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Experimental and modelling study on the influence of wood type, density, water content, and temperature on wood devolatilization

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Abstract

Wood devolatilization experiments in a single particle combustor and comparison with a 1D devolatilization model were carried out to investigate the effects of wood particle properties and operation conditions on wood particle devolatilization time. The experiments were conducted with 3 mm spherical/cubic and 4 mm spherical particles at gas temperatures of 1200-1450°C and oxygen contents of 0-4.4 vol%. Both experimental and modelling results showed that the devolatilization time increases linearly with particle density for raw, wetted, and torrefied wood particles. A sensitivity analysis done with the 1D devolatilization model showed that the biomass devolatilization time is sensitive to particle size, moisture content, gas temperature and particle density, and insensitive to volatiles fraction and gas velocity under the investigated experimental conditions. Using the same devolatilization kinetics, the 1D model could predict well the devolatilization time of different wood species with different particle size, density and moisture content. With this in mind, a simple correlation for devolatilization time has been developed based on the simulation data from the 1D model. The correlation uses a four-variable function with input of particle size, moisture content, gas temperature and particle density to determine the devolatilization time of biomass. Experimental devolatilization time found in literature could be predicted within $\pm 25\%$ for large particles (1 mm-10 mm) under high temperature conditions (1000°C-1600°C).

Keywords: biomass, devolatilization, particle density, single particle model

1. Introduction

Biomass devolatilization involves chemical reactions coupled with internal and external heat and mass transfer [1–4]. Devolatilization is an important step for both ignition and burnout of biomass particles during combustion. Several experimental studies [5–9] have been done to investigate biomass devolatilization under high-temperature conditions ($\geq 1200^\circ\text{C}$) that are representative for pulverized biomass combustion [5,7–9]. The existing studies found that the devolatilization time of biomass particles decreases with increasing gas temperature and oxygen concentration [5], and increases with increasing particle size [5–8], moisture content [7] and density [8,9]. However, to the authors' knowledge, a comprehensive comparison of the influences of the different factors on devolatilization time has not been carried out under pulverized biomass combustion conditions. To support fuel selection and burner optimization in pulverized biomass-fired power plants, it is important to identify the key parameters controlling the devolatilization time of biomass particles, and to develop reliable modelling tools to describe the devolatilization process.

Detailed one-dimensional (1D) models have been developed to describe the devolatilization of single biomass particles [10–18]. The existing models have been used to study the effects of particle shape [10], moisture content [10,14], particle size [18], heat flux [17,18] on the biomass devolatilization and validated mainly by experiments under relatively low-temperature conditions ($T_g < 1200^\circ\text{C}$). These models have only been validated to a limited extent under high temperature conditions ($\geq 1200^\circ\text{C}$) with respects to the effects of particle shape [19], particle size [4,19,20]. Other important factors, such as the moisture content and density of particles are rarely specifically studied by experiments and modelling. In order to develop a reliable model that is applicable in pulverized biomass combustion. Comprehensive experimental data with different particle density and particle moisture content at high-temperature are desirable to validate the model.

Beside the detailed 1D models, empirical correlations have also been developed to estimate the devolatilization time of biomass particles [7,21–25]. Most of the existing correlations primarily

use a power law to correlate the devolatilization time with particle size with a number of fitting parameters under fluidized bed combustors with relatively low temperature ($<1000\text{ }^{\circ}\text{C}$) [21–25]. Empirical correlations are rarely reported for biomass devolatilization under pulverized flame conditions. Mason et al. [7] correlated the devolatilization time as function of particle moisture content, particle size, and particle density at a temperature of 1550°C for 3 different woody biomass at suspension combustion conditions. However, the obtained coefficients of different woody biomass particle are significant different, and the developed correlation has only been validated with a limited number of experiments. Thus, a more generic correlation valid for different biomass properties and operation conditions is required.

The present work aims to investigate the effects of particle properties and reactor conditions on biomass devolatilization under pulverized biomass combustion conditions. Experiments with spherical and cubic wood particles having different density, size, wood type, and moisture content were carried out in a single particle combustor under different temperature and gas atmosphere conditions. A comprehensive 1D devolatilization model developed from our previous work [4,26] was used to model the experiments. Finally, a simple correlation based on the 1D devolatilization model was introduced to estimate the devolatilization time of wood particles at high temperatures.

2. Experiments

2.1 Single particle combustor

A single particle combustor (SPC), designed for combustion studies of fuel particles with local conditions similar to that in pulverized fuel fired boilers was used [5]. Detailed descriptions of the reactor and experimental procedures can be found elsewhere [5,8,9]. In the experiments, an individual wood particle was held by a 0.3 mm titanium wire on a ceramic sample probe and suspended in the flue gas from hydrogen flame. The combustion process of the single wood particle was recorded by a video camera. In the present work, the devolatilization time is sum of ignition and pyrolysis time, the method to estimate the ignition and pyrolysis time can be found in our previous work [5]. The detailed image post-processing for determining the

devolatilization time is described in reference [5].

2.2 Materials

In a pulverized wood-fired power plant, particles fed to the pulverized burners are in as size range of from 10 μm to 5 mm wood particles [27], The millimeter-size wood particles in a pulverized biomass combustor may result in unburned carbon in both bottom and fly ash, and therefore need special attention [28]. In addition, the experiments with millimeter-sized wood particles are relatively easy to be carried out. In the present study, millimeter-size wood particles have been chosen for experiments in the single particle combustor. Three types of pine, beech, and bamboo were selected as the raw material in the series I experiments. The particles used in series I experiments are all spherical and having two different sizes of ~ 4 mm and ~ 3 mm. The proximate analysis and the inorganic composition are shown in Table 1. The mass and diameter of individual particles were measured by using a microbalance (± 0.01 mg) and a caliper (± 0.05 mm). For ~ 4 mm wood particles, the measured mean particle diameters of pine, beech, and bamboo particles were 4.00 mm, 4.13 mm and 3.97 mm, respectively. In the case of ~ 3 mm spherical wood particles, the mean diameters were 3.12 mm and 3.03 mm of pine and beech wood, respectively. To investigate the effects of density on devolatilization time, particles with significantly different mass were selected in the experiments. The corresponding density ranges were 400-900, 600-1100, and 400-900 kg/m^3 for pine, beech, and bamboo, respectively. The “density” in the present work refers to “particle density on dry basis”. To produce wetted wood particles with different moisture content, selected particles were submerged into deionized water. Then they were taken out and exposed to air to obtain a specified moisture content (as received based: $\sim 15.0\%$, $\sim 30.0\%$, $\sim 50.0\%$). The actual moisture content of an individual wetted particle varies slightly ($< 4\%$) from the averaged moisture content.

Table 1. Proximate analysis and inorganic composition of the three wood particles used in series I experiments

Parameter	Unit	Pine	Beech	Bamboo
Moisture Content	ar%	6.9	4.9	5.2
Ash	db%	0.2	0.6	1.9
Volatiles	db%	86.6	83.7	79.0
Fixed carbon	db%	13.2	15.7	19.1
Al	mg/kg, db	10	<10	<10
Fe	mg/kg, db	42	29	38
P	mg/kg, db	82	70	82
Ti	mg/kg, db	<3	<3	<3
K	mg/kg, db	150	1700	8700
Na	mg/kg, db	20	<10	22
Ca	mg/kg, db	530	2000	<200
Mg	mg/kg, db	75	290	490
Si	mg/kg, db	<100	<100	290

In series II experiments, particles (~3 mm cubic) from five wood types with and without torrefaction pretreatment were used. The torrefaction was made using a 3-zone electrically heated tube oven [8]. After the oven was stabilized at 290°C, an Al₂O₃ boat (120×30×17 mm, without a lid) carrying 30 wood particles (6 samples of each wood species) was inserted into the center of the oven under a N₂ flow of 15 STP l/min for 1 hour. The proximate analysis and other properties of particles with and without torrefaction are shown in Table 2. The wood particles have small differences and variations in length, between 2.78 and 3.03 mm with a maximum standard derivation of 0.03 mm. The apparent wood particle densities were calculated to vary from 184 to 698 kg/m³ based on the weighted mass of particles.

Table 2. Properties of ~3 mm cubic wood particles with and without torrefaction

Parameter	Unit	Balsa	Paulownia	Pine	Beech	Sapele
Wood without torrefaction						
Moisture	ar%	5.0	4.9	6.4	6.3	7.7
Ash	db%	2.1	0.6	0.1	0.5	0.9
Volatiles	db%	81.1	80.2	82.1	80.4	74.3
Fixed carbon	db%	16.8	19.1	17.8	19.1	24.8
K	mg/kg, db	5522	2122	85	1060	65
Na	mg/kg, db	189	30	9	64	64
Ca	mg/kg, db	2318	467	250	1032	3399
Mg	mg/kg, db	644	27	61	203	457
Si	mg/kg, db	737	526	321	427	758
Mass	mg	6.70± 0.25	9.30± 0.35	11.70± 0.10	17.50±0.41	19.00± 0.69
Cube lengths	mm	3.02±0.03	3.03±0.02	2.97±0.03	2.96±0.03	3.01±0.03
Apparent density	kg/m ³	243	335	446	673	698
Wood with torrefaction						
Moisture	ar%	3.0	2.6	3.0	3.8	3.9
Ash	db%	3.0	0.8	0.1	0.8	1.1
Volatiles	db%	69.0	76.4	78.5	73.5	68.6
Fixed carbon	db%	28.0	22.8	21.4	25.7	30.3
Mass	mg	4.25±0.18	6.51±0.18	8.26±0.21	12.67±0.24	14.00±0.50
Cube lengths	mm	2.85±0.12	2.94±0.06	2.77±0.14	2.78±0.14	2.89±0.10
Apparent density	kg/m ³	184	256	389	589	583

2.3 Operating conditions

120 The operating conditions of experiment series I and II are shown in Table 3. Series I experiment
 121 has been carried out in the single particle combustor with different temperatures of
 122 1208/1221/1357/1400/1441°C, and oxygen concentrations of 0.0%/4.4%, while series II
 123 experiments have been carried out using a temperature of 1256°C and an oxygen content of
 124 2.8%. The extracted flue gas samples from the reactor outlet were dried and the O₂
 125 concentrations were measured. Based on the stoichiometry and the ideal gas assumption, the

concentrations of O₂ and H₂O in the reactor were calculated as shown in Table 3. According to our previous work [8], the difference between the calculated O₂ concentration and the measured value is small, therefore the calculated concentrations of O₂ and H₂O are used in the modelling. The averaged gas velocity in the single particle combustor was about 1.5 m/s as shown in Table 3. The wall temperature is assumed to be 200°C (estimated from the measured radial temperature distribution of our previous work [5,8]) lower than the gas temperature in our devolatilization model.

Table 3. Operating conditions of single particle combustor

No.	Measured gas temperature (°C)	Calculated gas velocity (m/s)	Calculated O ₂ concentration (wet basis, vol%)	Calculated H ₂ O concentration (wet basis, vol%)
Series I				
0% O ₂ / 1214°C	1221	1.49	0.0	26.8
0% O ₂ / 1357°C	1357	1.50	0.0	39.7
0% O ₂ / 1400°C	1400	1.42	0.0	39.1
0% O ₂ / 1441°C	1441	1.40	0.0	41.8
4.4%O ₂ / 1210°C	1208	1.43	4.4	25.7
Series II				
2.8% O ₂ / 1256°C	1256	1.50	2.8	27.0

3 Model description

3.1 Model assumption

The model used in the present work is originally developed by Johansen et al.[4] to study the influence of intraparticle heat transport on biomass devolatilization. It is further modified by including the effects of heat of devolatilization, and modifying the water drying model and the devolatilization kinetics in this paper. The model includes phenomena of internal and external heat transfer, water evaporation, and devolatilization kinetics. The general assumptions are listed as follows:

(1) The model is an one-dimensional model for spherical wood particle, which neglects the anisotropy of wood particles, even though the anisotropy of wood is expected to be important when the thermal conductivity along and across the fiber direction of wood particles is significantly different. A two- or three-dimensional model may be considered to implement the

anisotropy of wood particle. However, 2D or 3D model will results in much more complex and computationally intensive than a 1D model [2]. Moreover, the thermal conductivity along and across the fiber direction is not easily measured from experiments, while there are available and validated expression of effective dry wood conductivity. Furthermore, previous studies [10–18] have shown that appropriate devolatilization modelling can be obtained without consider the anisotropy of the wood. Thus, the anisotropy of wood is neglected in the present model.

- (2) No convective heat transport takes place inside the particle, only heat conduction;
- (3) No mass transfer limitation of the released volatiles is included;
- (4) The reactor walls contribute to the radiative heat flux between the particle external surface and the environment;
- (5) A fully devolatilized particle has a shrinkage factor of 0.2 (volume based) and the particle volume shrinks linearly with the devolatilization degree.

- (6) The devolatilization time is determined by 99% particle conversion (the amount of released moisture and volatiles divided by the amount of initial moisture and volatiles inside particle);

The assumptions above are commonly applied in the particle modelling literature [4,10,12,14,29].

3.2 Governing equations

The devolatilization model, which includes both internal and external heat transfer, is described as Eq. (1):

$$C_p \rho_p \frac{\partial T(t, r)}{\partial t} = \frac{1}{r^2} \left(r^2 \lambda_{eff} \frac{\partial T(t, r)}{\partial r} \right) - \frac{dX_w}{dt} \rho_{DB} Y_{w0} Q_w - \frac{dX_{vol}}{dt} \rho_{DB} Y_{vol0} Q_{pyro} \quad (1)$$

Here, C_p , ρ_p , λ_{eff} are the specific heat capacity (J/(kg K)), particle density (kg/m³), effective thermal conductivity (W/(m K)) of the biomass particle at time t , respectively. ρ_{DB} is the initial particle density (kg/m³) at $t=0$ s, r , the radial position (m), t , time (s), T , the particle temperature (K), Y_{w0} is the initial water mass fraction (dry basis), and Y_{vol0} is the initial mass fraction of volatiles (dry basis). Q_w and Q_{pyro} are the evaporation heat and devolatilization heat (J/Kg),

respectively. dX_w/dt and dX_{vol}/dt are conversion rates described by a drying model and a devolatilization model.

The boundary conditions of the model include both convection and radiation heat transfer are described by Eq. (2) and Eq. (3).

$$\left. \frac{\partial T}{\partial r} \right|_{r=0} = 0, \text{ all } t \quad (2)$$

$$\lambda_{eff} \left. \frac{\partial T}{\partial r} \right|_{r=R} = h_c (T_g - T_s) + \xi \sigma (T_w^4 - T_s^4) \quad t > 0 \quad (3)$$

Here, h_c is the convective heat transfer coefficient, $W/(m^2K)$, T_g , T_w , and T_s are gas, wall and particle external surface temperatures (K), ξ is the particle emissivity, which depends on many factors (e.g. temperature, wood type, surface structure). The typical values reported in literature are in a range of 0.7-1.0 [2]. Because of the difficulties in an accurate determination of the particle emissivity under different conditions, a fixed particle emissivity of 0.85 is selected in the 1D model. The effects of emissivity on modelling results is shown in the section of sensitivity analysis. σ is Stefan-Boltzmann constant ($5.6704 \times 10^{-8} \text{ J}/(m^2K^4s)$).

3.3 Physical properties

Table 4 summarizes the physical properties used in this work. The effective heat conductivity (λ_{eff}) of the biomass particle is expressed as a sum of the conduction in the solid phase (λ_p), gas phase ($\varepsilon_g \lambda_g$), liquid moisture ($\varepsilon_w \lambda_w$), and radiative conduction (λ_r) [30]. The solid phase heat conductivity λ_p is a function of volatiles conversion [4]. The conduction by radiation λ_r is a function of particle pore size and particle temperature [4,30], with the particle pore diameter (d_{pore}) assumed to vary linearly with the conversion [4]. When the moisture content is larger than Y_{fsb} (fibre saturation point), the heat required for water evaporation is the heat of vaporization, $\Delta_{vap}H$. When it is smaller than Y_{fsb} , the heat required is the sum of heat of vaporization and desorption of bound water [4,31]. The convective heat transfer coefficient (h_c) of a spherical particle is determined by Ranz and Marshall equation [32]. The shrinkage factor (ϕ , volume based) which is dependent of the experimental conditions and wood type as reported in previous studies [10,16,33], is assumed to be 0.2 in this work. All of the thermos-

physical properties described above are summarized in Table 4. The bulk gas physical properties are not shown in Table 4, but given in supplementary material.

Table 4. A summary of physical properties used in the particle-scale models for wood devolatilization

Parameters	Units	Description	Expressions	Ref.
λ_B	W/m/K	Dry wood conductivity	$0.13+3\times 10^{-4}(T-273)$, $T\leq 1006$ K 0.3 , $T>1006$ K	[4,34]
λ_C	W/m/K	Char conductivity	0.071	[10,16,35,36]
λ_p	W/m/K	Particle conductivity	$\lambda_B(1-X_{vol})+\lambda_C X_{vol}$	[4]
λ_g	W/m/K	Gas conductivity	0.0258	[4,11,16,17,36,37]
λ_r	W/m/K	Radiative conductivity	$\sigma d_{pore} T_p^3/\xi$	[4,10,11]
λ_w	W/m/K	Water conductivity	$0.6065(-1.4845+4.1229(T_p/298.15)-1.6387(T_p/298.15)^2)$	[38]
d_{poreB}	m	Wood pore diameter	3.2×10^{-6}	[4,39]
d_{poreC}	m	Char pore diameter	1.0×10^{-4}	[4,17,39]
X	-	Particle conversion	$(X_w Y_{w0} + X_{vol} Y_{vol0})/(Y_{w0} + Y_{vol0})$	
d_{pore}	m	Particle pore diameter	$d_{poreB}(1-X)+d_{poreC}X$	[4,17]
ε_g	-	Particle porosity	$1-\rho_{DB} Y_{w0}(1-X_w)/\rho_{true}/(1-\varphi)-\rho_{DB} Y_{vol0}(1-X_{vol})/1000/(1-\varphi)$	[29,33,39]
ε_w	-	Water volume fraction	$\rho_{DB} Y_{vol0}(1-X_{vol})/1000/(1-\varphi)$	
λ_{eff}	W/m/K	Effective conductivity	$\lambda_p+\lambda_{gas}\varepsilon_g+\lambda_r+\lambda_w\varepsilon_w$	[4,17]
ρ_g	kg/m ³	Gas density	$pM_w/R/T_g$	[36]
ρ_p	kg/m ³	Particle density	$\rho_{DB}(1+Y_{w0})(1-X)/(1-\varphi)$	[4]
C_{pc}	J/kg/K	Char heat capacity	$(1000R/11.3)(g(380/T)+2g(1800/T))$	[4,10,40]
C_{pB}	J/kg/K	Wood heat capacity	$(1000R/7.72)(g(380/T)+2g(1800/T))$ $g(x)=x^2\exp(x)/(\exp(x)-1)^2$	[4,10,40]
C_{pw}	J/kg/K	Water heat capacity	4180	[33]
C_p	J/kg/K	Particle heat capacity	Mass averaged	
$\Delta_{vap}H$	J/kg	Heat of vaporization	$1000(3179-2.5T_p)$	[4]
$\Delta_{ds}H$	J/kg	Heat of desorption	$0.4\Delta_i H(1-Y_w/Y_{fsp})^2$	[41]
Q_w	J/kg	Heat of water drying	$\Delta_{vap}H$, ($Y_w>Y_{fsb}$) $\Delta_{vap}H+\Delta_{ds}H$ ($Y_w\leq Y_{fsb}$)	[4,41]
Y_{fsb}	-	Fiber saturation point	$\text{Max}(Y_{fsb}=0.598-0.001T_p, 0.2)$	[31]
ξ	-	Emissivity	0.85	[4,10,17]
σ	J/(m ² K ⁴ s)	Stefan-Boltzmann constant	5.6704×10^{-8}	[42]
h_c		Convective heat transfer coefficient	$\lambda_{bulk_g}(2+0.6Re^{0.5}Pr^{(1/3)})/d_p$	[4,32]
d_p	m	Particle diameter	$d_{p0}(1-\varphi)^{1/3}$	
φ		Particle shrinkage	$0.2X$	[13]

3.4 Drying and devolatilization models

The drying process is described by a first order kinetic model as shown in Eq. (4) [33]:

$$\frac{dX_w}{dt} = k_w (1 - X_w) \quad (4)$$

The rate constant k_w follows an Arrhenius expression. The kinetic data are shown in Table 5.

Following Johansen et al. [4], the net devolatilization rate is described by Eq. (5) and Eq. (6)

$$\frac{dX_{vol}}{dt} = k_{vol} (1 - X_{vol}) \quad (5)$$

$$k_p = k_v + \min(k_t, k_{tv}) \quad (6)$$

k_v , k_t , and k_{tv} follows the Arrhenius expression. They are the rate constant of wood to volatiles by primary devolatilization, wood to tar by primary devolatilization, and tar to volatiles by secondary devolatilization, respectively. The net devolatilization rate constant is lumped as k_p as defined in Johansen et al. [4]. The kinetic data are derived by Wagenaar et al. [43] and have been widely used to simulate both small and large wood particles [4,10,26,44]. The kinetic parameters are listed in Table 5. Different values of reaction enthalpy, varying from 200 to 600 kJ/kg, have been reported for wood devolatilization [45]. In our model, a value of 418 kJ/kg is used based on reference [10], in which a similar experimental setup was used to study wood devolatilization and combustion.

Table 5. Kinetic parameters used in the devolatilization model

Parameters	Pre-exponential factor (s^{-1})	Activation energy (kJ/kg)	Reference
k_w	5.13×10^{10}	88	[33]
k_v	1.11×10^{11}	177	[43]
k_t	9.29×10^9	149	[43]
k_{tv}	4.28×10^6	107.5	[43]

4 Results and Discussion

4.1 Particle evolution

In order to analyze the particle evolution during drying and devolatilization, the radial distribution of particle temperature, moisture conversion, and volatiles conversion with specified particle conversion (defined as $(X_w Y_{w0} + X_{vol} Y_{vol0}) / (Y_{w0} + Y_{vol0})$) of 0.01, 0.5, and 0.9 are obtained under the conditions of $T_g = 1214^\circ\text{C}$ and 4 mm wood particle. As shown in Fig. 1 (a), when the total conversion is 0.01, the temperature of the particle outer layer between a radius of 1.2 mm and 2.0 mm is in a range of 100–600°C. A large amount of moisture is evaporated, while only a small amount of volatiles is released. When the particle conversion is 0.5, the temperature of the entire particle is higher than 100°C as shown in Fig. 1 (b), and the drying of moisture is almost finished. With a particle surface temperature of $\sim 850^\circ\text{C}$ and a center temperature of $\sim 200^\circ\text{C}$, significantly different conversion degrees are observed at different radius positions. When the particle conversion is 0.9, the particle center temperature is larger than 400°C. All moisture is evaporated, and the volatiles only remain in the particle center. From Fig. 1, it is also seen that the moisture front propagates inward to the center of the particle, followed by the volatiles released front. The results are consistent with other studies [29,45,46].

235

236 Figure. 1. Radial distribution of wood particle temperature (T), conversion of moisture (X_w) and

237 conversion of volatiles (X_{vol}) under different particle conversion (0.01, 0.5, and 0.9 corresponding to ta

238 residence time of 0.27, 3.37, and 7.77 s, Simulation conditions: $d_p = 4$ mm, Moisture = 4.9 ar%, Vol =

239 83.7 db%, FC = 15.7 db%, $T_g = 1214^\circ\text{C}$, $T_w = 1014^\circ\text{C}$, 0.0% O_2 , $\rho_{DB} = 700 \text{ kg/m}^3$).

4.2 Devolatilization time

In Fig. 2 (a) ~ (c), the experimental and predicted devolatilization times at different temperatures (1214/1357/1400/1441 °C) are compared for ~4 mm beech, pine, and bamboo wood. The devolatilization time decreases with increasing gas temperature due to an increased heat transfer, consistent with the results of other studies [5,12,22,47–49]. The predicted results agree with the experiments within about $\pm 25\%$ for all three woody biomass.

In Fig. 2 (d) ~ (f), the experimental and predicted devolatilization times of beech, pine, and bamboo wood with moisture content from 4.9~6.9% (raw wood particle) to ~50% at 1208 °C are compared. An increased devolatilization time is observed with an increase of moisture content for all the wood types. A higher moisture content results in a larger heat consumption for the drying process and thereby delays devolatilization. Again, the predicted devolatilization time agrees with the experimental data within $\pm 25\%$.

The effect of density on devolatilization time can also be observed in Fig. 2 (a) ~ (f). The devolatilization time increases with an increase of the particle density. The reason is that the devolatilization process is dominated by heat transfer for thermally-thick particles [3,26]. A higher density of the particles results in a lower heating rate, mainly due to an increased thermal capacity of the particles, and thereby increases the devolatilization time. Moreover, both the experimental and the model predicted results show that the devolatilization time increases linearly with an increase in the density, consistent with the study of Haseli et al. [18]. The results suggest that under the studied conditions, the density is the primary parameter that influences the devolatilization time of the biomass particles.

Figure. 2. A comparison between the experimental and model predicted devolatilization time with variation of gas temperature, moisture content and particle density for three different woods (beech, pine, bamboo) in series I experiments (spherical particle), Fig. 2 (a) ~ (c) show received particles devolatilized at different temperatures (1214/1357/1400/1441°C), Figure. 2 (d) ~ (f) show particles with different moisture content (as received particle basis, ~15 wt%, ~30 wt%, ~50% wt%) devolatilized at 1208°C.

Figure. 3 presents the experimental and predicted devolatilization time of ~3mm spherical wood particles (pine and beech) devolatilized with and without the presence of oxygen. With the presence of oxygen, the released volatiles are combusted near the particle, supplying extra heat and thereby leading to a small decrease in devolatilization time. However, the experimental

results in Fig. 3 show that the presence of 4.4% O₂ only decreases the devolatilization time slightly, compared to the case with 0.0% O₂. The particle density is still a key parameter affecting the devolatilization time almost in a linear trend as shown in Fig. 3.

Figure. 3. A comparison between the experimental and model predicted devolatilization time with a variation of wood types (Pine, Beech) and oxygen concentration (0.0% O₂, 4.4% O₂) in series I experiments (spherical particles), the particle diameter of pine and beech is 3.12 mm and 3.03 mm, respectively.

Figure. 4 shows the experimental and predicted devolatilization time of different woods with or without torrefaction in series II experiments (~3 mm cubic particles). The diameter used in modeling is based on the equivalent particle volume. The volume equivalent method is simple approximation which is proposed in previous studies [4,28]. The predicted devolatilization time for different wood types, torrefaction treatment, particle moisture content, and particle size conditions is in good agreement with measurements. The tendency in Fig. 4 further implies the significant influence of particle density on devolatilization time.

Figure 4. A comparison between predicted and experimental devolatilization time of different wood with or without torrefaction in series II experiments (cubic particles), the oxygen concentration of bulk gas is about 2.8% and the temperature is 1256°C.

4.3 Sensitivity analysis

4.3.1 Physical properties

There are several parameters in the model that may affect the predicted devolatilization time, such as emissivity (ε), gas conductivity (λ_g), char conductivity (λ_c), raw wood conductivity (λ_B), heat of devolatilization (Q_{pyro}), convective heat transfer coefficient (h_c), char pore size (d_{poreC}), raw wood pore size (d_{poreB}), raw wood thermal capacity (C_{pB}), char thermal capacity (C_{pC}), wood true density (ρ_{true}), shrinkage coefficient (ϕ), and fixed carbon content (FC). Figure 5 shows the results of a sensitivity analysis done by decreasing and increasing each parameter by 50% for a 4 mm wood particle devolatilized in 26.8% H₂O/73.2% N₂ at $T_g = 1214^\circ\text{C}$. The internal heat transfer related parameters (λ_c , λ_B , C_{pB}) and the heat of devolatilization show significant influences (>10%) on the devolatilization time, the external heat transfer related parameters (ε , h_c) show a limited effects (5% ~ 10%) on the predicted devolatilization time. Therefore the devolatilization process is internal heat transfer dominated and partially

controlled by external heat transfer for 4 mm particles [3,26]. Therefore, the assumption of using a constant emissivity in the modelling is reasonable in this work. The devolatilization time turned out to be insensitive to char pore size, gas conductivity, and raw wood pore size, due to its small contribution (<20%) to particle effective conductivity during the devolatilization process. The shrinkage coefficient also shows an insignificant impact on devolatilization time for the 4 mm wood particle, which is consistent with a previous study[37]. The fixed carbon content is found to have no significant influence on devolatilization time, and the results are consistent with the study of Bu et al. [13,15] as well as the experimental data shown in Fig. 3.

Figure 5. Sensitivity analysis of the model with respect to its physical properties ($T_g = 1214^\circ\text{C}$, $T_w = 1014^\circ\text{C}$, Moisture = 4.9 ar%, Ash = 0.6 ar%, $d_p = 4$ mm, $\rho_{DB} = 700$ kg/m³). For the emissivity of the particle, the maximum value with reasonable physical meaning is 1. Therefore, it is not 50% increase of the parameter.

4.3.2 Devolatilization kinetics

The influence of devolatilization kinetics is shown in Fig. 6, with Fig. 6 (a) showing the kinetic data and Fig. 6 (b) comparing the conversion history predicted by different kinetics. The kinetics of Wagenaar et al. [43] is derived by fast pyrolysis of pine wood sawdust in a drop tube reactor at temperatures (300 ~ 600°C) and commonly used in single particle modelling

[4,10,26,44]. The devolatilization kinetics of Johansen et al. [50] (HT) is derived from small wood particles (<0.1 mm) devolatilization in an entrained flow reactor at high temperatures (1200 ~ 1600°C). To cover a wide range of temperatures, Johansen et al. [4] proposed a combination of the low temperature kinetics ($T < 527^{\circ}\text{C}$, Wagenaar et al. [43]) and the high temperature kinetics ($T \geq 527^{\circ}\text{C}$, Johansen et al. (HT) [4]). The devolatilization kinetics of Roberts and Clough [51] was derived from a single beech wood particles devolatilization with a heating rate $20^{\circ}\text{C}/\text{min}$ at low temperatures ($275^{\circ}\text{C} \sim 435^{\circ}\text{C}$). The devolatilization kinetics of Johansen et al. [50] (TGA) was derived by TGA using a heating rate $2^{\circ}\text{C}/\text{min}$. According to Fig. 6 (b), the kinetics of Johansen et al. (HT) [4] underestimate the devolatilization time, because it is too fast at low temperatures (it is 10^6 times faster than that of Wagenaar et al. [43] when temperature is $< 400^{\circ}\text{C}$). The devolatilization kinetics of Wagenaar et al. [43] and Johansen et al. (Two) [4] lead to a similar particle conversion history. This implies that the volatiles are almost fully released at low temperatures ($< 600^{\circ}\text{C}$) during devolatilization of the 4 mm particle. Therefore, it is more reasonable to use the kinetics derived at low temperatures ($< 600^{\circ}\text{C}$) in the single particle model for large particles. Although the devolatilization kinetics of low temperature (Wagenaar et al. [43], Roberts and Clough [52], and Johansen et al. [50] (TGA)) are significantly different (a magnitude of -2 to 7, Wagenaar et al. [43] as basis), the devolatilization times predicted by different devolatilization kinetics (Wagenaar et al. [43]: 9.50 s, Roberts and Clough [52]: 11.71 s, Johansen et al. [50] (TGA): 12.45s) have a maximum difference of 31%. Therefore, for the devolatilization of large particles at high temperatures, low-temperature devolatilization kinetics should be chosen in the modelling, and the modelling results are not sensitivity to the selected low-temperature devolatilization kinetics.

Figure. 6. (a): five devolatilization kinetics (Wagenaar et al. [43], Johansen et al.[50] high temperature kinetic: Johansen et al. (HT), Johansen et al.[4] two regime kinetics ($T \geq 527^\circ C$, Johansen et al. (HT), $T < 527^\circ C$, Wagenaar et al.): Johansen et al. (Two), Johansen et al. [50] TGA kinetic: Johansen et al. (TGA), and Roberts and Clough's kinetic [52]); (b): The effects of five devolatilization kinetics on modelling results. (Beech wood, $T_g = 1214^\circ C$, $T_w = 1014^\circ C$, Moisture = 4.9 ar%, Vol = 83.7 db%, FC = 15.7 db%, Ash = 0.6 db%, $d_p = 4$ mm, $\rho_{DB} = 800$ kg/m³).

Figure.7 shows the results of scaling the devolatilization rate with 0.1 and 10 times of the Wagenaar et al. [43] for different size wood particles devolatilized at $1214^\circ C$. Again, the devolatilization rate has limited impact on the devolatilization time of large particles ($d_p = 1$ mm ($< \pm 25\%$) and $d_p = 10$ mm ($< \pm 15\%$)). The influence of devolatilization rate on devolatilization time becomes larger for a small particle (up to $\pm 60\%$). It indicates that the regime of biomass devolatilization transits from the heat transfer dominated regime to a kinetically controlled regime with decreasing particle size from 10 mm to 0.1 m.

Figure 7. Sensitivity analysis of the influence of devolatilization rate and particle size on devolatilization time. The dash (---) line are the $\pm 25\%$ deviation line based on the results of using Wagenaar et al. kinetics ($T_g = 1214^\circ\text{C}$, $T_w = 1014^\circ\text{C}$, Moisture = 4.9 ar%, Vol = 83.7 db%, FC = 15.7 db%, Ash = 0.6 db%).

5 Simple correlation for devolatilization time

According to the results and discussion in Section 4, the devolatilization time is sensitive to gas/wall temperature, moisture content, particle density, and particle size, and insensitive to volatiles content. The devolatilization time is found to increase linearly with the increase of particle density. A range of material properties (such particle density, size) can influence the devolatilization time, However, the different wood species seem to be relatively similar with respect to their material properties. If the change in wood density is accounted for, the devolatilization time can be calculated reasonably. Therefore, it is possible to derive a theoretical based simple correlation to estimate the devolatilization time based on our detailed devolatilization model. In this way, the devolatilization time can be estimated by readily measurable properties (such as particle density, size, and operation conditions).

5.1 Parametric analysis

To derive a correlation to predict devolatilization time, a parametric analysis of gas velocity,

gas temperature, and moisture content is described in the following section.

5.1.1 Effects of gas velocity

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

Figure. 8. Parametric analysis influence of gas velocity on modelling results of different particle size. ($T_g = T_w = 1200^\circ\text{C}$, Moisture = 0.0%, Vol = 88.0%, FC = 12.0%, Ash = 0.0%)

5.1.2 Effects of gas temperature

Figure. 9 shows the influence of gas temperature on predicted devolatilization time for different particle size ($d_p = 0.1$ mm, 1 mm, 10 mm) with variations of particle density. The predicted

devolatilization times decrease with an increase of gas temperature, consistent with other studies [4,21,22,24]. Moreover, the predicted devolatilization time increases linearly with the increase of particle density for all selected temperatures.

Figure. 9. Parametric analysis influence of gas temperature on modelling results of different particle size. ($V_g = 3$ m/s, Moisture = 0.0%, Vol = 88.0%, FC = 12.0%, Ash = 0.0%)

5.1.3 Effects of moisture content

Figure.10 show the results of model calculations for different particle size ($d_p=0.1$ mm, 1 mm, 10 mm) and moisture content (0.0 %, 20.0%, 50.0%) devolatilized at $T_g=1200^\circ\text{C}$. With the increase of moisture content from 0.0% to 50.0%, the devolatilization time is delayed 45%, 54%, and 68% for $d_p = 0.1$ mm, $d_p = 1$ mm, and $d_p = 10$ mm, respectively. The predicted devolatilized times increase with moisture content as also reported in previous studies [7,10,14].

Figure. 10. Parameter analysis influence of moisture content on modelling results of different particle size. ($V_g = 3$ m/s, $T_g = 1200^\circ\text{C}$, Vol = 88.0%, FC = 12.0%, Ash = 0.0 %)

5.2 Simple devolatilization time model

According to the sensitivity analysis in Section 4.3 and the parametric analysis in Section 5.1, we can conclude that the devolatilization time is most sensitive to particle size, gas temperature, moisture content, and particle density. According to the sensitivity analysis shown in Fig.5, it is seen that changing the fixed carbon content of 20% by $\pm 10\%$ does not have a significant influence on devolatilization time. The reason is that the devolatilization of millimeter-sized biomass particle is controlled by internal and external heat transfer and the heat of devolatilization, which is not significantly affected by volatile content. The devolatilization time is relatively insensitive to gas velocity as shown in Fig. 8, and the devolatilization kinetics have a limited influence on the predicted devolatilization time for large particles. According to the experimental results in Section 4.2 and the parametric analysis in Section 5.1, the devolatilization time increases linearly with the particle density when the gas temperature, moisture content, and particle size are constant. Therefore, it is possible to derive a simple correlation to predict devolatilization time,

$$\tau_{dev} = f(d_p, M_c, T_g) \rho_{DB} \quad (7)$$

Here, $f(d_p, M_c, T_g)$ is a slope to correlate particle density and devolatilization time. It can be correlated as a ternary function of particle size, moisture content, and gas temperature. To correlate the function of $f(d_p, M_c, T_g)$, a series of data with changing particle density, particle size, gas temperature, and moisture content are generated by using the detailed devolatilization model in Section 3. Then $f(d_p, M_c, T_g)$ is fitted from the data based on Eq. (7). The variation of particle density, particle size, gas temperature, and moisture content used to generate database are listed as below:

(1) Particle density: 50 ~ 800 kg/m³ with an increment step of 50 kg/m³, 900 ~ 1200 kg/m³ with an increment step of 100 kg/m³, the number of points is 20.

(2) Particle size: 0.1 ~ 1 mm with an increment of 0.1 mm, 1.5 ~ 10 mm with an increment step of 0.5 mm, the number of points is 37.

(3) Gas temperature: 800, 1000, 1100, 1200, 1300, 1400, 1500, and 1600 °C

(4) Moisture content: 6 moisture contents as received based 0%, 10%, 20%, 30%, 40%, 50%.

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

5.3 Discussion of $f(d_p, M_c, T_g)$

Figure. 11 (a) presents the effect of gas temperature on the value of $f(d_p, M_c, T_g)$. The $f(d_p, M_c, T_g)$ monotonically and nonlinearly decreases with temperature. A monotonically nonlinear function with the formulation of $(a+b/(T_g^c))$ is selected to represent the influence of gas temperature. Figure.11 (b) shows that the value of $f(d_p, M_c, T_g)$ monotonically and nonlinearly increases with moisture content. Thus, a polynomial function with the formulation of $(dM_c+eM_c^2)$ is selected to represent the influence of particle moisture content. According to Fig. 11 (a) and Fig. 11 (b), $f(d_p, M_c, T_g)$ monotonically and nonlinearly increases with particle size. A typical power-law expression: fd_p^n , as reported in references [21,22,24], is selected to represent the influence of particle size. The value of the coefficient n is in a range of 1 ~ 2 as discussed by Diego et al. [24]. Finally, the Eq. (8) is suggested to be used for the calculation of devolatilization time.

$$\tau_{\text{dev}} = f(d_p, M_c, T_g) \rho_{DB} = \left(a + \frac{b}{T_g^c} + dM_c - eM_c^2 \right) fd_p^n \rho_{DB} \quad (8)$$

Here a , b , c , d , e , f , and n are coefficients which can be regressed (“lsqcurvefit” function in MATLAB 2018a® used) from the devolatilization time calculated by using the devolatilization model. With some arrangement, the simple correlation to predict the devolatilization time can be expressed as Eq. (9).

$$\tau_{\text{dev}} = 0.0209(1000d_p)^{1.8600} \left(0.0072 + \frac{0.0591}{(T_g/1000)^{2.5313}} + 0.0440M_c - 0.0117M_c^2 \right) \rho_{DB} \quad (9)$$

Here, d_p is particle size, m, T_g is gas temperature, K, M_c is particle moisture content (dry based), and ρ_{DB} is particle density, kg/m³.

The value of n is 1.86 in good agreement with the range found in other studies [21,22,24]. Since the correlation is used to describe a spherical wood particle, d_p should be the equivalent particle diameter (diameter of a sphere having the same volume as the particle) multiplied by the shape factor (surface area of a sphere having the same volume as the initial particle/initial surface area of the particle) for non-spherical particle as suggested by Diego et al. [24]. In some cases, when the gas temperature is different from the wall temperature, a modification of using the average temperature of the gas and the wall is recommended.

Figure. 11. (a) the influence of gas temperature on the value of $f(d_p, M_c, T_g)$, (b), the influence of moisture content on the value of $f(d_p, M_c, T_g)$

5.4 Model validation

To evaluate the simple correlation, the devolatilization time calculated by Eq. (9) were compared with experimental data from other studies as shown in Fig. 12. The experimental data

include both single particle experiments with temperature higher than 1000°C [5,8,9,19,20] and lower than 1000°C [10,20]. Even though the experimental data from Lu et al. [8,9] were obtained from varying conditions (e.g., wood with and without torrefaction, torrefaction temperature and time, KCl content, etc.), the correlation gives a reasonable estimation of the devolatilization time. Although the generated database used to obtain Eq. (9) is for high-temperature ($> 1000^{\circ}\text{C}$), it still gives a reasonable estimation of devolatilization time in single particle combustor for the low-temperature cases as shown in Fig. 12 (b). Generally, the predicted results agree with the experiments within about $\pm 25\%$. While other empirical correlations [7,21,22,24] were obtained and validated by the specified experimental conditions, this simple correlation based on the 1D model validated by experimental data obtained from different experimental setup with different operating conditions, it appears to be applicable at a wide range of conditions with known operating temperature ($1000^{\circ}\text{C} \sim 1600^{\circ}\text{C}$), particle size (0.1 mm-10 mm), particle density and moisture content (0% ~ 50%). It should be noted that the simple correlation is only validated with the experimental particle size (1 mm ~ 10 mm.) in this work. The uncertainty of the simple model may increase for small particle size (e.g. 0.1 mm) which the effects of kinetics on devolatilization becomes significant.

Figure 12. Comparison of single particle experimental and predicted devolatilization time from various references: Fig. 13 (a): Momeni et al. [5] (d_p : 1.65 ~ 3.0 mm, $T_g = 1200^{\circ}\text{C}$, $T_w = 1000^{\circ}\text{C}$ (estimated)), Lu et al. (2016) [8] (d_p : 3.00 ~ 5.00 mm, $T_g = 1231^{\circ}\text{C}$, $T_w = 1031^{\circ}\text{C}$ (estimated)), Cereijo et al. [19] (d_p : 1.0 ~ 5.0 mm, $T_g = 1550^{\circ}\text{C}$, $T_w = 900^{\circ}\text{C}$), Lu et al. (2017) [9] (d_p : 3.00 ~ 5.00 mm, $T_g = 1225^{\circ}\text{C}$, $T_w = 1025^{\circ}\text{C}$ (estimated)); Fig. 13 (b): Anca-Couce et al. [53] (d_p : 9.9 mm, $T_g = T_w = 550 \sim 590^{\circ}\text{C}$); Remacha et al. [20] (d_p : 3.0 ~ 15.0 mm, $T_g = 1200^{\circ}\text{C}$, $T_w = 1200^{\circ}\text{C}$), Lu et al. [10] (d_p : 9.5 mm, $T_g = 777^{\circ}\text{C}$, $T_w = 1003^{\circ}\text{C}$); .

6 Implications and conclusions

Single particle devolatilization experiments with 8 different wood samples at temperatures from 1200 to 1450 °C were conducted with both spherical and cubic particles, and the influence of changes in moisture content, and particle density was also studied. A 1D wood particle devolatilization model based on the work of Johansen et al. [4] was modified. The model accounts for internal and external heat transfer, water evaporation and devolatilization kinetics. The detailed 1D devolatilization model was validated by using the experimental data, and both experiments and modelling show that the devolatilization time increases linearly with the increase of particle density.

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

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

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524 **Nomenclature**

C_p	Heat capacity of particle	J/kg/K
C_{pB}	Heat capacity of raw wood	J/kg/K
C_{pC}	Heat capacity of char	J/kg/K
d_p	Particle size	m
d_{poreB}	Raw wood pore size	m
d_{poreC}	Char pore size	m
FC	Fixed carbon	-
h_c	Convective heat transfer coefficient	W/m ² /s
m_p	Mass of particle	kg
M_c	Moisture content	-
Q_{pyro}	Heat of devolatilization	J/kg
Q_w	Heat of evaporation	J/kg
r	Radius	m
t	Time	s
T	Particle temperature	K
Vol	Volatiles	-
X	Total conversion	-
X_{vol}	Conversion of volatiles	-
X_w	Conversion of Moisture	-
Y	Mass fraction	-

525

526 Greek symbols

λ_g	Conductivity of gas	W/m/K
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λ_c	Conductivity of char	W/m/K
λ_B	Conductivity of apparent biomass particle	W/m/K
λ_p	Conductivity of particle	W/m/K
ε	Volume fraction	-
ρ_{true}	Wood true density	kg/m ³
ρ_{DB}	Particle density	kg/m ³
ξ	Emissivity	-
σ	Stefan-Boltzmann constant	J/(m ² K ⁴ s)
φ	Particle shrinkage	-
τ_{dev}	Devolatilization time	s

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