce pellets in a semi-industrial roller die type pelletizer. The detailed descriptions of the pelletizing processes can be found elsewhere [11,12].

2.2. Experimental procedure

A laboratory scale furnace was used to determine the combustion characteristics of single pellet. Similar equipment has been used for previously published single pellet combustion studies [8–10], but this furnace was also equipped with an analytical balance enabling using it as a macro-TGA. Fig. 2 presents schematic diagram of the furnace. The furnace was heated by PID controlled electrical wall heaters to reaction temperature prior to the experiments. Pre-heated air was continuously supplied to the furnace from the bottom through a distribution plate. The sample was hung in a Pt-basket connected to an analytical balance (±1 mg) with a steel wire, and kept in a cooling chamber with nitrogen flow before the and after the experiment. The cooling chamber was isolated from the radiation of the furnace by a slide hatch. Experiments started when the sample was inserted into the furnace from the cooling chamber using a pneumatic elevator device. The furnace had an observation window in front to record the
Combustion experiments were performed at the furnace temperature of 800 °C with 9 L/min of air flow at standard state. To examine the property of char, some experiments were terminated when the flaming pyrolysis completed (i.e. when the visible flame disappeared), and char sample was quenched with nitrogen flow in the cooling chamber. Morphological structure of both pellet and char samples were analysed by an Environmental Scanning Electron Microscope (ESEM) by Phillips (model XL30).

In addition to combustion of single pellet, thermogravimetric analysis (TGA) was performed on ground samples. Raw and pelletized biomass samples were ground to the particle size less than 0.1 mm for thermogravimetric analysis (TGA) to identify any chemical compositional changes of biomass due to thermal degradation during the pelletization process. TGA was performed under nitrogen atmosphere with nitrogen flow rate of 50 ml/min at standard state. The TGA was performed in a Q5000IR, TA Instruments, USA. Around 5 mg of sample was used for all TGA experiments. Initially, biomass samples were heated to 105 °C and kept for half an hour to remove moisture from biomass. Afterwards biomass samples were heated from 105 °C to 800 °C at a heating rate of 10 °C/min. The heating rate of 10 °C/min was chosen to ensure that the biomass particles were pyrolyzed under chemically controlled conditions.

### Table 1

<table>
<thead>
<tr>
<th>Particle size (mm)</th>
<th>&lt;0.25</th>
<th>0.25–0.5</th>
<th>0.5–1.0</th>
<th>1.0–1.4</th>
<th>1.4–2.0</th>
<th>2.0–2.8</th>
<th>2.8–3.15</th>
<th>&gt;3.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass fraction (wt.%)</td>
<td>10.6</td>
<td>16.2</td>
<td>44.3</td>
<td>23.3</td>
<td>5.1</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

3. Results and discussion

This section summarizes the effect of pelletizing die temperature and initial moisture content of biomass on fuel pellet conversion.

The combustion of single pellet was characterized into two regimes: flaming pyrolysis and char conversion. Flaming pyrolysis was considered from the moment when the pellet was inserted inside the furnace to the moment when the flame around the pellet disappeared. Therefore, it actually includes heating, drying, pyrolysis before ignition and flaming pyrolysis. The char conversion was considered from the moment when the flame around the pellet disappeared till the moment glowing of the char stopped. Fig. 3 shows a typical mass loss history of single pellet together with visual appearance at each regime. Major part of mass was released from the pellet during flaming pyrolysis with combustion of pyrolysis products in gas-phase. The char particle glowed during char conversion, which shows that combustion was taking place in the char particle.

Fig. 4 shows times for flaming pyrolysis and char conversion of single pellet, produced at various die temperatures (i.e. 20, 100, 150 and 200 °C) with initial moisture content of 12% (Fig. 4a) and 1% (Fig. 4b) in biomass. Time for char conversion varied more significantly than that of flaming pyrolysis. Char conversion time of pellets produced with oven-dried biomass i.e. 1% moisture (Fig. 4b) was significantly lower than pellets that were produced with wet biomass (12% moisture) (Fig. 4a). However, there was a similar trend in char conversion time against the change in mould temperature between pellets produced with oven-dried and wet biomass. In both moisture cases, char conversion time significantly increased when pelletizing temperature was raised from 20 °C to 100 °C and from 150 °C to 200 °C. However, char conversion time of pellets produced at the die temperature of 100 and 150 °C had negligible differences.

Pellets produced from biomass with 12% moisture at different pelletizing temperatures have different final moisture contents. The moisture content was in the range 2–6 wt.% [9]. To examine if moisture content of pellets have contributed to those differences in total conversion, pellets produced with wet biomass (12% moisture) was dried in an oven at 105 °C, and then combusted in the laboratory-scale furnace. Fig. 4c shows conversion times for those dried pellets. Char conversion time of dried pellets (Fig. 4c)
was identical to un-dried pellets (Fig. 4a) at the pelletizing temperature of 20, 100 and 150 °C. However, small difference in char conversion time was observed for pellet produced at 200 °C. Char conversion time of dried pellets increased significantly between the pelletizing temperature of 20 and 100 °C as well as between 150 and 200 °C pellets, which is in similar qualitative trend with un-dried pellets. In this study, moisture content in pellet did not influence its conversion time significantly. Therefore, the difference in conversion time between pellets from wet biomass (12 wt.% moisture; Fig. 4a) and dried biomass (1 wt.% moisture; Fig. 4b) can be explained by different pelletizing mechanism.

Combustion behaviour of thermally thick particle is controlled both by chemical and physical properties of fuel as was discussed previously.

First, thermogravimetric analyses were performed under chemically controlled atmosphere to examine if there was any chemical change in biomass during pelletization. Fig. 5 shows DTG of wood powder from raw biomass, single die pellets and semi-industrial pellets. In every occasion, the highest peak was observed at around 360 °C, corresponding to cellulose decomposition [13]. Peak intensities of ground pellets were slightly higher than that of raw biomass. Difference in DTG curves between ground pellets and raw biomass was negligible in the hemicellulose decomposition region (temperature range of 150 °C and 300 °C) and in the lignin decomposition region (temperature range of 350 °C to beyond 500 °C). These observations in the hemicellulose, cellulose and lignin decomposition region of DTG indicated that there was insignificant chemical change in biomass due to pelletization. Hence, difference in chemical property cannot account for the difference in char conversion time. Density (one of physical properties) is an important factor for fuel conversion [10]. Fig. 6a shows char conversion time standardized by the density of pellet (standardized char conversion time) vs. apparent density of pellet. Apparent density is calculated as the mass per unit volume of the pellet. The standardized char combustion time remained almost constant until pellet density reach around 1200 kg/m³. At the density of around 1200 kg/m³, on the other hand, standardized char conversion time scattered between 79 and 109 cm³/s/g. Fig. 6b shows relationship between pelletizing temperature and apparent density of pellets for different moistures in raw biomass (i.e. 12% and 1%). Apparent density of pellets increased with pelletizing temperature in the range 20–150 °C, but density hardly changed with further increase in temperature. Pelletizing temperature plays an important role in increase of pellet density through inter-particle bonding by allowing softening and flow of lignin (as discussed later). After reaching certain compaction level, increase in pelletizing temperature did not affect pellet density significantly although char conversion time increased. At this compaction level, fuel conversion was affected by other physical properties than density.

Three distinctions were observed when comparing combustion behaviour of semi-industrial pellet with that of single die pellet.

![Fig. 4. Comparison of the flaming pyrolysis and char oxidation time for pellets with different pelletizing temperatures (i.e. 20, 100, 150 and 200 °C) where pellet were (a) produced with 12 wt.% moisture in biomass, (b) produced with 1 wt.% moisture in biomass and (c) dried in an oven.](image1)

![Fig. 5. Comparison of DTG distribution among raw biomass, biomass from single die and semi-industrial pellets.](image2)

![Fig. 6. (a) Standardized char conversion time (cm³/s/g) vs. apparent pellet density and (b) apparent pellet density vs. pelletizing temperature.](image3)
First, when standardized char conversion time of semi-industrial pellet was plotted along with single die pellet in Fig. 6a, they were in the region where char combustion time was independent from apparent density of single die pellets. Second, char conversion time of semi-industrial pellet was significantly higher than any single die pellets. Finally, semi-industrial pellets shrank during flaming pyrolysis while single die pellets swelled. Fig. 7 shows SEM images of char from semi-industrial and single die pellet. Particles in semi-industrial char were tightly connected to each other after flaming pyrolysis (Fig. 7a) while char particles in single die pellet had loose connections among particles. It means that the bonding mechanism of semi-industrial pellets may be somewhat different from single die pellets even though the apparent density of semi-industrial pellet was similar to that of some single die pellets.

To examine the difference in particle bonding between semi-industrial and single die pellet (below density 1200 kg/m$^3$), SEM images of semi-industrial pellet and single die pellet (pelletizing temperature at 100°C with 12% moisture in biomass) were taken in cross section as shown in Fig. 8 (Fig. 8a: semi-industrial pellet; Fig. 8b: single die pellet). Particles in semi-industrial pellet were severely distorted and there was surface adhesion and fibre inter-locking in tracheid. In addition to that, inter-particle bonding in radial direction of pellet was evident in semi-industrial pellet (see Fig. 8a). On the other hand, particles in single die pellet lacked both surface adhesion in tracheid of a particle and inter particle connectivity (see Fig. 8b).

Biomass densification process can be separated into two different stages, i.e. particle arrangement, deformation (elastic/plastic) [14–19]. Particle bonding nature observed from SEM images (Fig. 8) shows that both semi-industrial and single die pellets experienced plastic deformation. However, the degree of plastic deformation was higher in semi-industrial than in single die pellet. High degree of plastic deformation in semi-industrial pellet was probably due to high pressure in industrial scale pelletizer as the aspect ratio of the industrial press is extremely high compared with single die pellet press [14]. In fact, it is impractical to achieve such high pressure in single die pellet press due to practical limitations [14,17]. Moreover, lack of fibre adhesion and radial direction inter-particle connectivity in single die pellet is probably due to difference in biomass flow pattern. In single die pelletizer, biomass particle flows along the direction of the piston. In contrary, in industrial scale pelletizer, biomass is compressed in layers and those layers of biomass travels gradually through a narrow neck of the die. This facilitates particles to bond to each other in radial direction [20].

Pelletizing temperature plays a key role in inter-particle bonding by softening and flow of lignin and by wetting of the fibre wall. However, the magnitude of pressure and biomass flow mechanism is also essential for inter-particle bonding [14]. This might be the reason why combustion behaviour of single die pellets with the density of around 1200 kg/m$^3$ was different than semi-industrial pellet i.e. inter-particle bonding was weaker in single die pellet than semi-industrial pellet.

4. Conclusions

We examined the effect of pelletizing conditions on fuel conversion behaviour by combusting single pine pellet in a laboratory-scale combustion furnace.
Time required for single pellet combustion generally increased with pelletizing temperature. However, temperature had little effect on combustion time in the pelletizing temperature range of 100°C and 150°C. Pellets produced with wet biomass (moisture content: 12%) required longer combustion time than pellets produced with oven-dried biomass (moisture content: ~1%). The change in fuel conversion time was explained by the physical property because chemical property (intrinsic reactivity) was not affected by pelletizing condition.

During the densification processes, pelletizing temperature and moisture content played significant role in the increase of pellet density. However, particle deformation could not be explained only by these pelletizing conditions. Possible explanations are pelletizing pressure and change in particle flow pattern by the shape of dies.

In the low density region (<1200 kg/m³), fuel conversion time (especially char combustion time) standardized by apparent density of pellets remained constant. At the density of around 1200 kg/m³, fuel conversion time seems to be affected more by morphological changes than by density.

Our future research will address (1) how the pelletizing pressure and the shape of dies affect the morphology of pellets (interaction of biomass particles); (2) how morphology of pellets affects fuel conversion time; and (3) how wider variation in moisture content in the biomass, prior to pelletization, influence pellet combustion for different wood species.

Acknowledgment
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References
Paper III
Simplification of devolatilization models for thermally-thick particles: Differences between wood logs and pellets

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Abstract

Many phenomena affects devolatilization of relatively large wood particles, e.g. wood pellets and logs, including mass and heat transfer, chemical reactions and physical transformation such as shrinkage. Many studies investigated the importance of these phenomena through detailed mathematical models at particle scale, but the models need to be simplified at a certain degree to be implemented into large-scale simulation for gasifiers and boilers. This paper first presents how each physical and chemical parameter should be modelled for wood logs (low density and anisotropic) and wood pellets (high density and isotropic) through parametric studies with a detailed particle simulation. They required different sub-models for effective thermal conductivity and heat of reactions due to the difference in isotropy of particles between pellets and logs. Then, we demonstrated that a constitutive equation, i.e. analytical solution of the shrinking core model, is sufficient to express devolatilization rate of thermally-thick particles at the temperature of 1173 K with proper sub-models of physical and chemical parameters. The constitutive equation agreed better with experimental data of wood log than wood pellets, mainly because of the error caused during the consideration of the effect of convective cooling of char layer on thermal conductivity. Both detailed and simplified particle models were validated with the experimental data in an isothermal macro thermogravimeter allowing devolatilization of large particles.

Key Words:

Woody biomass
Devolatilization
Thermally-thick particle
Isotropy
Detailed particle simulation
Shrinking core model

1. Introduction

Thermochemical conversion of biomass such as combustion and gasification has attracted a lot of attention as a promising technology for an alternative to fossil fuel based technologies. Numerical simulation is a powerful tool for optimization of reactor designs and operational conditions. However, it is a big challenge to develop simulation models that are sufficiently accurate and computationally efficient because it is necessary to treat highly complicated multi-scale, multi-phase and multi-physics problems [1]. One of such complexities appears when relatively large biomass particles such as wood chips, logs, pellets, and briquettes are used as fuel. Heat conduction inside the particles affects apparent devolatilization rate of such particles, so-called thermally thick particles. Hence, it is essential to address particle-scale mass and heat transfer when describing the fuel conversion of thermally-thick particles in the reactors.

Some recent studies have implemented particle-scale mass and heat transfer models into reactor-scale simulation models of biomass gasification and combustion either with representative particle model [2–3] or discrete particle model [4]. These models solve particle-scale mass and heat transfer equations numerically in parallel with reactor-scale equations, leading high computational load. For example, introduction of n particles with N grid points into reactor-scale simulation with M grids would yield total number of grids as $(N + 1) \times M$ for RPM and $n \times N + M$ for DPM. It is still...
unknown how complex the particle-scale models should be to express fuel conversion sufficiently. Some studies showed that it is important to consider not only intra-particle mass and heat transfer but also gas flow surrounding the particle [6,7], particle shrinkage [8,9], particle shape [10], and internal microstructure [11, 12]. On the other hand, some studies demonstrated that the detailed particle model such as internal mass transport phenomena are necessary to acquire the accurate predictions. In fact, some studies have shown that simple particle models agreed with the experimental data sufficiently well by considering only conduction and devolatilization reactions [14, 15].

Simultaneous numerical solution of particle-scale and reactor-scale models is a time consuming process [16]. Therefore, some studies have tried to decrease the computational load by using some simplification such as applying shrinking core model, SCM (i.e. assumption of infinitely thin reaction zone or sharp interface) [17–22]. The shrinking core model assumes that the devolatilization of biomass particle proceeds as the propagation of infinitely thin reaction front from the surface to the centre of particles. Experimental studies have supported this assumption by showing the propagation of reaction front over the time [23, 24]. Such simplifications have demonstrated the improved computational performance. However, a comparison study of various multi-scale models for a packed-bed catalytic reactor showed that the most effective way to decrease the execution time of multi-scale simulation without the loss of accuracy is to derive constitutive equations for particle-scale. Constitutive equations are usually derived either by finding analytical solution of the differential equation or by expressing the independently solved numerical solution with polynomial functions.

The objective of this paper is to demonstrate the methods to simplify the model for fuel conversion of thermally thick particles during devolatilization, especially the suitability of the constitutive equation of the shrinking core model (SCM). We modified the SCM derived either by finding analytical solution of the differential equations for particle-scale. Constitutive equations are usually derived by finding analytical solution of the differential equation or by expressing the independently solved numerical solution with polynomial functions. The objective of this paper is to demonstrate the methods to simplify the model for fuel conversion of thermally thick particles during devolatilization, especially the suitability of the constitutive equation of the shrinking core model (SCM). We modified the SCM in order to account for the effects of convective heat transfer and gas flow. The SCM is used to predict the temperature, pressure, and concentration profiles within the particle. The model is solved numerically using a finite difference method. The results are compared with experimental data to validate the model.

2. Experimental

2.1. Sample

Cylindrical-shaped wood logs of Cercidiphyllum japonicum (Katsura tree) and wood pellets (90 wt.%) pine and 10 wt.% spruce, Bioenergi i Luleå AB were used. The particle diameters of wood logs were 9.5 and 14.5 mm with various length-to-diameter (L/D) ratios. Particle diameters of wood pellets were 6 and 8 mm with the L/D ratio of 1–4. The mean apparent density of wood logs was around 500 kg m$^{-3}$ and that of wood pellets was around 1100 kg m$^{-3}$. The sample was dried in an oven at 368 K for more than 8 h prior to the
Table 1
Proximate and ultimate analysis of sample.

<table>
<thead>
<tr>
<th></th>
<th>Logs</th>
<th>Pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile matter(^1), wt.%</td>
<td>85.1</td>
<td></td>
</tr>
<tr>
<td>Fixed carbon(^2), wt.%</td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>Ash(^1), wt.%</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>C(^2), wt.%</td>
<td>47.5</td>
<td>50.6</td>
</tr>
<tr>
<td>H(^2), wt.%</td>
<td>5.6</td>
<td>6.1</td>
</tr>
<tr>
<td>N(^2), wt.%</td>
<td>0.3</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>O (diff.)(^2), wt.%</td>
<td>46.6</td>
<td>43.3</td>
</tr>
</tbody>
</table>

\(^1\) Dry basis.

\(^2\) Dry ash free basis.

3. Models

3.1. Detailed particle model

Detailed particle simulation was carried out as a numerical solution of the set of transport equations inside the particle with sub-models for chemical reactions and physical parameters such as thermal conductivity. The simulation model was built based on ref [10] with more reasonable physical parameters as described in Section 3.1.2. It was one-dimensional transient model under the assumption of local thermal equilibrium between gas and solid phases.

3.1.1. Governing equations

Fuel particles are divided into a certain number of cells, whose size is adjusted to reflect the change in the size of fuel particles due to the shrinking caused by the devolatilization as described later. In the current model, two species (raw wood and char) were considered in solid phase. The mass conservation of raw wood and char can be described as

\[ \frac{\partial (\rho_{w}V)}{\partial t} = -(k_1 + k_2 + k_3)\rho_{w}V \quad \text{and} \quad \frac{\partial (\rho_{c}V)}{\partial t} = k_1\rho_{c}V + \phi\rho_{c}V. \]  

On the other hand, gas phase inside the particle was lumped into inert gas (N\(_2\)), light gases, and tars (high molecular weight gases). Since we considered both convective and diffusive mass transfer, mass and species (inert and tar) transport equations can be written as:

\[ \frac{\partial (\rho_{g}V)}{\partial t} = \frac{1}{T} \frac{\partial (\rho_{g}U)}{\partial t} - (k_1 + k_2 + k_3)\rho_{g}V - \phi\rho_{g}V \quad \text{and} \quad \frac{\partial (\rho_{g}V)}{\partial t} = k_1\rho_{g}V + \phi\rho_{g}V. \]

The kinetic scheme and kinetic constants of devolatilization can be found in Table 2. It should be noted that the densities of solid were defined based on the control volume while densities in gas phase was determined with gas volume. We assumed that the particle can be considered as porous medium and Darcy’s law can express the flow field inside the particle. In addition, we approximated the behaviour of total gas in the particle by ideal gas law.

\[ U = \frac{\partial \rho_{g}V}{\partial t}, \]

\[ P = \rho_{g}RT. \]

We used one overall energy balance equation by assuming the local thermal equilibrium between solid and gas phases:

\[ \frac{\partial (\rho_{c}h_{c} + \rho_{g}h_{g} + \phi\rho_{c}h_{c} + \phi\rho_{g}h_{g})}{\partial t} + \frac{1}{T} \frac{\partial (\rho_{c}h_{c} + \rho_{g}h_{g})}{\partial t} = \frac{1}{T} \frac{\partial (\rho_{c}h_{c} + \rho_{g}h_{g})}{\partial t} \]

\[ \frac{\partial (\rho_{c}h_{c} + \rho_{g}h_{g} + \phi\rho_{c}h_{c} + \phi\rho_{g}h_{g})}{\partial t} + \frac{1}{T} \frac{\partial (\rho_{c}h_{c} + \rho_{g}h_{g})}{\partial t} = -\frac{1}{T} \frac{\partial (\rho_{c}h_{c} + \rho_{g}h_{g})}{\partial t} \]

Fig. 1. Schematic diagram of the isothermal macro-thermogravimetric analyser (ITG).
3.1.3. Numerical methods

A set of partial differential equations (PDEs), which consists of the conservation equations for solid, gas, momentum and energy inside the particles, was discretized on a staggered grid by finite volume method. The particles were discretized into 200 control volumes with constant radial distances, and time steps were chosen to satisfy Courant–Friedrichs–Lewy condition for implicit method dependent on the particle size. A fully implicit scheme was applied for transient terms in PDEs and diffusion/convection terms were discretized by the power law scheme [36]. Discretized form of each differential equation was solved by using TDMA (tri-diagonal matrix algorithm) method. Pressure–velocity coupled system of equations were solved by SIMPLE (Semi-Implicit Method for Pressure Linked Equations) algorithm. The program was written in Matlab. Initial and boundary conditions are shown in Table 3.

3.2. Analytical solution of the shrinking core model (SCM)

This section describes the analytical solution of shrinking core model (SCM) to express apparent devolatilization rate of biomass particle. Pioneer work on the analytical solution of the SCM was carried out for sphere coal particles by Chern and Hayhurst [24]. They enabled the analytical solution by assuming that the heat flow at the particle surface, conductive heat flow inside the char layer and reaction heat of devolatilization are balanced at any time of devolatilization. This study suggests the improvement of the model aiming at application for biomass particles by (1) considering accumulation of heat inside the particles, (2) reformulating for cylindrical shapes (common shape for biomass particles), (3) suggesting a method to calculate the devolatilization temperature, and (4) deriving conversion rate to be directly applicable for reactor simulations.

Fig. 2 shows the schematic description of biomass particles during devolatilization under the assumptions of the SCM. The formulation of SCM is based on the assumption that infinitely thin reaction zone, which travels from the particle surface to centre during devolatilization, divides the particles into char layer and biomass core. At the particle surface, char surface receives heat from the surrounding environment. Then, heat conducts through the char layer from the surface to the centre while accumulation of heat in char layer is considered as negligible. Biomass core is assumed to remain as the initial temperature and temperature to rise to devolatilization temperature at the reaction front, where devolatilization occurs. Volatiles formed during devolatilization are assumed to leave the particle instantly as it is formed (i.e. to longitudinal direction). Therefore, the sensible heat of volatiles was ignored in the model while it is possible to consider via relaxation factor of thermal conductivity as discussed in Section 4.2. Biomass particles were assumed to be infinitely long cylindrical particles and not shrink by devolatilization. We also assume that physical properties remain constant against the change in temperature.

Heat flow rate from the environment to the particle surface, $Q_e$, is expressed as

$$Q_e = 2\pi r L H_0 (T_e - T_i),$$

where effective heat transfer coefficient takes into account for both convective and radiative heat transfer, i.e. $\alpha_{\text{er}} = \alpha_{\text{conv}} + \alpha_{\text{rad}}$, and $T_e$ is the temperature of heat at given position inside the char layer, $Q_e$, is

$$Q_e = 2\pi r L T_i \rho_i C_i.$$  

Although heat transfer is transient phenomena, we can apply pseudo–steady state approximation when the accumulation of heat in char layer is much smaller than heat flow. By assuming that char

<table>
<thead>
<tr>
<th>Initial conditions</th>
<th>Boundary conditions</th>
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<tr>
<td>$T(r,0) = T_i$</td>
<td>$T(0,t) = T_0$</td>
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<tr>
<td>$\rho_i(r,0) = \rho_w$</td>
<td>$\rho_w = \rho_w(T_i - T_e)$</td>
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<tr>
<td>$\nu_i(r,0) = 0$</td>
<td>$\nu_i = \nu_i(T_i - T_e)$</td>
</tr>
<tr>
<td>$T(r,0) = T_i$</td>
<td>$T(0,t) = T_0$</td>
</tr>
<tr>
<td>$P_i(r,0) = P_{\text{amb}}$</td>
<td>$P_i = P_{\text{amb}}$</td>
</tr>
<tr>
<td>$u_i(r,0) = 0$</td>
<td>$u_i = u_i(T_i - T_e)$</td>
</tr>
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</table>

$T_i$ and $T_e$ are initial and boundary conditions of temperature, $\rho_w$ is the density of water, $\nu_i$ is the kinematic viscosity, $P_i$ is the ambient pressure, $u_i$ is the velocity. 

### Table 3

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A_i$</th>
<th>$E_i$</th>
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<tbody>
<tr>
<td>Biomass → Gas ($k_1$)</td>
<td>4.38×10^4</td>
<td>152.7</td>
</tr>
<tr>
<td>Biomass → Char ($k_3$)</td>
<td>1.08×10^10</td>
<td>146.8</td>
</tr>
<tr>
<td>Tar → Gas ($k_6$)</td>
<td>3.27×10^8</td>
<td>111.7</td>
</tr>
<tr>
<td>Tar → Char ($k_7$)</td>
<td>2.6×10^8</td>
<td>108</td>
</tr>
<tr>
<td>Tar → Char ($k_8$)</td>
<td>1.0×10^8</td>
<td>108</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Sub-models</th>
<th>Refs.</th>
</tr>
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</table>
| Differences in isotropic wood pellets and anisotropic wood logs. The model developed by Kollmann and Cote [31,32], which attributes the contribution of gas-phase, solid-phase, and radiation across the pore on the overall thermal conductivity by porosity. We applied the weighting bridge-factor to account for the macroscopic pore structure, which can be expressed as the mixture of the direction parallel to and perpendicular to fibers. Thermal conductivities in the ideal directions (parallel/ perpendicular) can be expressed in the same way as the electrical conductance of parallel and series circuits. The bridge factor for wood pellets was 0.33 [33], and wood logs was 0.68 [34].

Different methods are available to incorporate particle shrinkage in the particle model [9,35,27]. We assumed that radial direction of shrinkage occurs uniformly over the particle during conversion because of numerical stability. Temporary radius of the particle was simply calculated as the product of initial radius, final shrinkage ratio, and the temporary overall conversion. The final shrinkage ratio, the ratio of the particle radius before and after the devolatilization, was experimentally determined in this study, which was around 0.75 for wood pellets and 0.8 for wood logs.

<table>
<thead>
<tr>
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<tr>
<td>Tar → Char ($k_8$)</td>
<td>1.0×10^8</td>
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</table>

<table>
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<th>Refs.</th>
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<tbody>
<tr>
<td>$k_1$</td>
<td>$[26]$</td>
</tr>
<tr>
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<td>$[27]$</td>
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<tr>
<td>$k_8$</td>
<td>$[27]$</td>
</tr>
</tbody>
</table>
conductivity can be represented by mean value inside the char layer, Eq. (12) becomes a separable differential equation. By integrating across the char layer from the reaction front, $t_{\text{dev}}$, to the particle surface, $R$, $Q_c$ can be rewritten as

$$Q_c = -2\pi r_0 \rho \bar{D} p_0 (T_{\text{dev}} - T_0) + \Delta h_{\text{dev}} \frac{\partial t_{\text{dev}}}{\partial r}$$

where $T_{\text{dev}}$ is the characteristic temperature of devolatilization. The sum of the rate of heat accumulation by raw biomass and heat of reaction of devolatilization, $Q_a$, at the reaction front is

$$Q_a = -2\pi r_0 \rho \bar{D} p_0 (T_{\text{dev}} - T_0) + \Delta h_{\text{dev}} \ln \left(\frac{T_{\text{dev}}}{T_0}\right)$$

Here, we assume that the amount of these three heat flow rate, i.e., $Q_c$, $Q_a$, and $Q_0$, give the same values. From the Eqs. (11), (13) and (14), we can eliminate $T_r$, $Q_r$, $Q_0$ and obtain the following relationship between the reaction time, $t$, and the radius of unreacted core, $r_{\text{unreact}}$:

$$1 - \frac{t}{t_{\text{dev}}} = \frac{1}{2B_\text{SCM}} \left(1 - \frac{T_{\text{dev}}}{T_0}\right)^2 - 2B_\text{SCM} \frac{T_{\text{dev}}}{T_0} \frac{1}{2B_\text{SCM} + 2} \ln \left(\frac{T_{\text{dev}}}{T_0}\right)$$

where $B_\text{SCM} = (\bar{D} \rho_0 \bar{p})$ is the dimensionless number with the same form as the Biot number, which expresses the ratio of the internal to external heat transfer resistance. Here, we should note that this dimensionless number (SCM-Biot number) uses conductivity of char, Eq. (15) can be rewritten as a function of conversion of biomass particle, $X$, using the relation with the radius of unreacted core, i.e., $X = 1 - (r/r_{\text{unreact}})^2$ for cylindrical particle as

$$\frac{t}{t_{\text{dev}}} = X + \frac{B_\text{SCM}}{B_\text{SCM} + 2} (1 - X) \ln \sqrt{1 - X}$$

while the conversion rate, $dX/dt$, is

$$\frac{dX}{dt} = \frac{B_\text{SCM} + 2}{2B_\text{SCM}(1 - B_\text{SCM}) \ln \sqrt{1 - X}}$$

Here, total time of devolatilization is

$$t_{\text{dev}} = \frac{\rho_0 R^2}{2\pi \rho \bar{D} p_0 (T_{\text{dev}} - T_0) + \Delta h_{\text{dev}} \frac{B_\text{SCM} + 2}{B_\text{SCM}}}$$

Many studies show that the overall reaction heat of devolatilization can be neglected while the reactions of volatile generation are endothermic and those of char generation are exothermic [9,14]. Under such conditions, Eq. (18) can be simplified to

$$t_{\text{dev}} = \frac{R^2}{2B_\text{SCM} (T_{\text{dev}} - T_0)} \left(\frac{B_\text{SCM} + 2}{B_\text{SCM}}\right)$$

where $B_{\text{SCM}}$ is the number with the same form as thermal diffusivity ($\bar{D}/(\rho \bar{C_p})$). Again, we should note that this number (SCM thermal diffusivity) is calculated by char conductivity. The detailed derivation of the SCM can be found in Supplementary material while the calculation methods for the devolatilization temperature are discussed in Section 4.3.

4. Results and discussion

4.1. Effect of length-to-diameter ratio on devolatilization rate

One of the most important simplification steps in the particle model is the assumption that the effect of mass and heat transfer in axial direction is negligible. Hence, it is important to examine if there is any difference in devolatilization time when length-to-diameter $(L/D)$ ratio changes. Previous studies have shown that the cylindrical particles can be treated as one dimensional if the $L/D$ is larger than 3 [37]. Fig. 3 shows relationship between devolatilization time and particle $L/D$ for both wood logs and pellets. Devolatilization time was independent of $L/D$ ratio when $L/D$ was above 2 for wood logs and above 3 for pellets. This ensures that wood logs and wood pellets can be treated as infinitely long cylinder at $L/D > 2$ and $L/D > 3$, respectively. When using particles with smaller $L/D$ ratio, it is recommended to use a shape correction factor [37]:

$$t_{\text{dev}}^{\text{shape factor}} = P(L/D) t_{\text{dev}}$$

4.2. Valid assumptions for the simplification: differences in wood logs and pellets

The results from the detailed particle model were compared to the experimental data to identify which assumptions we can apply for the simulation of the models. The necessities of intra-particle convective heat transfer, heat of reaction, and shrinkage in the particle model were examined. Other forms of physical changes such as particle cracking and fragmentation were not considered since particle cracking was observed only with 14.5 mm wood log at the temperature of 1173 K. We carried out 12 cases of particle simulation per experimental condition for this purpose. For each type of wood particle, the particle model agreed reasonably with experimental data using one set of physical models, which was set as a base case in the following part. The complete set of experimental and simulation data can be found in Supplementary material for the validation of particle model. Then, the thickness of the reaction zone was examined to identify the validity of the shrinking core model assumption. We should note that the present model did...
not contain any fitting parameter, but only theoretical sub-models with literature values or measured values.

Fig. 4 shows the comparison of experimental data to particle simulation with and without the consideration of convective transport of the outflow gases inside the particle. The model results for wood logs showed reasonable agreement with experiments without convective heat transfer while significant error was observed with convective heat transfer. In contrast, the consideration of convective heat transfer was essential part of the particle model for wood pellets. The difference between wood logs and pellets would be their anisotropic and isotropic natures. Relatively cold volatile gases cool down relatively hot char while they travel through the char layer to the particle surface. This phenomenon reduces effective thermal conductivity of the particle. Janse et al. [12] argued that the cooling effect of volatiles can be neglected when the direction of heat flux is perpendicular to the gas flow field. This argument agrees with our modelling results for wood logs. We can speculate that volatile gases left wood logs only in longitudinal direction while volatiles in wood pellets flowed in both radial and longitudinal directions. This also agrees with the pore structures of these fuels. Therefore, simplified particle models should consider convective cooling when using wood pellets while it can be simply ignored for wood logs. One simple method to consider the effect of convective cooling on intra-particle heat transfer is to use relaxation factor in thermal conductivity. Fig. 4b also shows the simulation results of the detailed particle model with relaxation factor of 0.35 although residual mass systematically deviated from the experimental data. Therefore, applying relaxation factor to thermal conductivity may be a reasonable approach for simplified model to consider convective cooling with the notion of systematic deviation.

Modelling heat of reaction in particle models is highly complex because devolatilization can be either endothermic to exothermic while it is important part of chemical-physical interaction inside the particle. Milosavljevic et al. [38] observed that high heating rate was in favour of volatile formation than char formation. On the other hand, low char yield is known to be in favour of endothermicity, which in turn can lower the heating rate from the local heat balance. Therefore, three different approaches for heat of reactions were examined in this study. First, devolatilization was assumed to be endothermic. Second approach set heat of reactions of devolatilization as zero. The last approach correlated heat of reaction to the char yield. Effect of heating rate on the favoured reaction pathway was included in the model via kinetic constants (Table 2) while the effect of reaction pathway on local heat balance was considered only in the last approach. However, the last approach caused significant discrepancy from the experimental results, so the result was omitted here.

Fig. 4. The effect of convective heat transfer by outflow of volatiles on time vs. residual mass curves at \( T_r = 1073 \) K. (a) Wood logs with the diameter of 14.5 mm, and (b) wood pellets with the diameter of 8 mm.

Fig. 5. Comparison of different models for heat of reactions of devolatilization in time vs. residual mass curves at \( T_r = 1073 \) K. (a) Wood logs with the diameter of 14.5 mm, and (b) wood pellets with the diameter of 8 mm.
Fig. 5 shows the comparison of the model to experimental data. Devolatilization of wood logs was represented well with endothermic reactions while devolatilization of wood pellets showed closest agreement with thermal neutral approach. Two possible reasons are the effect of heating rate and the presence of secondary reactions. In our experiments, wood logs experienced lower heating rate than wood pellets as seen from slower mass loss while wood pellets showed slightly higher char yield both in experiments and simulations. Hence, it is highly likely that exothermic secondary reactions were responsible for the differences in char yield and heat of reactions between wood logs and pellets. It is reasonable because volatiles from wood logs leave particles in longitudinal direction while volatiles from wood pellets diffuse in all directions. We recommend the assumption of devolatilization being endothermic in wood logs and thermally neutral in wood pellets. However, it should be noted that the applicability of this assumption should be examined when the model is applied in new conditions. Further model development of kinetic schemes and heat of reaction is also recommended.

The effect of shrinkage in the particle model was also investigated since it affects effective thermal conductivity inside the particle. Fig. 6 shows the comparison of residual mass against reaction time with and without shrinkage in the detailed particle model. The existence of shrinkage in the model showed relatively small effects on the fuel conversion for both wood logs and pellets. This shows that shrinkage is not an essential part of particle model when overall fuel conversion is considered.

The shrinking core model (SCM) in Section 3.2 assumes that devolatilization progresses at an infinite thin reaction zone moving from the surface to the centre of the particle. To investigate the validity of this assumption, Fig. 7 shows the local reaction rate at various overall conversions. For both wood logs and pellets, we can observe the progress of the reaction zone from the surface to the centre. This means that the SCM assumption would be a reasonable assumption to simplify the particle model. However, reaction zone became relatively thick at the late stage of the conversion. For 14.5 mm wood logs, local reaction rate at the centre of the particle stayed below 25% of that at reaction front when the overall conversion was 90%, while the number was 46% for 8 mm wood pellets. This implies that the SCM assumption may cause more significant error to wood pellets than it does to wood logs.

4.3. Devolatilization temperature

Devolatilization temperature is characterized as the local temperature where the maximum rate of devolatilization appears throughout the particle at any given time (see Fig. 7). It is important information because we assume that the devolatilization temperature remains constant regardless the location of reaction front
in the SCM. Fig. 8 shows the devolatilization temperature at various overall conversions obtained from the detailed particle simulation. It stayed almost constant temperature throughout the conversion, showing that constant devolatilization temperature is a reasonable assumption. Therefore, method for the estimation of devolatilization temperature is necessary for the application of the SCM. Several methods were found in the literature [16,39]. However, no method gave reasonable values compared with the devolatilization temperature of detailed particle simulation (Fig. 8).

The temperature at the maximum rate of devolatilization can be correlated to heating rate [40] for the first-order reaction as:

$$
\frac{dT}{dT} = \exp\left(-\frac{E}{RT}\right).
$$

This equation indicates that the higher the heating rate is, the higher the devolatilization temperature becomes. Therefore, the devolatilization temperature should have the correlation with the physical parameters that affect the local heating rate of wood particles.

When the surface temperature is constant at reactor temperature, the numerical solution of heat conduction inside infinite cylindrical particles with constant thermal diffusivity can be expressed as:

$$
T - T_e = erf\left(\frac{r}{2\sqrt{D_0 t}}\right)
$$

This assumption is valid because the particle simulation indicated that the surface temperature approached to the gas temperature rapidly and remained constant. Derivation of Eq. (22) gives heating rate of any given position and time in the wood particle as:

$$
\frac{dT}{dT} = \frac{(T_e - T_0)\sqrt{2\pi \alpha}}{2(\alpha D_0^{1/2} - \alpha D_0^{1/2} erf\left(\frac{r}{2\sqrt{D_0 t}}\right))}.\tag{23}
$$

This formula shows that the heating rate is affected by both position and time. Here, the detailed simulation showed that the devolatilization temperature from the particle simulation was close to the average of initial and gas temperatures. We can obtain the time to reach the average temperature, \((T_e + T_0)/2\), using Eq. (22) as:

$$
t_e^{1/2} = \frac{2\sqrt{\pi}}{\alpha D_0^{1/2}} erf^{-1}(0.5) - \frac{r^{1/2}}{\alpha D_0^{1/2}}\tag{24}
$$

By substituting Eq. (24) to Eq. (23), the heating rate of any given position inside the particle at average temperature can be correlated to reaction conditions as:

$$
\frac{dT}{dT} \bigg|_{T_0} \approx \frac{2}{\alpha D_0^{1/2}} \left(T_e - T_0\right).\tag{25}
$$

Eqs. (21) and (25) indicate that the devolatilization temperature has correlation with the physical constant, \(\alpha D_0^{1/2}\), and reactor temperature, \(T_e\), although it was obtained with extended amount of use.

![Fig. 8. Overall particle conversion (X) vs. temperature at the location of maximum devolatilization rate throughout particle (devolatilization temperature). (a) Wood logs, and (b) wood pellets.](image)

![Fig. 9. The dependency of devolatilization temperature on (a) physical parameter, \(\alpha D_0^{1/2}\), and (b) reactor temperature, \(T_e\).](image)
simplification. In fact, the devolatilization temperature obtained by the average value of particle simulation (see Fig. 8) had clear correlation to the physical constant and reactor temperature as shown in Fig. 9. Wood pellets and wood logs seem to have same correlations when convective cooling was considered with relaxation factor for thermal conductivity. Regression analyses showed that the correlation can be expressed as the following equation with $R^2 = 0.9923$:

$$ T_{\text{dev}} = -0.1265T_e + 18.28 \ln \left( \frac{x}{D} \right) + 695 $$

(26)

Here, we should note that the correlation might change by different biomass samples because devolatilization temperature can be affected by kinetic parameters as shown in Eq. (21).

4.4. The validity of the shrinking core model (SCM)

The results of the shrinking core model (SCM) were compared to the experimental results for validation. Fig. 10 shows the residual mass of wood logs plotted over the reaction time of the particle. Fig. 11 shows the same plots for wood pellets. Experimental data is shown as markers and results from the SCM model are shown as lines. We applied the simplification methods for physical parameters and calculation methods of devolatilization temperature as described in Sections 4.2 and 4.3, respectively. In other word, we did not carry out parameter fitting for the SCM to fit the experimental data.

The SCM results agreed with the experimental data well at high reactor temperature with respect to the overall devolatilization time for all the examined samples. It is reasonable considering that high reactor temperature is favourable for the assumption of infinitely thin reaction zone. The shape of time to residual mass curve by the SCM was deviated from the experimental data although it is acceptable difference considering the degree of simplification. The model might improve its performance if the effect of initial heating period is considered. Comparing the particle types, the SCM results of wood logs agreed with the experimental data better than those for wood pellets. This might be because of the systematic deviation of residual mass when applying relaxation factor on thermal conductivity instead of calculating the convective heat transfer (see Fig. 4b). After all, the SCM with proposed calculation methods for the physical parameters could be a suitable particle model for thermally-thick wood particles when considering a large number of particles in the reactor simulation.

5. Conclusion

The detailed particle simulation including mass and heat transfer and devolatilization showed that wood pellets and wood logs need different strategies for the simplification of models due to the difference in directions of volatile flow. The model for wood...
logs should exclude convective heat transfer by volatiles if the fibres align to longitude direction while it is important part in the models for pellets. However, the effect of convective heat transfer can be incorporated by simply multiplying a relaxation factor to thermal conductivity. Devolatilization of wood logs was expressed as endothermic reactions while the model results showed best agreement with experimental data of wood pellets when the heat of reaction was assumed to be zero, possibly due to the secondary reactions. The effect of the shrinkage on the mass loss rate was negligible for both wood logs and pellets.

At the examined reaction conditions, devolatilization of both wood pellets and logs occurred at very thin reaction zone, showing the validity of so-called the shrinking core model (SCM). Therefore, the constitutive equation of the SCM was reformulated for the wood particles. Empirical correlation was also derived to estimate devolatilization temperature as a function of reactor temperature and characteristic time of heat conduction. The SCM showed good agreement with experimental results at the reactor temperature of 1173 K without parameter fitting by using proposed methods to estimate physical parameters semi-empirically.

Major uncertainties of this study lie on incomprehensiveness of kinetic scheme as well as application of one dimensional model for three dimensional anisotropic phenomena. Therefore, further model development is recommended to consider three-dimensional internal microstructure of biomass particles and kinetic schemes that capture complex chemical-physical interaction inside the particle. Such model may be used to examine the validity of the simplification strategy suggested in this study. In addition, char particles generated during devolatilization of thermally-thick particle generally experience char combustion and gasification under the influence of mass diffusion limitation. Therefore, it would be beneficial if the SCM can be integrated with simplified models of char combustion and gasification considering the effect of mass transfer.

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Appendix A
Sub-models used in the detailed particle model
As described in Section 3.1.2, we selected the chemical and physical sub-models to express some critical phenomena precisely. Table A1 shows the summary of the equations used in the detailed particle simulation of this study.

Appendix B. Supplementary data
Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/jcej.2015.03.131.

References

Table A1 Values and correlations for physical properties.

<table>
<thead>
<tr>
<th>Property</th>
<th>Correlation/value</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Molecular mass of gases, kg kmol⁻¹</td>
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<td></td>
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<tr>
<td>Reaction rate, kg m⁻³ s⁻¹</td>
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<tr>
<td>Effective thermal conductivity parallel to the fibre, W m⁻¹ K⁻¹</td>
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<td>Effective thermal conductivity perpendicular to the fibre, W m⁻¹ K⁻¹</td>
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<tr>
<td>Thermal conductivity of biomass parallel to the fibre, W m⁻¹ K⁻¹</td>
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<tr>
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<td>Radiative heat transfer through the pore, W m⁻¹ K⁻¹</td>
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<td>Effective pore diameter, m</td>
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<td>Char pore diameter, m</td>
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<td>Molecular diffusivity of gases, m² s⁻¹</td>
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<td>Density</td>
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Paper IV
Apparent combustion rate of large wood char particles

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Abstract

Apparent combustion rate of large char particles, e.g. wood pellets and wood logs, are affected by both chemical reactions and transport phenomena. This study investigates how devolatilization conditions and the initial macroscopic pore structure affect the apparent char reactivity of large wood particles, not only by changes in intra-particle mass diffusion but also by the change in the intrinsic reactivity of char. We have performed char oxidation experiments both under chemically and mass transfer controlled conditions, and have developed a one-dimensional char oxidation model to examine the fundamentals of large particle combustion. We found that devolatilization conditions (i.e. temperature and particle diameter) had influence on the intrinsic reaction rate, but it did not play significant role on the overall conversion of large particle. The increase in reaction temperature resulted in the thin reaction zone. As a result, overall oxidation rate of large char particles became temperature insensitive.

Keywords: wood pellets, char combustion, pore structure, reaction rate
1. Introduction

Combustion and gasification are efficient and well established processes for converting biomass to useful energy. Modelling of such thermochemical combustion processes, especially with computational fluid dynamics (CFD) simulation, has become reliable and powerful tools for the optimization of design and operation [1–3]. Char oxidation or gasification is normally the rate limiting step of fuel conversion, and its reaction rate varies largely with small changes in macroscopic pore structure [4]. Hence, it is important to have an accurate model based on deep understanding of the reaction process. Under most industrially relevant conditions, relatively large biomass particles (5–20 mm) are supplied to reactors such as fixed bed, grate fired or fluidized-bed reactors. Char oxidation/gasification of large particles occurs under the influence of intrinsic reaction kinetics, mass diffusion and non-uniform temperatures inside the particles. While a number of studies have investigated char reactivity under chemically controlled regime [5–7], few studies have discussed the fundamentals of large particle oxidation or gasification [8–14]. Apparent char reactivity of large char particles is affected by local reaction conditions inside particles change. Mermoud et al [10] argued that simplified approaches such as the shrinking core model or a homogeneous model is inadequate to model large particle conversion since mass transfer is limiting the gasification process.

Difference in the macroscopic pore structure may also affect the intrinsic reaction rate of char combustion and gasification. Our previous study [15] showed that the differences in isotropy of wood logs and pellets affected intra-particle phenomena such as convective transport of heat, local heating rate and secondary cracking of tar during devolatilization. It is well known that devolatilization conditions affect intrinsic char reactivity. Identified important parameters are heating rate [16], holding time (annealing or the loss of ash) [17], temperature, existence of cooling and reheating, cooling rate, reaction atmosphere during devolatilization [18], and the presence of volatile-char interactions [19–21]. However, most studies have been conducted in laboratory scale reactors with small particles to isolate the effect of each parameter. In large particles, local conditions of these parameters change dependent on the type of particles (log or pellet), particle size, and devolatilization conditions. However, the effect of overall devolatilization reaction conditions on intrinsic char reactivity of large particles has not been studied well despite its possible importance for the overall
char oxidation/gasification time. Furthermore, the relative importance of each parameter has not been explored for large particles.

The main objectives of this study are to experimentally examine how devolatilization conditions (i.e. temperature and diameter) affect the char reactivity, and to numerically compare the relative importance of mass transfer and reaction rate on the oxidation of large char particle. We performed char oxidation experiments both under chemically and mass transfer controlled conditions, and developed a one-dimensional char oxidation model to examine fundamentals of large particle combustion. Identification of local reaction conditions during combustion was possible using the detailed particle simulation previously published in [15].

2. Experimental methods

2.1 Raw sample and char preparation

Cylindrical-shaped wood logs of Cercidiphyllum japonicum (Katsura tree) and wood pellets (90 wt.% pine and 10 wt.% spruce, Bioenergi i Luleå AB) were used. The particle diameter of wood log was 9.5 mm and those of wood pellets were 6 and 8 mm with length-to-diameter ($L/D$) ratios of 3. The mean apparent density of wood logs was around 500 kg m$^{-3}$ and that of wood pellets was around 1100 kg m$^{-3}$. The samples were dried in an oven at 368 K for more than 8 h prior to char preparation and kept in a desiccator cabinet with silica gel beads to minimize the re-adsorption of moisture. Proximate and ultimate analyses of the sample are found in supplementary material.

An isothermal macro-thermogravimeter (iTG) was used to prepare char samples. Detailed description of the iTG can be found in ref [11] and supplementary material. The reaction zone was pre-heated to target temperatures (973, 1073 and 1173 K) and was purged with nitrogen at 7 L min$^{-1}$ at standard state. The sample was held in a basket made of two nickel–chromium wires to minimize the disturbances of gas flow and radiation, caused by the basket. The sample basket was kept in the cooling zone, and then moved to the reaction zone by lowering the wire. It was devolatilized until the mass became stable (approximately 100 seconds). For intrinsic reaction rate experiment, hot char particles were moved to the cooling zone and quenched by N$_2$ flow. For the apparent reaction rate
experiments, char particles were kept inside the reactor and the gas was switched from inert to
oxidizing.

2.2 Experimental procedure

Two types of experiments have been carried out: measurements of the intrinsic reaction
rate and the apparent reaction rate.

2.2.1 Intrinsic reaction rate

After devolatilization in iTG, hot char particles were cooled and grounded to the size
less than 75 μm to study the intrinsic reaction rate. A thermogravimetric analyser, TGA (Q5000IR, TA
Instrument, USA), was used for the measurement of the intrinsic reaction rate. A mixture of oxygen
and nitrogen was supplied to the TGA at a flow rate of 50 ml min\(^{-1}\) at standard state. Approximately
0.5 mg of sample was used for each experiment at the TGA. Initially, the char samples were heated to
378 K and kept for 15 min to ensure the removal of moisture from char. Next, the char samples were
heated from 378 to 923 K at constant heating rates. Three volume fractions of oxygen (i.e. 5, 10, and
15 vol.% in nitrogen) and three heating rates (i.e. 5, 10, and 15 K min\(^{-1}\) ) were used to determine the
kinetic parameters of chars from both wood pellets and logs. In addition, some experiments were
conducted at 10 vol.% of O\(_2\) and 10 K min\(^{-1}\) of heating rate on both types of chars to examine the
effects of devolatilization temperature and particle size on intrinsic char reactivity.

2.2.2 Apparent reaction rate

The apparent reaction rates of char combustion were measured for large char particles
in iTG (see supplemental material for schematic of iTG) at the reaction temperature without extracting
char from the reactor. In these experiments, single wood particles (log of 9.5 mm and pellet of 6 and 8
mm) were first pyrolyzed in a 7 L min\(^{-1}\) (standard state) nitrogen flow. Then, the reaction environment
was switched to oxidizing atmosphere by changing the gas composition to 10 vol.% of O\(_2\) in nitrogen
while keeping the total gas flow rate constant. The temporal mass of the sample basket were recorded
to a PC every two seconds during the experiments.
3. Modelling methods

3.1 Estimation of intrinsic kinetic parameters

The reaction scheme for char oxidation was approximated with a one-step global reaction. It was chosen due to its simplicity and the presence of only one distinguishable peak in derivative of thermogravimetric analysis (see supplement material). The absence of other peaks or shoulders indicates that there were at least no intermediate devolatilization stages, and that the only prominent reaction was the oxidation of char. The one-step global reaction model applied in this study can be written as:

\[ \text{char} + O_2 \rightarrow CO_2. \tag{1} \]

The products of combustion was lumped to only CO$_2$ because combustion of char in TGA was completed at around 773 K, at which the molar fraction of CO$_2$ stays above 95vol.% \[22]\]. We should note that the current approach to obtain kinetic parameters may introduce errors when applied at higher reaction temperatures due to the change in dominant reaction pathways \[21]\]. Nevertheless, this approach was utilized since the intrinsic rate experiments were limited to low temperature region to avoid thermal runaway due to the heat of reactions.

The reaction rate of char combustion is usually related to the partial pressure of oxygen and pore surface area \[6\]. In this study, we applied the rate expression as:

\[ R = \frac{dx}{dt} = A \exp(-E/RT) P^{m_{O_2}} (1 - X_e)^n, \tag{2} \]

where

\[ X_e = \frac{m_e - m}{m_o - m_f}. \tag{3} \]

The evolution of the pore surface area during combustion was described by a simple power law expression of the mass fraction of char \[5\]. Since the reaction order with respect to oxygen is usually in the range of 0.8 to 1 for wood char \[5\], the value of the exponent m was taken as unity for simplicity. The sample temperature is a known function of time, hence, expressed as:

\[ T = T_0 + ht. \tag{4} \]
The kinetic parameters were estimated by a least square method for the absolute errors of residual mass \((Y_c=1-X_c)\) [5], weighted by the number of data points in each experimental condition.

\[
F = \sum_{j=1}^{J} \sum_{k=1}^{K} \frac{\sum_{l=1}^{N}(Y_{exp,l} - Y_{sim,l})^2}{N}.
\]  

(5)

\(J\) and \(K\) are the numbers of experimental conditions with respect to heating rates and oxygen concentrations, respectively. The estimated parameters were activation energy, pre-exponential factor, and coefficient of power function for residual mass \((1-X_c)\). First, mass conservation equation, Eq. 2, was integrated by implicit Euler method. Then, an objective function, Eq. 5, was minimized by using the matlab “fminsearch” function. The detailed of this method can be found can be in ref [5].

3.2 Particle simulation

Detailed particle simulations were carried out as numerical solutions of the set of transport equations inside the particle with sub-models for chemical reactions and physical parameters (see supplementary material). It was a one-dimensional model under the assumption of local thermal equilibrium between gas and solid phase. In the current model, two species (char and ash) were considered in solid phase. The mass conservation of char and ash can be described as:

\[
\frac{\partial (\rho_c Y_c)}{\partial t} + \frac{1}{r} \frac{\partial (\rho_c Y_c u)}{\partial r} = -S_c, \text{ and}
\]

(6)

\[
\frac{\partial (\rho_a Y_a)}{\partial t} = 0.
\]

(7)

The gas species inside the particles were lumped into inert gas \((N_2)\), oxygen, and carbon dioxide. Since we considered both convective and diffusive mass transfer, mass balance and species transport equations can be written as:

\[
\frac{\partial (\rho_c Y_c)}{\partial t} + \frac{1}{r} \frac{\partial (\rho_c Y_c u)}{\partial r} = \frac{1}{r} \frac{\partial}{\partial r} (\rho_c D_{eff} \frac{\partial Y_c}{\partial r}) + S_{c,t}, \text{ and}
\]

(9)

\[
\frac{\partial (\rho_a Y_a)}{\partial t} + \frac{1}{r} \frac{\partial (\rho_a Y_a u)}{\partial r} = \frac{1}{r} \frac{\partial}{\partial r} (\rho_a D_{eff} \frac{\partial Y_a}{\partial r}) - S_{a,t}.
\]

(10)
We assumed that the particles can be considered as porous medium, and that Darcy’s law can express the flow field inside the particle. In addition, we approximated the behaviour of the gas in the particles by the ideal gas law.

\[
\begin{align*}
U &= -\frac{\mu}{\rho_g} \frac{\partial P}{\partial r} \\
P &= \frac{\rho_g R_g T}{W_c}.
\end{align*}
\]

(11)

(12)

We used one overall energy balance equation by assuming the local thermal equilibrium between solid and gas phases.

\[
\begin{align*}
\frac{\partial}{\partial t} \left[ \rho_c h_c + \rho_a h_{ash} + \Phi \left( \rho_N h_N + \rho_O h_O + \rho_{CO2} h_{CO2} \right) \right] + \frac{1}{r} \frac{\partial}{\partial r} \left( r \lambda_{ef} \frac{\partial T}{\partial r} \right) + \Delta h S_g &= \\
\frac{\rho_c h_c + \rho_a h_{ash} + \Phi \left( \rho_N h_N + \rho_O h_O + \rho_{CO2} h_{CO2} \right)}{\rho} \frac{\partial \rho}{\partial t}.
\end{align*}
\]

(13)

A fully implicit scheme was used for the transient term and the power law scheme was used to discretize for the convection and diffusion terms. Each discretized PDE was solved by using the TDMA (tri-diagonal matrix algorithm). The SIMPLE algorithm [23] was used to solve the pressure-velocity coupled system of equation. A detailed description of the numerical method can be found in our previous publication [11]. Table 1 shows the initial and boundary condition.

4. Results and discussion

4.1 Effect of devolatilization conditions on intrinsic char reactivity

The apparent reaction rate of thick char oxidation can be affected both by intrinsic reaction rate and intra-particle mass diffusion as discussed previously. This section shows the experimental data for the effect of devolatilization conditions on the intrinsic reaction rate. The investigation is important to differentiate the effect from that on apparent char reactivity by intra-particle mass transfer. Char particles were prepared at different reactor temperatures (i.e. 973, 1073 and 1173 K) in an iTG, and intrinsic reactivity tests were performed with grounded char particles in a TGA at 10 K min\(^{-1}\) with 10 % of O\(_2\).

Fig 1 shows char conversion versus temperature for both pellet and wood log chars at various reactor temperatures during char preparation. For the devolatilization temperature between 973
and 1073 K, char reactivity was not significantly affected for both wood logs and pellet. However, wood pellet char produced at 1173 K was much less reactive than other pellet chars. The possible reason is the secondary char deposition on active sites of the particle during devolatilization at 1173 K. Tar from pyrolysis of wood pellets can flow in all direction and allows secondary intra-particle cracking during pyrolysis, especially at high temperatures [11].

Fig 2 shows how particle size during devolatilization affects the intrinsic char reactivity. The intrinsic reaction rate was hardly affected by the change of pellet diameter (see fig 4a), although small particle showed somehow lower reactivity. In contrast, the intrinsic reactivity of wood log char was reduced with the increase of log diameter. A possible explanation for this reduction of char reactivity is the deposition of secondary char on active site of the particle, a mechanism affected by heating rate and initial pore structure. Our previous study[15] indicated that tar from wood logs follows the natural longitudinal vacuole, leaving the particle without secondary cracking. Therefore, the main reason of reactivity reduction seen here may be an increase in secondary tar formation induced by the difference in heating rate during pyrolysis.

In summary, the intrinsic reactivity of wood char was affected by both devolatilization temperature and particle diameter. How this change in intrinsic reaction rate impacts the prediction of apparent reaction rate of large wood particles are discussed in section 4.4.

4.2 Kinetic parameters

The kinetic parameters were estimated for chars of both wood log and pellet. The devolatilization temperature was 1073 K and particle size was 8 and 9.5 mm for wood pellet and log, respectively. The kinetic constants of char oxidation can be found in Table 2.

The activation energies were very high with 218 kJ mol\(^{-1}\) for wood log and 258 kJ mol\(^{-1}\) for pellet, respectively. High activation energies have been previously reported for chars that are produced under severe pyrolysis condition. For example, previous studies have estimated the activation energies of 208 and 229 kJ mol\(^{-1}\) for chars from high temperature (i.e. 873 K) and high heating rate (e.g. 15 K/min), respectively [5,21,24], with the high activation energies attributed to the
severity of the devolatilization conditions. Our devolatilization conditions were more severe (i.e. 1073 K) than those found in the literatures (between 573 K to 873 K [21]), and the produced char was as reactive as those produced at high heating rate.

Activation energies varied significantly between wood log and pellet. Two possible reasons are the species and heating rate. Our previous study indicated that wood pellet experiences higher heating rate than wood log during devolatilization [11]. Since effect of wood species on char reactivity is known to be less significant [5], it is likely that difference in heating rate caused the activation energies to vary significantly between wood log and pellet.

4.3 Validation of the particle model

The particle model was validated using iTG data of time vs. residual mass as shown in Fig. 3. The model matched very well with the experimental data of wood pellets. About 99% of the pellet conversion was estimated properly by the particle model. In contrary, the model can predict only up to ca. 45% of wood log conversion. Similar discrepancy was observed for wood log particles, especially for big particles [10], and consideration of peripheral fragmentation demonstrated to improve the model performance [25]. We observed particle fragmentation only during devolatilization of wood logs. Wood logs and wood pellets may require different particle models because the difference in integrity of intra-particle structure [15] influenced the existence of fragmentation during char combustion. Our model did not consider the fragmentation of the particle prior to and during the fuel conversion. Although development of the model with fragmented particle was out of the scope of this study, we recommend including this effect for future studies. In addition, it may become important to consider the reactor specific fragmentation mechanisms such as collapsing char in fuel beds or attrition in fluidized beds [26,27].

4.4. Effect of chemical and physical parameters on apparent particle conversion

Since the model had a good performance with wood pellets, the effect of chemical and physical parameters, namely kinetic parameter and tortuosity, on model performance was investigated for wood pellets with various particle diameters and combustion temperatures. The intrinsic reaction
rate was affected by the change in pyrolysis temperature and particle diameter as discussed in section 4.1. Fig 4 shows a comparison of experiments and particle simulation for time vs. conversion, using original kinetic parameters and tortuosity. Original kinetic parameters presented in section 4.2 were estimated on 8 mm wood pellet char pyrolyzed at 1073 K. Particle model showed reasonable agreement with experiments when the reactor temperature was 1173 K without modifying kinetic parameters or tortuosity. In other words, although the intrinsic reaction rate was influenced by the reactor temperatures, their effect on overall conversion was limited when oxidization temperature is high. However, significant error was observed after 80% conversion when the reactor temperature was 973 K. It is likely due to change in fuel morphology (e.g. fragmentation, pore growth) since it can predict up to 80% conversion with original kinetic parameters and tortuosity. As shown in the next section, char combustion proceeded throughout the particle at 973 K unlike at higher temperatures. Further investigation is required on the changes of fuel morphology dependent on the reaction front.

An additional parameter (i.e. tortuosity), other than kinetic constants, was adjusted in order to fit the experimental data of char conversion with simulation result for the 6 mm particle (see Fig. 4C). The tortuosity value was 1.5 for 8mm pellet while it was 1.35 for 6 mm pellet. It implies that the diffusional resistance was small in smaller pellet.

The results showed that it is valid to use constant kinetic parameters for particle simulation of char combustion at different conditions, although the differences in devolatilization conditions may vary the resulting kinetic parameters. However, it does not necessary justify to apply kinetic parameters from literature, which tend to vary significantly [21].

4.4 Effect of reaction temperature on apparent reaction combustion rate of large particle

The experimental results of char conversion with time at three different reactor temperatures (i.e. 973, 1073 and 1173 K) at 10 % of oxygen pressure are plotted in Fig.5 for the 8 mm pellets. The reactor temperature had a profound effect on the char conversion time. The apparent reaction rate increased largely with the increase of reactor temperature from 973 K to 1073 K, but a further increase of reactor temperature to 1173 K did not influenced the apparent reaction rate significantly. Similar observation was found for wood logs (shown in supplementary material). Our
simulation results showed the same tendency against the change in reaction temperature, which made it enable to explore this unusual behaviour.

Fig. 6 shows the predicted local char conversion and partial pressure of oxygen within the particle at various overall conversions. The data is shown for 8mm wood pellets exposed at 973, 1073 and 1173 K. We observed that the char combustion was taking place throughout the particle at different overall conversion when the reactor temperature was 973 K. In fact, local char conversion increased nearly uniformly throughout the particle as the overall conversion increased. At the temperatures of 1073 and 1173 K, on the other hand, the reaction took place at the surface of the particle and progressed toward the particle centre as the local conversion shows. Local partial pressures of O$_2$ showed that the oxygen could not reach to the centre of particles either at 1073 K or 1173 K, while oxygen was present at the particle centre throughout the reactions at 973 K. It means that the reaction progressed phenomenologically in the manner of regime 2 (intra-particle diffusion control).

The change in local conversion also indicates why the particle simulation had discrepancy with experimental data at 973 K in the previous section (see Fig. 6). Since local conversion increased similarly throughout particles at the temperature of 973 K, it is likely that the pore structure altered as the reaction progressed. It means the tortuosity (currently set constant as 1.5) might have decreased as the reaction progressed, leading to an acceleration of reaction. Further studies are recommended for the change in particle morphology such as macroscopic pore structure, e.g. using X-ray tomography [28], as it may be possible to describe the model discrepancy at higher conversions under such conditions if the model incorporates the change in macroporous structure according to the reaction progress.
5. Conclusions

The influences of devolatilization conditions (temperature and particle diameter) on both intrinsic and apparent reaction rates of char oxidation were investigated. The intrinsic char oxidation rate was influenced by devolatilization conditions, but this change of intrinsic reaction rate had limited effect on apparent reaction rate, according to the estimation by particle model. Under certain conditions, the particle model showed discrepancy against experimental data in the reaction progress at high char conversion (e.g. wood logs and 973 K). It is thought to be due to the absence of sub-models describing fragmentation or change in macroscopic pore structure. Hence, we recommend future studies for experimental investigations on the changes in particle morphology.

The experimental observations suggested that conversion time was not influenced significantly by increase of reactor temperature from 1073 K to 1173 K. Particle simulation showed that the consumption rate of oxygen was higher than the diffusion rate and the reaction front became thinner as the reactor temperature was increased above 1073 K.

Some aspects of the particle model need further improvement in the future, such as consideration of more comprehensive chemical kinetic scheme and gas phase combustion at external boundary layer and inside pores.

Acknowledgments

We thank Bio4Energy, a strategic research environment appointed by the Swedish government, and Swedish Energy Agency for supporting this work.
References


Captions

**Fig 1:** Comparison of char conversion of wood chars, produced at different reactor temperature during pyrolysis, under chemical controlled atmosphere a) wood log b) wood pellet.

**Fig 2:** Comparison of char conversions of wood char produced from different diameter of the particle, under chemical controlled atmosphere a) wood log b) wood pellet. The pyrolysis temperature was 1073 K and chars were oxidized in TGA under 10 % of O₂.

**Fig 3:** Comparison of experimental and simulated results for the residual masses

**Fig 4:** Time vs. char conversion of wood pellet a) at reactor temperature of 973 K and 1173 K. b) 6 mm wood pellet at 1073 K

**Fig 5:** Experimental char conversion with time at different reactor temperature wood pellet. The oxygen partial pressure was 10 %.

**Fig 6:** Profiles of (left) local conversion and (right) partial pressure of oxygen within the particle at various overall conversions at. (a) 973 K (b) 1073 K (c) 1173 K
Table 1: Initial and boundary conditions

<table>
<thead>
<tr>
<th>Initial conditions</th>
<th>Boundary conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t=0; \quad r=0; \quad r=R;$</td>
<td>$r=0; \quad r=R;$</td>
</tr>
<tr>
<td>$\rho_w(r, 0) = \rho_{wo}$</td>
<td>$\frac{\partial T}{\partial r} = 0 \quad \lambda_{eff} \frac{\partial T}{\partial r} = h_{eff} (T_e - T_s)$</td>
</tr>
<tr>
<td>$\rho_s(r, 0) = 0$</td>
<td>$\frac{\partial Y}{\partial r} = 0 \quad D_{eff} \frac{\partial Y}{\partial r} = h_m (Y_e - Y_s)$</td>
</tr>
<tr>
<td>$T(r, 0) = T_0$</td>
<td>$\frac{\partial P}{\partial r} = 0 \quad P_s = P_{atm}$</td>
</tr>
<tr>
<td>$P(r, 0) = P_{atm}$</td>
<td></td>
</tr>
<tr>
<td>$U_s(r, 0) = 0$</td>
<td></td>
</tr>
<tr>
<td>$Y_s(r, 0) = 1$</td>
<td></td>
</tr>
</tbody>
</table>

$^*h_{eff} = h_{conv} + \varepsilon \sigma (T_e + T_s)(T_e^2 + T_s^2)$
Table 2: kinetic constants for wood log and pellet

<table>
<thead>
<tr>
<th></th>
<th>Log</th>
<th>pellet</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, s(^{-1}) kPa(^n)</td>
<td>7.48×10(^7)</td>
<td>1.16×10(^{11})</td>
</tr>
<tr>
<td>E, kJ mol(^{-1})</td>
<td>218</td>
<td>258</td>
</tr>
<tr>
<td>n, -</td>
<td>1.49</td>
<td>1.95</td>
</tr>
</tbody>
</table>
Fig 1: Comparison of char conversion of wood chars, produced at different reactor temperature during pyrolysis, under chemical controlled atmosphere a) wood log b) wood pellet.
Fig 2: Comparison of char conversions of wood char produced from different diameter of the particle, under chemical controlled atmosphere a) wood log b) wood pellet. The pyrolysis temperature was 1073 K and chars were oxidized in TGA under 10 % of O₂.
Fig 3: Comparison of experimental and simulated results for the residual masses
Fig 4: Time vs. char conversion of wood pellet a) at reactor temperature of 973 K and 1173 K. b) 6 mm wood pellet at 1073 K
Fig 5: Experimental char conversion with time at different reactor temperature wood pellet. The oxygen partial pressure was 10%.
Fig 6: Profiles of (left) local conversion and (right) partial pressure of oxygen within the particle at various overall conversions at (a) 973 K (b) 1073 K (c) 1173 K.
Supplement material

Fig A1: Schematic of isothermal macro TG

Fig A2: Derivative thermogravimetry of char oxidation at chemically controlled environment. Chars were produced at reactor temperature of 973 K.
Fig A3: Experimental char conversion for wood log at different reactor temperatures.

Table A1: Fuel analysis of the 8 mm and 6 mm pellets

<table>
<thead>
<tr>
<th>Sample</th>
<th>8 mm pellets</th>
<th>6 mm pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td>C [wt.%]</td>
<td>50.6</td>
<td>50.6</td>
</tr>
<tr>
<td>H [wt.%]</td>
<td>6.2</td>
<td>6.1</td>
</tr>
<tr>
<td>N [wt.%]</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>O (by difference) [wt.%]</td>
<td>42.69</td>
<td>42.82</td>
</tr>
<tr>
<td>Ash content [wt.%]</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Property</td>
<td>Correlation/value</td>
<td>Ref</td>
</tr>
<tr>
<td>---------------------------------------------------</td>
<td>-----------------------------------------------------------------------------------------------------</td>
<td>-----------</td>
</tr>
</tbody>
</table>
| Molecular mass of gases, kg kmol⁻¹                 | \[
\frac{1}{W_G} = \sum \frac{Y_i}{W_i}
\]                                                                 | -         |
| Reaction rate, kg m⁻³ s⁻¹                          | \[
\omega_j = A_i \exp\left(-\frac{E_i}{RT}\right)\rho_i
\]                                                                 | -         |
| Effective thermal conductivity, W m⁻¹ K⁻¹         | \[
\lambda'_{eff} = \xi\lambda_T + (1 - \xi)\lambda_L
\]                                                                 | [24]      |
| Effective thermal conductivity parallel to the fibre, W m⁻¹ K⁻¹ | \[
\lambda_L = \left(1 - \phi\right)\lambda_{\parallel} + \phi\left(\lambda_{\perp} + \lambda_{rad}\right)
\] | [24]      |
| Effective thermal conductivity perpendicular to the fibre, W m⁻¹ K⁻¹ | \[
\lambda_{\perp} = \left(\frac{1 - \phi}{\lambda_{\perp}} + \frac{\phi}{\lambda_{\parallel} + \lambda_{rad}}\right)^{-1}
\] | [24]      |
| Thermal conductivity of biomass parallel to the fibre, W m⁻¹ K⁻¹ | \[
\lambda_{b,parallel} = 0.87
\]                                                                 | [25]      |
| Thermal conductivity of biomass perpendicular to the fibre, W m⁻¹ K⁻¹ | \[
\lambda_{b,perpendicular} = 0.43
\]                                                                 | [25]      |
| Thermal conductivity of char, W m⁻¹ K⁻¹            | \[
\lambda_{c,}\lambda_{c,parallel} = 1.47 + 0.0011T
\]                                                                 | [26]      |
| Radiative heat transfer through the pore, W m⁻¹ K⁻¹ | \[
\lambda_{rad} = 13.56\sigma_{rad}T^\frac{3}{2}/\epsilon
\]                                                                 | [27]      |
| Effective pore diameter, m                         | \[
d_{\text{por},w} = 5 \times 10^{-5}
\]                                                                 | [28]      |
| Wood pore diameter, m                              | \[
d_{\text{por},c} = 1 \times 10^{-4}
\]                                                                 | [28]      |
| Char pore diameter, m                              | \[
\epsilon = 0.90
\]                                                                 | [28]      |
| Emissivity, –                                      | \[
\epsilon = 0.90
\]                                                                 | [28]      |
| Thermal conductivity of gas, W m⁻¹ K⁻¹             | \[
\lambda_{g} = 25.77 \times 10^{-3}
\]                                                                 | [27]      |
| Void fraction of solid, –                          | \[
\phi = 1 - \frac{\rho_w}{\rho_c} = 1450
\]                                                                 | [26]      |
| Intrinsic density of wood, kg m⁻³                  | \[
\rho_w = 1950
\]                                                                 | [26]      |
| Intrinsic density of char, kg m⁻³                  | \[
\rho_c = \frac{1430 + 0.355T - 7.32 \times 10^7T^{-2}}{1500 + T}
\]                                                                 | [29]      |
| Specific heat of wood, J kg⁻¹ K⁻¹                  | \[
C_{P_w} = 1800 - 800\exp(-0.0055T)
\]                                                                 | [24]      |
| Specific heat of char, J kg⁻¹ K⁻¹                  | \[
C_{P_c} = 770 + 0.629T + 0.000191T^2
\]                                                                 | [24]      |
| Specific heat of gases, J kg⁻¹ K⁻¹                 | \[
\phi_{\text{por}} = \eta\phi_w + (1 - \eta)\phi_c
\]                                                                 | [30]      |
| Effective permeability of solid, Darcy             | \[
\phi_c = 1
\]                                                                 | [8]        |
| Permeability of wood, Darcy                        | \[
\phi_c = 100
\]                                                                 | [8]        |
| Permeability of char, Darcy                        | \[
D = D_{ab}(T/298)^{1.75}
\]                                                                 | [8]        |
| Mass diffusivity m² s⁻¹                            | \[
D_{ab} = \frac{\phi\theta}{T} (D_{ab} = 3 \times 10^{-5})
\]                                                                 | [8]        |
| Dynamic Viscosity of gases, kg m⁻³ s⁻¹             | \[
\mu = 4.847 \times 10^{-7}T^{-0.64487}
\]                                                                 | [31]      |
| Nusselt number, –                                  | \[
Nu = \left[ 0.376 R_{e}^{1/2} + 0.057 R_{e}^{2/3} \right]^{1/3} R_{e}^{1/3}
\]                                                                 | [32]      |
|                                                                 | \[
4.18 R_{e}^{1/3} - 0.92 \ln \left( \frac{4.85372}{R_{e}} \right) + 1
\]                                                                 | [32]      |
Paper V
Effect of the bed compaction on fixed bed combustion

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Abstract

Fixed bed combustion is widely used in small scale wood pellet or log fired boilers and grates. The bulk density of fuel bed has significant effect on combustion behavior, but it is true effect is not clear because it is highly dependent on particle size, shape and apparent particle density. This work investigated how the bulk density of fixed bed influences combustion behavior (i.e. conversion mass flux, flame velocity). Experiments were performed in a laboratory scale reactor using wood pellets with constant particle density. Bulk density was changed only by void fraction to eliminate the influence of particle density. Wood pellets of two diameters (6 and 8 mm) were sorted into two length-to-diameter ratios (1 and 3). Temporal mass of fuel bed and bed temperatures at several locations were measured to calculate conversion mass flux and flame velocity. A numerical simulation of fixed bed combustion was conducted in order to support experimental observation and to understand the detailed bed dynamics. The results indicated that void fraction had minor effects on overall bed conversion of wood pellet within the experimental conditions. On the other hand, simulation results indicated that the change in flame velocity, usually reported as the effect of bulk density, can be simply explained by the change of apparent particle density. It implies that apparent density of particles is important parameters of bed combustion.

Keywords: CFD, wood pellet, combustion, fixed bed
1. Introduction

Fixed bed combustion in a counter current mode (i.e. combustion front moves against the supplied air) is used mainly in small scale wood pellet or log fired boilers and grates. Several laboratory scale studies have been conducted in order to understand the dynamics of the fixed bed combustion (e.g. flame velocity, conversion mass flux) [1–3]. Important parameters are mainly fuel composition, operating condition and fuel morphology [1]. Although primary air supply is the most influential parameters [4], the reaction front speed is also correlated to fuel composition and packing structure of bed [2,5].

Bulk density of the bed is determined by void fraction and apparent particle density, where void fraction is affected by the packing structure of the bed due to the difference in particle size and shape. In addition, same bulk bed density can be formed with loose packing of high-density particle and dense packing of low-density particles. In a bed, where void fraction is unevenly distributed, the fluid flow is influenced by the resistance force put by the solid body. It can affect the development and distribution of flame in the bed. Therefore, special attention is required during investigation of the effect of bed morphology on bed combustion. Horttanainen et al. observed that increases of wood pellet diameter reduces flame mass flux [6]. Li et al. observed that flame front velocity decreases with increase of corn stalk length [7]. Yang et al. [8] conducted experiment on pinewood cubes and observed that ignition time increased and burning rate decreased with increase of fuel particle size. Thunman and Leckner showed that large particle size results in lower burning rate while particle density has no effect, which contradicts with our observation as shown later [3]. Therefore, it is unclear how void fraction and apparent particle density affect propagation of reaction front.

This study investigated how the dynamics of fixed bed combustion (i.e. conversion mass flux, flame velocity) changes due to the change of bed bulk density. Especially, the relative importance between particle density and packing conditions were investigated by experiments of different bulk density from same particle density, followed by sensitivity study of both particle density and bulk density by numerical simulation. Bulk density was changed by using wood pellets with two diameters (6 and 8 mm) and two length-to-diameter ratio (1 and 3). Wood pellet beds were combusted in a laboratory scale reactor and temporal mass of fuel bed, bed temperatures were measured. A numerical simulation was conducted in ANSYS fluent in order to understand the detailed bed dynamics.
2. Experimental

2.1 Sample

Wood pellets (mixture of spruce and pine) with the diameter of 6 mm and 8 mm (called 6 mm pellets and 8 mm pellets in this paper) were purchased from Bioenergi i Luleå AB for the experiment. Table 1 shows the ultimate analysis of the two biomass pellets. We sorted the pellets manually according to their length to vary the bulk density of bed. Two length-to-diameter ratios (L/D ratio) were chosen as the possible extreme conditions within the European standard of pellets production (i.e. L/D<4). The 8 mm pellets had L/D ratios of 2.51 and 1.2, corresponding to the bulk densities of 670 and 650 kg m\(^{-3}\), respectively. On the other hand, the L/D ratios were 2.87 and 1.37 with bulk densities of 635 and 625 kg m\(^{-3}\) for 6 mm wood pellet.

2.2 Experimental procedure

Fig 1 shows the schematic figure of a laboratory pot furnace used in this study. A detailed description of the laboratory furnace was published previously [9,10]. It consists of a cylindrical retort with 335 mm in height and internal diameter of 120 mm. It was electrically heated by PID controllers. Biomass sample was placed inside a cylindrical holder and placed inside the retort. Air was introduced from the bottom of the reactor. The retort was surrounded by thick wall of firebricks and was sealed to avoid surrounding air coming inside the reactor. The wall temperature of the lower part of the reactor, corresponding to the location of the bed, was kept at 723 K and that of upper part, corresponding to the freeboard, was kept at 1023 K. The cylindrical pot was placed on a scale and the temporal mass of fuel was recorded. Four thermocouples were placed inside the fuel bed to measure bed temperature.

2.3 Mathematical modeling

A fixed-bed combustion model by Gomez et al [11] was modified and used to study combustion of wood pellet in a packed bed. The model was two dimensional with assumption of porous zone of the bed. Standard porous media CFD (computational fluid dynamics) code in ANSYS fluent was modified with different sub-models by using the user defined function platform to account for solid phase. The main assumptions of the model are

- Porous bed is a disperse media.
- Thermally thin spherical-equivalent particles are assumed in the bed.
The particle density decreases during drying and devolatilization while the particle diameter shrinks during char oxidation.

The rate of drying changes against temperature according to the Arrhenius law.

Devolatilization can be approximated by three lumped reactions.

The solid and gas phases exchange heat by both convection and radiation. The gases released by the solids are introduced in the gas phase at the same temperature as the solid phase.

The gas mixture is incompressible and follows ideal gas law.

The presence of solid phase in the packed bed influences the flow, hence, the development of the flame. Commercially available CFD code for porous zone does not have the necessary sub-models to present packed bed combustion in solid phase (e.g. solid conversion, effect intra-particle mass and heat transfer on conversion, void fraction development). Hence, such sub-models were implemented to the CFD code through user defined functions, UDF, written in C++. The combustion chamber was divided into two separate zones. First zone describes the bed where both solid and gas phases exist and their interaction was considered by model described below. The second zone describes freeboard, and only gas phase was modelled. In this model, six variables were externally defined to describe the properties of the solid phase: 1) temperature 2) the solid fraction 3) the moisture density 4) the dry biomass density 5) the char density 6) the particle characteristic volume. Table 2 shows governing equations for solid phase variables and their source terms are listed in Table 3.

Table 4 shows the kinetic parameters for drying, pyrolysis and char oxidation. The product of pyrolysis was assumed to be CO, CO2, H2, H2O, CH4 and C6H6. Product gas of pyrolysis was calculated by the method presented by Thunman et al [12]. The gas phase reactions were modeled with finite rate/eddy dissipation model with Magnussen Constant, A=0.6 [13]. Table 5 shows the gas phase reactions and kinetics. The turbulence was modeled with the realizable k – ε model with enhanced wall treatment for the near wall region. The flow through the solid phase was formulated based on physical velocity formulation.

The effect of solid phase on gas phase was modeled by adding mass, species, energy, momentum, turbulent kinetic energy and turbulent dissipation rate sources. The masses, species and energies that are produced as a result of heterogeneous reactions were added to the cells where reaction takes place in the gas phase. The momentum equation was modified
through addition of viscous and inertial resistance [14]. Turbulent kinetic energy and turbulent
dissipation rate due to the presence of solid particles were added [15] as:

\[
S_k = \rho \epsilon_m (1 - \epsilon)
\]

\[
S_\epsilon = C_{\mu} \frac{\epsilon^2}{k_m} (1 - \epsilon)
\]

\[
\epsilon_m = 3(1 - \epsilon)^2 \alpha^2 \frac{dM}{d\rho}
\]

\[
k_m = 3.7(1 - \epsilon)^{2.5} \alpha
\]

The heat and mass exchange between phases are modeled in a formulation analogous to the
experimental correlation of Wakao and Kaguei for Nusselt and Sherwood number [16]. Equivalent
diameter, a function of particle length and diameter, was considered as the
characteristic length of the particle. As a result, mass and heat exchange between phases is
influenced by the particle shape and size. Detailed description about thermal conductivity,
diffusivity and other model parameters can be found in Gomez et al., [11].

The radiative heat transfer was modeled with discrete ordinate model (DOM) and was
modified to account the presence of solid phase in the model[11,17]. Standard CFD code
solves a transport equation for radiation (RTE) and adds a source term in the gas phase. The
effect of solid phase on RTE was included by modification of the solid phase absorption and
scattering coefficients and adds one additional source term in the solid phase energy equation.
The detailed description of this method is described in ref [11,17]. Eq. 25 shows the modified
RTE considering both gas and solid phases. Eq. 26 and 27 shows the source terms for gas and
solid phases energy equations, respectively.

\[
\nabla I(r,s) + \left( a_s + a_g + \sigma_s + \sigma_g \right) I(r,s) = \left( \frac{a_s n^2 \sigma_s}{\pi} + \frac{a_g n^2 \sigma_g}{4\pi} \right) \int_0^{4\pi} I(r,\theta) \Phi(r,\theta) d\theta
\]

\[
S_{r,rad} = \int_0^{4\pi} \left( a_s I(r,s) - \frac{a_s n^2 \sigma_s}{\pi} \right) d\theta
\]

\[
S_{g,rad} = \int_0^{4\pi} \left( a_g I(r,s) - \frac{a_g n^2 \sigma_g}{\pi} \right) d\theta
\]

Transport equations were solved by built-in algorithm of the commercial CFD software. The
spatial and transient discretization was solved with the second order upwind and second order
implicit method, respectively. The pressure-velocity coupling was solved with SIMPLEC
(Semi-Implicit Method for Pressure Linked Equations-Consistent) method. The time step was 0.1 sec in the simulation.

3. Results and discussion

This section discussed about the effect of bed density on combustion of pellet in a bed. Experimental results show the effect of bulk density due to the change in bed packing at constant particle density. Figure 2 shows relation between flame velocity and bulk densities of the bed at two different air flows. The flame velocity was experimentally measured from a distance between two thermocouples and the time elapsed since the first one reaches 800 K until the second one is at the same temperature [11]. Flame velocity was increased with increase of the bulk density from 625 to 635 kg m\(^{-3}\) but flame velocity was less influenced by bulk densities when it varied between 635 to 670 kg m\(^{-3}\). In contrary, the flame velocity was significantly affected by the increase of air flow rate from 20 to 30 l min\(^{-1}\) of bulk densities when the bulk density was higher than 635 kg m\(^{-3}\). However, it was little affected by air flow rates when bed density was 625 kg m\(^{-3}\).

Fig 3 shows conversion mass flux as a function of bulk density of the bed. The conversion mass flux was estimated only between 10 to 90% of conversion. The effect of bulk density on conversion mass flux was not evident as it varies abruptly with the bed density. Air flow rate, on the other hand, affected the conversion mass flux significantly. It is likely due to increase of mass transfer rate at high flow rate.

Bulk density of the bed, in our experiments, had insignificant influence on the overall conversion of the bed. In addition, flame velocity was only affected by bulk density when it was varied between 625 and 635 kg/m\(^3\). It implies that the early stage of fuel conversion (e.g. ignition, drying) might be affected at low bulk density of the bed.

We varied bulk densities of the bed by changing particle lengths and diameters during experiment. It makes bed having different void fraction with identical particle density. We developed a CFD model to estimate if particle density, other than void fraction, has any influence on flame velocity. Fig. 4 shows relation between flame velocity and bulk density of the bed when void fraction of the bed was kept constant (i.e. 51%) and particle density was varied. Flame velocity decreased with the increase in bulk density between 300 and 650 kg/m\(^3\) but approaching towards an asymptotic value at high density. This tendency is in agreement with the previous experimental observation by Porteiro et al. [2]. Fig. 5 and 6 shows the
particle density and solid temperature in the bed at simulation time of 1000 seconds. Both particle density and temperature showed that devolatilization front moved faster in low density condition (i.e. $\rho_{\text{bulk}} = 300 \text{ kg/m}^3$) than in high density fuel condition (i.e. $\rho_{\text{bulk}} = 585 \text{ kg/m}^3$). More mass is available in a cell-volume for high density than low density fuels. Energy required for heating up, drying and devolatilization was also higher in high density than low density fuels. As a consequence, the local temperature increase was delayed for high density. It reduces the heat transfer inside the bed from hot to cold part. Relatively large amount of gas was produced in the same volume during drying and pyrolysis, which made the local gas mixture to be fuel rich. As a result, the ignition of the volatiles is delayed.

4. Conclusions

Bulk density of the bed depends on both void fraction and particle density. The results under the experimental conditions in this study indicated that void fraction had small effect on conversion behavior of fixed bed during combustion of wood pellet. In contrary, our simulation results indicated that apparent particle density significantly affected the flame velocity. It implies that apparent density of particles is an important parameters of bed combustion. On the other hand, the effect of air flow rate on conversion of the wood pellet in a bed was equally important as apparent particle density.

There are some limitations in the present model that can introduce major uncertainties. The limitations are the two dimensional representation of the reactor, no shrinkage of the bed, no movement of mass and energy in solid phase, no influence of particle movement on turbulence, incomprehensive devolatilization kinetic model and absence of proper definition of porosity distribution close to the wall. The effect of those limitations was obviously reflected on the estimation by the model. For instance, the CFD model underestimated the flame velocity. However, it managed to show a flame velocity and bulk density relationship which is similar to the previously published experimental data. This implies that the model can provide good qualitative than quantitative information. Further improvement on above mentioned limitations may also make the model quantitatively accurate.
Acknowledgments

We thank Bio4Energy, a strategic research environment appointed by the Swedish government, and Swedish Energy Agency for supporting this work.
References


Captions

Figure 1: A schematic of the experimental setup for bed combustion

Figure 2: Flame velocity with bulk density of the bed. The apparent density of the particle was 1170 kg/m$^3$.

Figure 3: Conversion mass flux against bulk density of the bed

Figure 4: Simulated flame velocity against bulk density of the bed. The void fraction was 51% in all simulations. The air flow rate was 20 l/min.

Figure 5: Wood density contour in fuel bed at three different bulk densities. Simulation time was 1000 sec. The air flow rate was 20 l/min.

Figure 6: Solid temperature contour in fuel bed at three different bulk densities. Simulation time was 1000 sec. The air flow rate was 20 l/min.
### Notations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_p$</td>
<td>specific heat</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$C_2$</td>
<td>turbulence model constant</td>
<td></td>
</tr>
<tr>
<td>$d$</td>
<td>diameter</td>
<td>m</td>
</tr>
<tr>
<td>$E$</td>
<td>activation energy</td>
<td>J mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta h^o$</td>
<td>heat of reaction, J kg$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$I$</td>
<td>irradiation</td>
<td>W m$^{-2}$</td>
</tr>
<tr>
<td>$R$</td>
<td>ideal gas constant</td>
<td>J K$^{-1}$ mol$^{-1}$</td>
</tr>
<tr>
<td>$M$</td>
<td>molecular weight</td>
<td>kg kmol$^{-1}$</td>
</tr>
<tr>
<td>$r$</td>
<td>particle radius</td>
<td>m</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>s</td>
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### Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>$\alpha$</td>
<td>absorption coefficient, m$^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>solid fraction, -</td>
</tr>
<tr>
<td>$\varepsilon'$</td>
<td>turbulence dissipation, (m$^2$s$^{-3}$)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>thermal conductivity, W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density, kg m$^{-3}$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stefan-Boltzmann constant, W m$^2$ K$^{-4}$</td>
</tr>
<tr>
<td>$\sigma_{scat}$</td>
<td>scattering coefficient, m$^{-1}$</td>
</tr>
<tr>
<td>$\omega$</td>
<td>rate of reaction, kg m$^{-3}$ s$^{-1}$</td>
</tr>
</tbody>
</table>

### Subscript

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$c$</td>
<td>char</td>
</tr>
<tr>
<td>$conv$</td>
<td>convection</td>
</tr>
<tr>
<td>$eff$</td>
<td>effective value</td>
</tr>
<tr>
<td>$g$</td>
<td>gas</td>
</tr>
<tr>
<td>$i$</td>
<td>specie i</td>
</tr>
<tr>
<td>$j$</td>
<td>reaction j</td>
</tr>
<tr>
<td>$S$</td>
<td>source</td>
</tr>
<tr>
<td>$s$</td>
<td>solid</td>
</tr>
<tr>
<td>reac</td>
<td>reaction</td>
</tr>
<tr>
<td>------</td>
<td>----------</td>
</tr>
<tr>
<td>p</td>
<td>particle</td>
</tr>
<tr>
<td>0</td>
<td>initial</td>
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</table>
Table 1: Fuel analysis of the 8 mm and 6 mm pellets

<table>
<thead>
<tr>
<th>Sample</th>
<th>8 mm pellets</th>
<th>6 mm pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td>C [wt.%]</td>
<td>50.6</td>
<td>50.6</td>
</tr>
<tr>
<td>H [wt.%]</td>
<td>6.2</td>
<td>6.1</td>
</tr>
<tr>
<td>N [wt.%]</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>O (by difference)</td>
<td>42.69</td>
<td>42.82</td>
</tr>
<tr>
<td>Ash content [wt.%]</td>
<td>0.50</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Table 2: Governing equations of solid phase variables

<table>
<thead>
<tr>
<th>Equation Description</th>
<th>Equation</th>
</tr>
</thead>
</table>
| Solid temperature                         | \[
\frac{d\left(p_C^e T_C\right)}{dt} = \varphi \left(\lambda_C e \nabla T_C\right) + S_e
\] |
| Solid fraction                             | \[
\frac{dx}{dt} = - \frac{\omega_{\text{char}}}{\rho P} C_p x
\] |
| Third power of particle diameter           | \[
\frac{dD}{dt} = - \frac{\omega_{\text{char}}}{\rho P} D x
\] |
| Moisture density                           | \[
\frac{d\left(p_{\text{moist}}\right)}{dt} = -\omega_{\text{moist}} C_p x
\] |
| Dry wood density                           | \[
\frac{d\left(p_{\text{wood}}\right)}{dt} = -\omega_{\text{wood}} C_p x
\] |
| Char density                               | \[
\frac{d\left(p_{\text{char}}\right)}{dt} = \left(\omega_{\text{char}} - \Delta \omega_{\text{char}}\right) C_p x
\] |
| Particle total density                     | \[P_P = p_{\text{moist}} + p_{\text{wood}} + p_{\text{char}}\] |
| Energy equation source                     | \[S_e = S_{\text{conv}}^e + S_{\text{conv}}^e + S_{\text{conv}}^{\text{loss}} + S_{\text{conv}}^{\text{loss}}\] |
Table 3: Source terms for the solid phase governing equations.

<table>
<thead>
<tr>
<th>Source Term</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying rate</td>
<td>( \omega_{\text{moist}} = \rho_\text{moist} A \exp \left( -\frac{E}{RT} \right) ) (9)</td>
</tr>
<tr>
<td>Devolatilization rate</td>
<td>( \omega_{\text{wood}} = \rho_\text{wood} \sum_{i=1}^{i=2} A_i \exp \left( -\frac{E_i}{RT} \right) ) (10)</td>
</tr>
<tr>
<td>Char generations</td>
<td>( \omega_{G,\text{char}} = \rho_\text{wood} A_3 \exp \left( -\frac{E_3}{RT} \right) ) (11)</td>
</tr>
<tr>
<td>Char consumption rate</td>
<td>( \omega_{C,\text{char}} = K_{\text{glob}}^G A_V[O_2] M_e + K_{\text{glob}}^{G1} A_V[CO_2] M_e ) (12)</td>
</tr>
<tr>
<td>Char consumption rate</td>
<td>( + K_{\text{glob}}^{G2} A_V[H_2O] M_e )</td>
</tr>
<tr>
<td>Global char constants</td>
<td>( K_{\text{glob}}^G = \frac{1}{\gamma^G} ) (13)</td>
</tr>
<tr>
<td>Char oxidation parameter</td>
<td>( \varphi = \frac{2 + 4.3 \exp \left( \frac{-3390}{T} \right)}{2 \left( 1 + 4.3 \exp \left( \frac{-3390}{T} \right) \right)} ) (14)</td>
</tr>
<tr>
<td>Reaction heat</td>
<td>( S_r^{\text{react}} = -\omega_{\text{moist}} \cdot \epsilon \cdot \text{LH}<em>\text{moist} - \omega</em>{\text{wood}} \cdot \epsilon \cdot \text{LH}_\text{dev} + S_r^{\text{char}} \cdot \epsilon ) (15)</td>
</tr>
<tr>
<td>Char</td>
<td>( S_r^{\text{react}} = \left( K_{\text{glob}}^G A_V[O_2] M_e [2(\varphi - 1) \Delta H_{\text{CO}<em>2} + 2(\varphi - 1) \Delta H</em>{\text{CO}_3}] \right. ) (16)</td>
</tr>
<tr>
<td></td>
<td>( + K_{\text{glob}}^{G1} A_V[CO_2] M_e \Delta H_{\text{g1}} )</td>
</tr>
<tr>
<td></td>
<td>( + K_{\text{glob}}^{G2} A_V[H_2O] M_e \Delta H_{\text{g2}} )</td>
</tr>
<tr>
<td>Loss of energy from solid phase</td>
<td>( S_r^{\text{react}} = \left( \omega_{\text{moist}} + \omega_{\text{wood}} \cdot \epsilon + \omega_{C,\text{char}} \right) \cdot \epsilon \cdot \left( \frac{C_p}{T_0} \right) (1 - \Delta t) ) (17)</td>
</tr>
</tbody>
</table>
Table 4: kinetics of the heterogeneous reactions (solid phase) and gas phase reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Kinetic parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis and drying</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry wood → Gas</td>
<td>$4.38 \times 10^9 \exp(-152 \times 10^3/RT)$</td>
<td>[18]</td>
</tr>
<tr>
<td>Dry wood → tar</td>
<td>$1.08 \times 10^{10} \exp(-148 \times 10^3/RT)$</td>
<td>[18]</td>
</tr>
<tr>
<td>Dry wood → Char</td>
<td>$3.27 \times 10^{9} \exp(-111 \times 10^3/RT)$</td>
<td>[18]</td>
</tr>
<tr>
<td>Water → Vapor</td>
<td>$5.13 \times 10^7 \exp(-88 \times 10^3/RT)$</td>
<td>[19]</td>
</tr>
<tr>
<td>Heterogeneous char reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$CO_2 + \varphi O_2 \rightarrow 2(1 - \varphi)CO$ + $(2\varphi - 1)CO_2$</td>
<td>$K^{0.5} = 1.7185.T_e \exp(-9000/T_e)$</td>
<td>[11]</td>
</tr>
<tr>
<td>$C + CO_2 \rightarrow 2CO$</td>
<td>$K^{0.5} = 3.42.T_e \exp(-1.56 \times 10^9/T_e)$</td>
<td>[11]</td>
</tr>
<tr>
<td>$C + H_2O \rightarrow CO + H_2$</td>
<td>$K^{0.5} = 5.7114.T_e \exp(-1.56 \times 10^9/T_e)$</td>
<td>[11]</td>
</tr>
<tr>
<td>Gas phase reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_6H_6 + 4.5 O_2 \rightarrow 6CO + 3H_2O$</td>
<td>$R_{1,\text{kin}} = 1.3496 \times 10^8 \exp\left(-\frac{1.3496 \times 10^8}{RT}\right)[C_6H_6]^{1.5}[O_2]^{1.185}$</td>
<td>[11]</td>
</tr>
<tr>
<td>$CH_4 + 1.5 O_2 \rightarrow CO + 2H_2O$</td>
<td>$R_{2,\text{kin}} = 5.012 \times 10^{11} \exp\left(-\frac{2 \times 10^8}{RT}\right)[CH_4]^{1.5}[O_2]^{1.185}$</td>
<td>[11]</td>
</tr>
<tr>
<td>$H_2 + 0.5 O_2 \rightarrow H_2O$</td>
<td>$R_{3,\text{kin}} = 9.87 \times 10^9 \exp\left(-\frac{3.1 \times 10^7}{RT}\right)[H_2][O_2]$</td>
<td>[11]</td>
</tr>
<tr>
<td>$CO + 0.5 O_2 \rightarrow CO_2$</td>
<td>$R_{4,\text{kin}} = 2.239 \times 10^{12} \exp\left(-\frac{1.702 \times 10^8}{RT}\right)[H_2O]^{0.5}[O_2]^{0.25}[CO]$</td>
<td>[11]</td>
</tr>
<tr>
<td>$H_2O + CO \rightarrow H_2O + CO$</td>
<td>$R_{5,\text{kin}} = 2.780 \exp\left(-\frac{1.255 \times 10^7}{RT}\right)[CO][H_2O]$</td>
<td>[11]</td>
</tr>
<tr>
<td>$CO_2 + H_2 \rightarrow H_2O + CO$</td>
<td>$R_{6,\text{kin}} = 93690 \exp\left(-\frac{4.659 \times 10^7}{RT}\right)[CO_2][H_2]$</td>
<td>[11]</td>
</tr>
</tbody>
</table>
Figure 1: A schematic of the experimental setup for bed combustion, adopted from Ramin et. al [9]
Figure 2: Flame velocity with bulk density of the bed. The apparent density of the particle was 1170 kg/m$^3$. 
Figure 3: Conversion mass flux against bulk density of the bed
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