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Highlights

The Influence of Size and Morphology on Devolatilization of Biomass Particles

Anna Leth-Espensen, Tian Li, Peter Glarborg, Terese Løvås, Peter Arendt Jensen

- Biomass devolatilization model describing both spherical and cylindrical particles.
- Devolatilization kinetic scheme account for both high and low heating rate kinetics.
- Influence of particle properties on devolatilization time for particles 79 μm -3.1 mm.

The Influence of Size and Morphology on Devolatilization of Biomass Particles

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Abstract

This modeling study examines the effect of particle morphology on devolatilization of biomass particles at conditions relevant for suspension firing. A model, which can calculate devolatilization times and particle temperatures for both spherical and cylindrical particles is established, and modeling predictions are compared to experimental data from literature relevant for suspension firing with good consistency. The model predicts devolatilization times, which vary with more than two orders of magnitude in the particle size range ($d_p = 0.2$ - 3 mm) used in suspension firing. For the relevant gas temperature ($T_g = 1300$ - 1900 K) and density ($\rho = 400$ - 1000 kg/m³) intervals, the devolatilization times vary with approximately a factor of two in both cases. Variations in moisture content primarily influence the time for onset of devolatilization, which may affect flame stability in suspension fired boilers. When modeling cylindrical biomass particles as spheres, the model further shows that it is

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more accurate to keep the diameter of the cylinder than to adjust the radius to create a sphere with the same volume as the original cylinder. Finally, the present study includes an analysis of the relative effect on devolatilization time of relevant physical parameters for three particle sizes ($d_p = 78.8\mu\text{m}$, $400\ \mu\text{m}$, and $1560\ \mu\text{m}$). The analysis shows that a 30 % decrease in T_g increases devolatilization times by 82 % for small particles, but only by 11 % for larger particles.

Keywords: High heating rate, Devolatilization model, Particle Morphology, Biomass, Suspension Firing

1. Introduction

Increased interest in climate change has given rise to the use of biomass as a fuel in suspension firing units. Typically, suspension firing is conducted at high temperatures ($> 1000\ \text{K}$), high heating rates ($> 1000\ \text{K/s}$), and with small particles ($d_p < 3\ \text{mm}$). Suspension firing has traditionally been done with coal, but due to the wanted reduction in net CO_2 emission, biomass has been introduced. Biomass particles differ from coal in size, shape, chemical composition and volatile fraction.[1–4] Models for coal particle combustion have often assumed an isothermal, zero dimensional (0D)[5] or one dimensional (1D) spherical geometry.[6] This approach is not suitable for elongated biomass particles, where the increased size results in internal temperature gradients, which cannot be neglected. Thus, with the transition from coal to biomass particles, modeling is required to include particles of different morphologies.[7–10] Compared to other morphologies, it is recommended by Trubetskaya[11, 12] to model biomass particles as cylinders in devolatiliza-

16 tion models. Typical aspect ratios ($AR = L/d_p$) for wood[13] are 2-3 and up
17 to approximately 14 for herbaceous material.[11]

18 Experimental studies have illustrated the importance of representing par-
19 ticle gradients accurately. It is well known that thermal conversion of larger
20 particles involves significant internal gradients. Larfeldt et al.[14] conducted
21 experiments with large cylindrical particles ($d_p = 50$ mm, $L = 300$ mm) at
22 moderate temperatures (973 K) in an electrically heated furnace, and Pi-
23 lar Remacha et al.[15, 16] conducted experiments in a flat flame burner for
24 medium sized, spherical particles ($d_p = 3-15$ mm) at $T_g = 1380$ K. Both of
25 these experimental studies showed internal temperature gradients for large
26 particles, and it was concluded that an isothermal 0D approach is not suffi-
27 cient to describe devolatilization in larger particles. However, even for par-
28 ticle sizes relevant for suspension firing, it may be important to account for
29 gradients. Bharadwaj et al.,[17] who conducted experiments in a downfired
30 turbulent flow combustor at $T_w = 1523$ K, with a particle sieve size of 0.707-
31 0.841 mm and aspect ratio 2-3, showed that both intraparticle heat and mass
32 transfer are necessary to account for biomass particle devolatilization for par-
33 ticle sizes relevant for suspension firing. Based on model work, Johansen et
34 al.[18] came to the same conclusion valid for all particle sizes under conditions
35 relevant for suspension firing.

36 Bharadwaj et al. [17] further show that the aspect ratio decreases during
37 devolatilization for both wood (red oak) and herbaceous material (alfalfa).
38 The same conclusion was drawn for small softwood particles (sieve size 45-75
39 μm) by Lewis and Fletcher[19] in a flat flame burner at $T_g = 1163-1433$ K. Lu
40 et al.[8] have looked at devolatilization of three different particle shapes (d_p

41 = 0.32-16 mm) in an entrained flow reactor and a single particle reactor and
42 conclude that particle morphology influences devolatilization times and con-
43 version rates due to the increase in surface to volume ratio for non-spherical
44 particles. The corresponding model developed by Lu et al. indicates that
45 particle morphology effects are important for particles exceeding 200-300 μm .
46 Another devolatilization model describing both spherical particles and other
47 geometries has been presented by Thunman et al.[20], and further developed
48 by Ström and Thunman.[21] This model was validated against experimen-
49 tal data relevant for fluidized beds (d_p 10-40 mm, $T_g < 1123$ K, HR $\lesssim 10$
50 K/s). Gubba et al.[22] presented a model to account for intraparticle heat
51 and mass transfer for co-firing with biomass, which can be implemented into
52 CFD. However, their model was only validated with experimental data for
53 large particles ($d_p = 9.5$ mm) at intermediate temperatures ($T_g = 1050$ K), so
54 it is not necessarily applicable for the smaller particles utilized in suspension
55 firing. To the knowledge of the authors, no model exists, which is validated
56 against relevant experimental data and can adequately predict devolatiliza-
57 tion times for small particles ($d_p < 3$ mm) at high temperatures and heating
58 rates for different morphologies.

59 Even though particle devolatilization is described extensively in the lit-
60 erature, work that illustrates the effect of biomass particle morphology on
61 particle ignition and devolatilization time for conditions relevant for suspen-
62 sion firing is scarce. The purpose of this paper is to further develop the model
63 by Thunman, Ström, and coworkers[7, 21] to be relevant for suspension fir-
64 ing conditions, i.e. to be able to predict devolatilization behavior in smaller
65 particle sizes at higher temperatures and heating rates. Firstly, this is done

66 by a modification to the model, so it now include sink and source terms
67 for the energy required to heat water vapor and devolatilization gasses after
68 reactions. Secondly, a new kinetic scheme incorporating both low and high
69 heating rate Arrhenius kinetics is implemented, and submodels accounting
70 for particle specific heat capacity and particle thermal conductivity are cho-
71 sen according to the physico-chemical condition in a suspension firing unit.
72 Thirdly, the model presented here is compared to experimental data from the
73 literature in both the lower and the upper end of the suspension firing fuel
74 size range. In this way, it is ensured that the improved model can describe all
75 particle sizes in the relevant size range ($d_p = 0.1-3$ mm). Furthermore, this
76 paper also illustrates the influence of key biomass properties' effect on de-
77 volatilization time. The effect of morphology, gas temperature, particle size,
78 density, and moisture content on pyrolysis for three representative particle
79 sizes ($d_p = 79$ μm , $d_p = 0.8$ mm, and $d_p = 3$ mm) has been investigated. The
80 effect of these parameters on ignition time and flame stability in suspension
81 fired units is discussed.

82 **2. Method**

83 The model adopted here, is originally by Thunman et al.[20] and Ström
84 and Thunman.[21], and is developed for combusting particles in fluidized
85 and fixed beds, i.e. for larger particles at lower temperatures than what is
86 typically the case for suspension firing. In this paper the model is further
87 developed to be able to describe single particle devolatilization under sus-
88 pension firing conditions. Section 2.1 describes the structure of the model
89 as it is put forward by Thunman, Ström and coworkers.[20, 21] Section 2.2

90 describes the new additions to the model, by presenting submodels and the
 91 kinetic scheme, chosen here, in order to expand the model to include de-
 92 volatilization of smaller particles at suspension firing conditions.

93 *2.1. Model Description*

94 The model is constructed as a shell model, comparable in structure to an
 95 onion. It is a combination of a sharp interface model and a finite reaction
 96 zone model.[23] At $t = 0$ the particle primarily consists of moist wood, with
 97 infinitesimally thin outer layers of dry wood and char. As time progresses
 98 the outer regions of the particle are dried and devolatilized. Consequently,
 99 at time t , the particle consists of three concentric shells; an outer char shell,
 100 a middle dry shell, an inner moist shell. A sketch of the shell structure can
 101 be seen in figure 1.

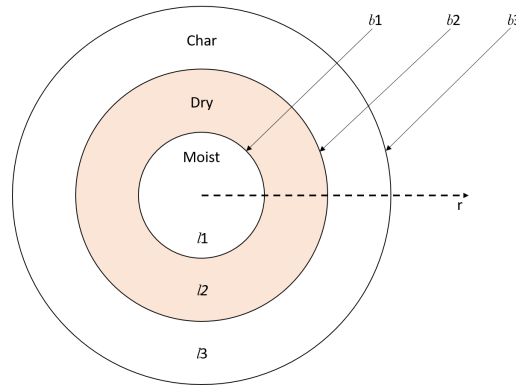


Figure 1: Sketch of shell structure. Adapted from Ström and Thunman.[21]

102 The evaporation of water happens at the interface between the moist and
 103 the dry zone. The devolatilization takes place in the dry zone, marked by
 104 the light peach colored area in figure 1. The heat balance for the outer shell
 105 includes external radiation and convection. The heat balances of the model

106 can be seen in equation 1 through 3, and the mass balances can be seen in
 107 equation 4 through 6. There are some slight modifications to the originally
 108 developed equations[21] marked in blue in equation 1 and 2. Q_{l2} is a source
 109 term for the energy required to heat the water released during evaporation
 110 and the energy required to heat the wood, from which the water has been
 111 released. The water vapor is heated from the release temperature, T_{b1} , to
 112 the temperature where it is transferred to the next shell, T_{b2} . The newly
 113 dried wood is heated from the release temperature, T_{b1} , to the temperature
 114 of the dry wood layer, T_{l2} . In the same fashion, Q_{l3} is a source term for
 115 the energy required to heat the gas released from the devolatilization, the
 116 energy required to heat the water released during evaporation (which has
 117 been transported through the dry layer), and the energy to heat the char, in
 118 which the devolatilization has taken place. The volatiles and the water vapor
 119 are heated from the temperature at the shell boundary, T_{b2} , to the outer shell
 120 temperature, T_{b3} . The newly devolatilized wood (now char) is heated from
 121 the boundary temperature, T_{b2} , to the char layer temperature, T_{l3} .

$$\frac{dT_{l3}}{dt} = \frac{\alpha_{l3}}{V_{l3}} \left(A_{b3} \frac{dT}{dr} \Big|_{b3,l3} - A_{b2} \frac{dT}{dr} \Big|_{b2,l3} \right) + \frac{Q_{l3}}{C_p \rho V} \quad (1)$$

$$\frac{dT_{l2}}{dt} = \frac{\alpha_{l2}}{V_{l2}} \left(A_{b2} \frac{dT}{dr} \Big|_{b2,l2} - A_{b1} \frac{dT}{dr} \Big|_{b1,l2} \right) + \frac{Q_{l2}}{C_p \rho V} \quad (2)$$

$$\frac{dT_{l1}}{dt} = \frac{\alpha_{l1} A_{b1}}{V_{l1}} \frac{dT}{dr} \Big|_{b1,l1} \quad (3)$$

$$\frac{dm_{l3}}{dt} = \gamma \omega_{b2} \quad (4)$$

$$\frac{dm_{l2}}{dt} = \omega_{b1} / Y_{m,db} - \omega_{b2} \quad (5)$$

$$\frac{dm_{l1}}{dt} = -\omega_{b1} / Y_m \quad (6)$$

The boundaries (b) and shell layers (l) are numbered from the center outwards, so $l1$ is the wet layer, $b1$ is the boundary between wet and dry layer and so on. T_{li} is the temperature of layer i , α is the thermal diffusivity, V is the layer volume, A is the surface area, m is the layer mass, γ is the char yield, ω_{wb1} is the drying reaction rate, ω_{b2} is the pyrolysis reaction rate, and Y_m is the mass fraction of moisture. Boundary conditions for the heat balances are given in equation 7 through 9, assuming no heat accumulation at the boundaries.

$$hA_{b3}(T_g - T_{b3}) + \sum \epsilon_1 \sigma A_{b3}(T_w^4 - T_{b3}^4) = k_{p3} A_{b3} \left. \frac{dT}{dr} \right|_{b3,l3} \quad (7)$$

$$k_{l3} A_{b2} \left. \frac{dT}{dr} \right|_{b2,l3} = k_{l2} A_{b2} \left. \frac{dT}{dr} \right|_{b2,l2} + Q_{rxn,b2} \quad (8)$$

$$k_{l2} A_{b1} \left. \frac{dT}{dr} \right|_{b1,l2} F_{b1} = Q_{rxn,b1} \quad (9)$$

122 Here h is the heat transfer coefficient, ϵ is the emissivity, σ is the Stefan-
 123 Boltzmann constant, k is the thermal conductivity, and Q_{rxn} is a reaction
 124 heat flow. F_{b1} is an empirical parameter, which determines the ratio of the
 125 heat transferred to the drying front for water evaporation to that used to
 126 heat up the wet wood layer.

127 The model can describe devolatilization of both spherical and cylindrical
 128 particles. The sizes of the particles are characterized by the initial radius
 129 R for the sphere, and by both an initial radius, R , and a length, L , for the
 130 cylinder. The one-dimensional geometry of the sphere and an assumption of
 131 isotropy means that changes in size for the spherical particles can be char-
 132 acterized only by one time-dependent variable, the radius r . The cylindrical
 133 particles are two-dimensional, but can also be described using only one vari-
 134 able, r , plus the two constant parameters for the initial dimensions, R and

135 L . The length of the cylindrical particle is defined as a function of r as
136 $l = L - 2(R - r)$. The implementation of the model is only made for cylin-
137 ders with $L > 2R$. A sketch of the cylindrical particle can be seen in figure
138 2. By assuming that the reduction in diameter of a given shell equals the
139 reduction in length, the number of variables needed to describe a cylinder
140 can be reduced to one, assuming isotropy in the angular direction. This ap-
141 proach is a simplification of the end effects, but it allows for a simpler model.
142 A model with a more detailed description of the end effects would have a
143 devolatilization time higher than that for a sphere, but lower than the one
144 predicted for a cylinder with the model presented here. As will be shown
145 in section 4.2, the devolatilization time for a sphere and a cylinder with AR
146 = 1.01 are practically the same, so describing the end effects at a higher
147 computational cost is not relevant here. The same one variable approach to
148 describe cylinders has been utilized by Porteiro et al.[24]. Yang et al.[25]
149 have, using a two variable approach, described the end effects in more detail
150 by allowing a faster release of volatiles at the cylinder ends. However, this
151 approach typically yields greater computational costs, thus it has not been
152 pursued here.

153 The model as presented by Thunman, Ström, and co-workers[20, 21]
154 has been validated against experimental data with different morphologies
155 (spheres, cylinders, and parallellipeds), but only for large particles ($d_p >$
156 9.5 mm) at moderate temperatures ($T_g < 1276$ K). Thus, the original model
157 has a verified capacity to predict biomass devolatilization under these condi-
158 tions. However, larger particles at moderate temperatures are primarily heat
159 transfer controlled. In contrast, the smaller particles utilized at suspension

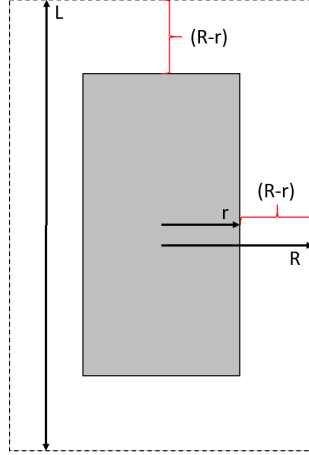


Figure 2: Sketch of geometry of cylindrical particle. Dashed line is initial outline of particle layer, solid grey figure is particle at $t > 0$.

160 firing will be kinetically controlled or in the transition region between kineti-
 161 cally controlled and heat transfer limited devolatilization. For the purpose of
 162 expanding the model to be able to predict devolatilization under suspension
 163 firing conditions, alternative submodels and expression for relevant physico-
 164 chemical properties are put forward in the subsequent section.

165 2.2. Model Input Parameters

An overview of the model parameters used in this study can be seen in table 1. The kinetic scheme builds on Arrhenius equations with different kinetic parameters for low and high heating rates, which can be seen in equation 10 through 12.

$$k_L = k_{L1} + k_{L2} + k_{L3} \quad (10)$$

$$k_{Lj} = A_{Lj} \exp(-E_{a,Lj}/(RT)), \quad j = 1, 2, 3 \quad (11)$$

$$k_H = A_H \exp(-E_{a,H}/(RT)) \quad (12)$$

166 The low heating rate kinetics are described by Wagenaar et al.[26] as three
167 competing reactions and the high heating rate kinetics are described by a
168 single first order reaction (SFOR) by Johansen et al.[27]. In this paper both
169 low and high heating rate kinetics are treated as SFORs. The low heating
170 rate kinetics are combined to a single rate constant as shown in equation
171 10, in order to ensure that the obtained char yield is not dependent on three
172 competing reactions, relevant only for low temperatures. The transition from
173 the low to the high heating rate should happen around 800 K.[28] It is here
174 chosen to be linear, with the transition temperature interval between 750
175 and 950 K. An Arrhenius plot of the pyrolysis rates of different studies and
176 the combined function utilized here can be seen in figure 3. Compared to
177 the kinetics utilized here, the figure shows that at low temperatures the
178 high heating rate kinetics predicts the reaction rate to be high, and at high
179 temperatures the low heating rate kinetics also predicts the reaction rate to
180 be high. The discrepancies between low and high heating rate kinetics also
181 show that it is necessary to have different kinetic schemes when covering a
182 large temperature span.

183 The specific heat capacities for wood and char are sensitive to temper-
184 ature. Relations for C_p should not be extrapolated outside the interval, in
185 which they have been derived without careful consideration. Comparison of
186 some examples of C_p values for both dry wood and char can be seen in figure
187 4. Extrapolation of the linear C_p expressions result in extreme values for the
188 specific heat capacities, especially at high temperatures. The only pair of
189 related C_p values, which do not increase significantly by extrapolation to the
190 relevant temperature interval are behold by Merrick et al.[37], hence they

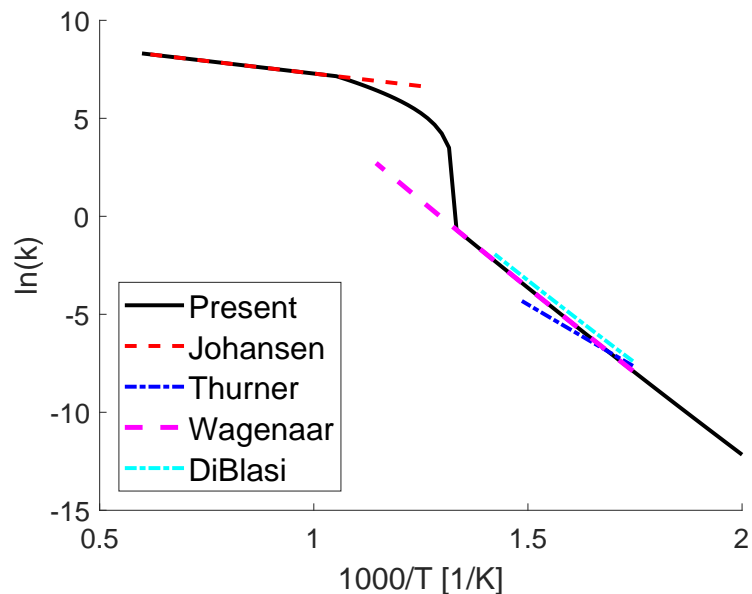


Figure 3: Arrhenius plot for kinetic scheme used in this model and literature models for high heating rate kinetics from Johansen et al.[27] and low heating rate kinetics from Wagenaar et al.[26], DiBlasi and Branca[42], and Thurner and Mann.[43]

191 have been chosen in the present work, even though they have originally been
 192 derived for coal. An expression for the specific heat capacity for wet wood is
 193 derived by TenWolde et al.[39], and is dependent on both moisture content
 194 and the C_p of dry wood. This expression is utilized here, using the expression
 195 for dry wood C_p developed by Merrick et al.

196 The change of enthalpy as a result of the desorption of water from a coal
 197 particle has been addressed by Callanan et al.[33] for multiple samples, all
 198 giving similar results. An average value of the provided data, 3.61 kJ/g,
 199 has been utilized here. The value is connected with some uncertainty as the
 200 data are obtained for coal particles, but the water content is low in the ex-
 201 periments investigated here (0-6 wt % wb) and in suspension firing units in

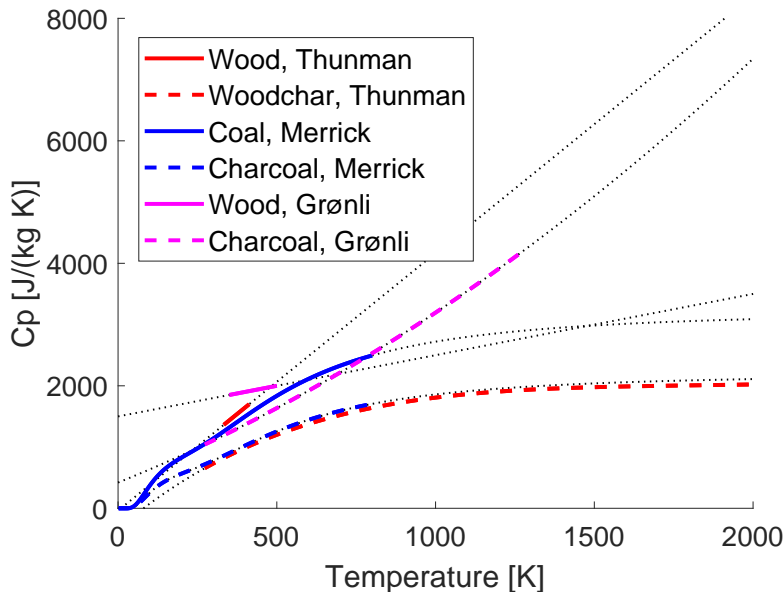


Figure 4: Comparison of C_p values from Thunman et al.[20], Merrick[37] and Grønli and Melaaen.[44] Black dotted lines are extrapolation of models.

202 general, meaning that the effect of any uncertainties are assumed insignifi-
 203 cant. The change in enthalpy as a function of devolatilization reported in
 204 literature varies from being highly endothermic at 611 J/g wood[45] to being
 205 exothermic at -222 J/g.[46]. There seem to be little consensus in literature
 206 on any value for the heat of devolatilization, and most sources provide both
 207 exothermic and endothermic values.[21, 46] The discrepancy is likely due
 208 to differences in biomass, differences in operating conditions, and a differ-
 209 ent definition on how the devolatilization process is delimited. Most sources
 210 do, however, report the process to be slightly endothermic. In this work
 211 different heat of devolatilization values have been tested and compared to
 212 experimental results, and a value of 200 J/g has been chosen as it represents

213 experimental data well. The influence of changes in heat of devolatilization
214 is tested in section 4.1.

215 The thermal conductivity of virgin wood is normally considered to be con-
216 siderably higher than that of char,[40] but Brown[47] has shown that the ther-
217 mal conductivity of char at elevated temperatures is twice that of virgin wood
218 at ambient temperature, consequently both must be determined accurately.
219 The thermal conductivity employed in this work builds on the correlation set
220 forward by Koufopoulos et al.[40]. They developed an empirical expression
221 for the devolatilization of wood particles ($d_p = 20$ mm) under moderate tem-
222 peratures ($T_g < 873$ K), that has been widely adopted, also for high heating
223 rate experiments.[28, 48] No thermal conductivity correlation for wood at
224 higher temperatures has been found in literature. Thermal conductivity for
225 wet wood is approximately 15 % higher than that of dry wood according to
226 table values for multiple wood species from the WoodHandbook[41], thus a
227 15 % increase in wet wood thermal conductivity has also been applied here.

228 The heat transfer coefficient, h , is an input parameter, which, regardless
229 of particle shape, is estimated as described by Leth-Espensen et al.[29] h
230 is calculated from the Nusselt number, which is not defined for free falling
231 cylindrical particles in turbulent gas streams, hence a spherical correlation
232 has been employed. Duan et al.[49] propose to relate the heat transfer coeffi-
233 cient to the drag coefficient and determine h in this way in order to avoid the
234 dependence on the Nusselt number. Although possible, a limited number of
235 experiments relating drag and heat transfer for cylindrical particles in free
236 fall are available and therefore, a spherical assumption using the correlation
237 for the Nusselt number is currently employed.

238 The model predicts both the temperature of each of the three particle
239 boundaries (moist wood, dry wood, and char) as shown in figure 5 and the
240 temperature and mass of each of the three particle layers. In figure 5a the
241 mass of each of the three layers and the total mass of the particle can be seen.
242 It can be seen that the mass of the moist layer decreases over time, whereas
243 the dry wood layer first increase as water is evaporated, and subsequently
244 decreases as the wood is devolatilized. The char layer steadily increases until
245 it reaches the specified char yield. The total mass of the particle decreases
246 over time until only char is left. Figure 5b shows the temperature on the
247 outer surface of each shell. The surface temperature is thus identical to the
248 char boundary temperature, T_{b3} , in this figure. The dry layer temperature
249 is increasing as the particle is heated, but stagnates during devolatilization
250 as the process is endothermic. The moist boundary temperatures, T_{b1} , is
251 close to the center temperature as the entire moist layer is slowly heated to
252 the boiling temperature, and remains at T_{boil} during water evaporation. The
253 moist layer temperature, T_{l1} , is the average temperature in the moist layer
254 and is plotted in the remainder of this paper as a substitute for the particle
255 center temperature, which is not obtained in this model.

256 **3. Model Validation**

257 This section covers the validation of the model with experimental data
258 relevant for suspension firing for both spherical and cylindrical particles. The
259 model is validated against data sets involving particles in the diameter range
260 78.8 μm to 9.5 mm. The degree of devolatilization in the following graphs is
261 release of volatiles excluding the water present in the particle.

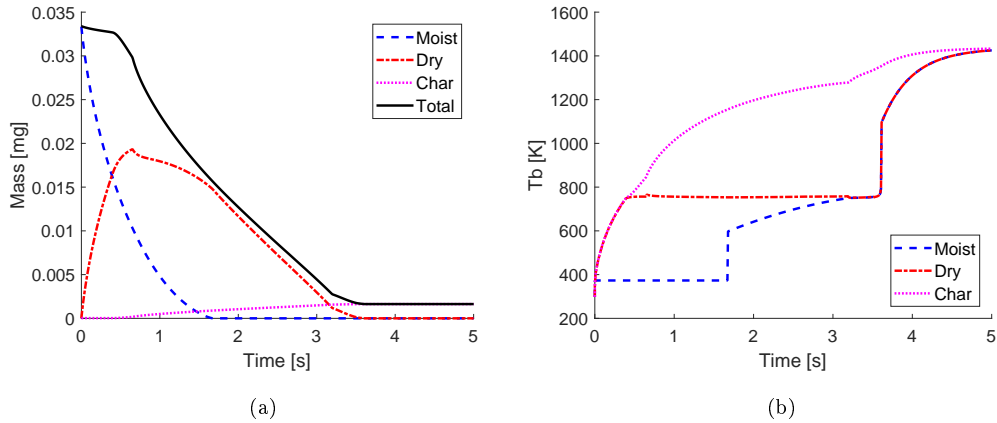


Figure 5: Example of mass and temperature profiles provided by the model. Here for a particle with $AR = 2$, $\rho = 700 \text{ kg/m}^3$, $T_g = 1600 \text{ K}$, $T_w = 1400 \text{ K}$, moisture content = 4 wt% wb, and $r_{ini} = 1560 \text{ }\mu\text{m}$.

262 3.1. Summation of Model Validation

263 The model is validated for particles in the parameter intervals give in table
 264 2. The model is validated in the entire size interval relevant for suspension
 265 firing, also the main part of the parameter ranges for moisture content, gas
 266 temperature, and density are covered. For the aspect ratio the relevant range
 267 for wood particles is covered.

268 3.2. Particles with $d_p = 78.8 \text{ }\mu\text{m}$

269 Experiments with small wood particles have been performed by Johansen
 270 et al.[27, 50]. The experiments were conducted in a laminar entrained flow
 271 reactor with fuel feed rates low enough to create single particle conditions.
 272 The maximum gas temperatures were 1405-1667 K, the heating rate was in
 273 the order 10^5 K/s , and the residence time from 0-100 ms. The applied experi-
 274 mental parameters are given in table 3. The char yield is estimated using the

275 method described by Leth-Espensen et al.[29], and the length is estimated
276 based on recommendations from Masche et al.[13]. Figure 6 shows the com-
277 parison between experimental results for pine wood and model predictions
278 for $T_g = 1405$ K and $T_g = 1667$ K. Also experimental data from four other
279 biomass samples devolatilized under the same conditions in the same equip-
280 ment have been included in the figure. The fuel types (pine, mischanthus,
281 doped pine, leached mischanthus) all behave very similarly, and the major
282 difference is the char yield. The four additional fuel types aid in describing
283 the very rapid heating of particles of this size, where data points are scarce.
284 The devolatilization of the particles happen within the first 20 ms in the
285 reactor.

286 The figure shows consistency between experimental and model data. The
287 small particles are rapidly devolatilized after an initial, short heating period.
288 The relatively small diameter of the particles entails that these particles
289 mimic isothermal particles. For an isothermal particle a short heating period
290 would also be expected, before a rapid devolatilization commences.

291 3.3. Particles with $d_p = \sim 3$ mm

292 Experiments with 3 mm particles have been conducted by Lu et al.[52] in
293 a single particle combustor. The particles are fixed on a small wire, located
294 in a hot fluegas above a flame, and the devolatilization time is determined by
295 video registration. The particles have been carved to near-spherical shapes,
296 and are modeled as such. The temperature in the gas phase is $T_g = 1487$ K,
297 and the initial heating rates are in the order $10^2 - 10^3$ K/s. The experimental
298 data are given in table 4. Figure 7 shows the comparison of the devolatiliza-
299 tion times for 3 mm spherical particles of different density for pine and beech

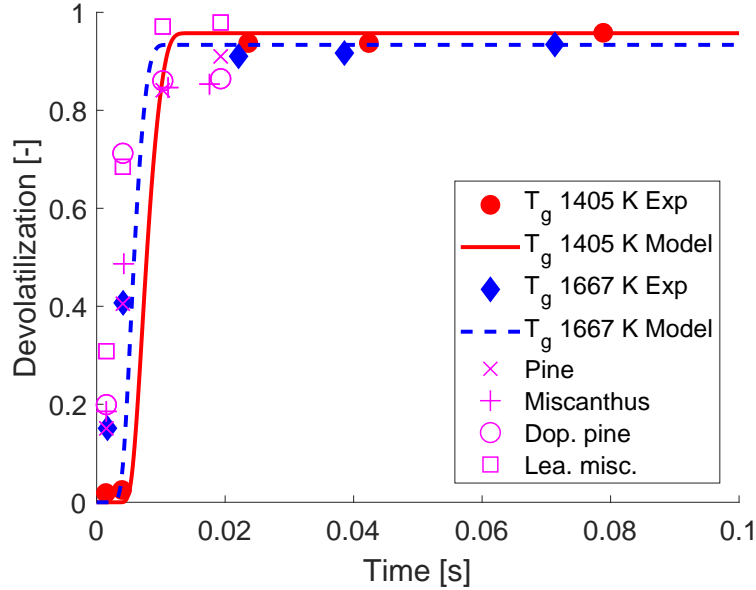


Figure 6: Comparison of model predictions to literature data for pine from Johansen et al.[27]. $d_p = 78.8 \mu\text{m}$, $\text{AR} = 2$, $\rho = 591 \text{ kg/m}^3$, moisture content ≈ 0 . Additional input parameters to the model are given in table 3. The pink data points are for four biomass types (pine, miscanthus, KCl doped pine, leached miscanthus) devolatilized under identical conditions as reported by Johansen et al.[50]

300 wood. The wood type is indirectly a parameter in the model as the char yield
 301 varies depending on the wood sort. The char yield was estimated using the
 302 method described by Leth-Espensen et al.[29] The particles also vary slightly
 303 in diameter.

304 The measured pyrolysis time increases with increasing density in the ex-
 305 perimental dataset in agreement with the model predictions. The model is
 306 particularly accurate for the beech samples, but for both wood species, the
 307 trend is captured well. Complete devolatilization of the 3 mm particles was
 308 obtained after 3.5 to 6.5 seconds.

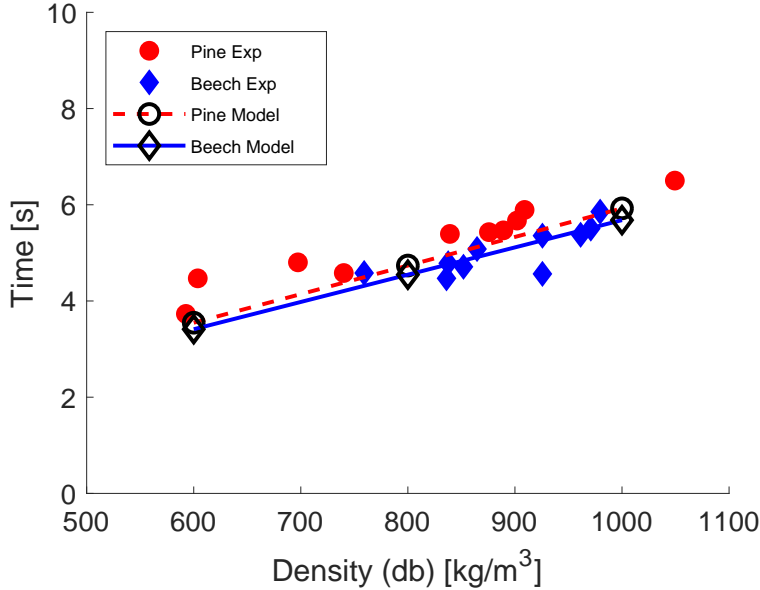


Figure 7: Comparison of devolatilization time for 3 mm spherical particles of different density. Experimental data from Lu et al.[52] $T_g = 1487$ K, $T_w = 1187$ K (estimated value), moisture content = 5.5 wt % wb. Additional input parameters to the model are given in table 4.

309 *3.4. Particles with $d_p = 9.5$ mm*

310 Lu[53] has conducted experiments with spherical and cylindrical parti-
 311 cles, both 9.5 mm in diameter, and the cylinders have a length of 38 mm.
 312 The experiments were conducted in a single particle combustor, and each
 313 experiment was repeated three to four times. For the spherical particles the
 314 settings were the same in all three repetitions. For the cylindrical particles
 315 the settings were the same except that the thermocouple measuring the cen-
 316 ter temperature was placed radially in experiment 1 and 2, and axially in
 317 experiment 3 and 4. The maximum gas temperature in the experiments was
 318 1276 K, and the initial heating rate was in the order of $10^1 - 10^2$ K/s. The

319 experimental data are given in table 5.

320 The temperatures in the devolatilization experiment for the cylindrical
321 particle have previously been compared to the model presented by Ström
322 and Thunman[21], and these results are also included in figure 9b. The two
323 models show similar results for the temperatures of these large particles.
324 Ström and Thunman have, however, not reported the degree of devolatiliza-
325 tion related to the temperature measurements, and the comparison of experi-
326 mental data from devolatilization of spherical and cylindrical poplar particles
327 at identical conditions in the same set-up have not been made either. The
328 latter is the reason of interest for this study.

329 Figure 8a and figure 8b show the degree of devolatilization and the tem-
330 perature measurements for the spherical particles. The devolatilization of
331 the spherical 9.5 mm particles take approximately 35 seconds. Figure 9a and
332 figure 9b show the degree of devolatilization and the temperature measure-
333 ments for the cylindrical particles. For the 9.5 mm cylindrical particle the
334 devolatilization time is approximately 50 s. For both the spherical and the
335 cylindrical particles, the thermocouple influences the devolatilization. The
336 conducting material of a thermocouple may cause measurement errors of
337 up to 300 K for millimeter-sized particles in high temperatures ($T_g = 1653$
338 K).[15] It is especially critical for the center temperatures, which are thus
339 likely measured above the temperature in an unaffected particle.

340 The devolatilization is predicted well by the model both for the spherical
341 and cylindrical particles, albeit the model prediction is slightly faster than
342 the experimental results. The surface temperature is also predicted well.
343 The center temperature is predicted reasonably by the model. The parti-

344 cle center temperatures measured experimentally are likely an overestimate
 345 as they have been measured with a thermocouple, which entails the short-
 346 comings described above. The particle center temperatures predicted by the
 347 model are likely an underestimate, as e.g., the moist layer temperature is
 348 defined as equal to T_{boil} until all water is evaporated. However, the stepwise
 349 temperature profile for drying is also observed by Pilar Remacha et al.[16]
 350 during drying of alumina particles in a flat flame burner at 1573 K, so the
 351 assumption is expected to be reasonable. The combination of overprediction
 352 of experimental temperatures and underprediction of model temperatures is
 353 the reason for the small discrepancies seen in figure 8b and 9b. The results
 354 of the quaduplicate experiments also show that the experimental variation
 355 is considerable.

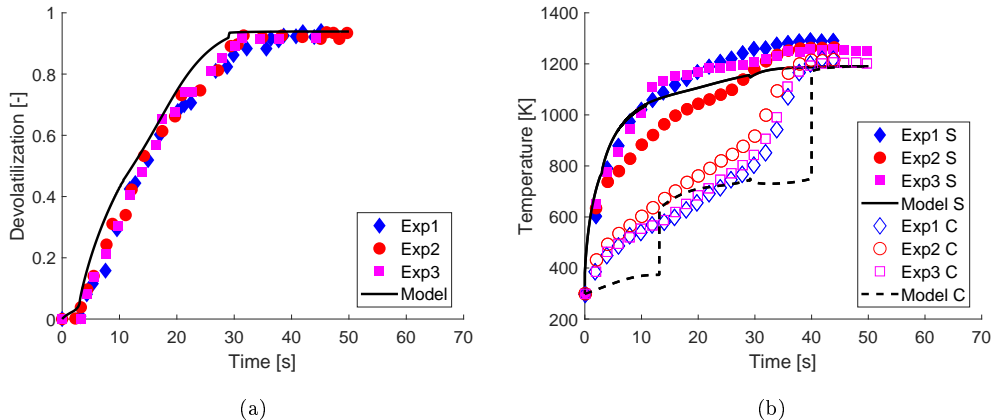


Figure 8: Comparison of model to experimental data of spherical particles from Lu et al.[53] $d_p = 9.5\text{mm}$, $\rho = 580\text{ kg/m}^3$, $T_g = 1276\text{ K}$, $T_w = 1176\text{ K}$ (estimated value), moisture content = 6 wt% wb. Additional input parameters to the model are given in table 5. The small fluctuation in the graphs around $t = 30\text{ s}$ is due to the change in kinetic scheme. S = surface temperature, C = Center temperature.

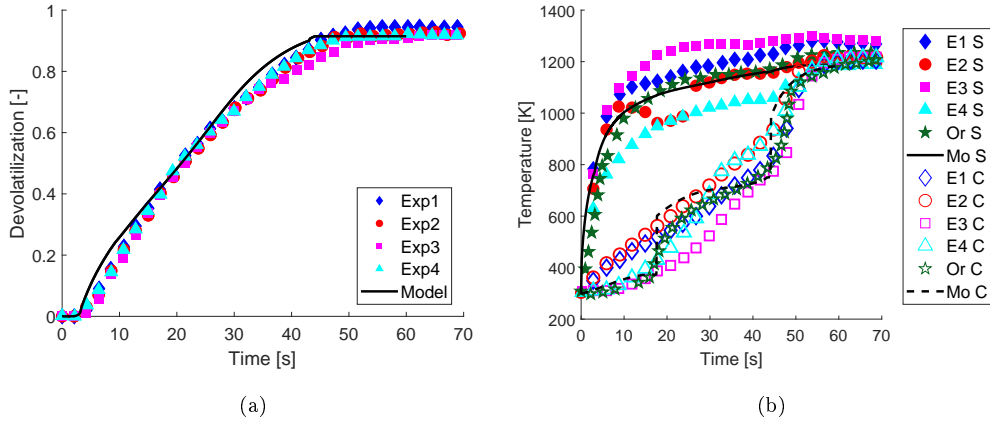


Figure 9: Cylindrical particles modeled with current model (Mo) compared to model results from Ström and Thunman (Or) and experimental data from Lu et al.[53] $d_p = 9.5$ mm, $AR = 4$, $\rho = 580$ kg/m³, $T_g = 1276$ K, $T_w = 1176$ K, moisture content = 6 wt% wb. Input parameters to the model are given in table 5. S = surface temperature, C = Center temperature.

356 4. Model predictions

357 4.1. Sensitivity Analysis

358 To investigate the influence of the material value properties and some
 359 particle and boundary conditions a sensitivity analysis with respect to de-
 360 volatilization time has been conducted. The influence of particle properties
 361 and devolatilization conditions is tested for three different particle sizes (d_p
 362 = 79 μ m, 800 μ m, and 3.12 mm), since the influence of the model parameters
 363 varies depending on size. The other applied particle parameters can be seen
 364 in table 6.

365 The smaller particles are kinetically controlled, whereas the devolatiliza-
 366 tion process for the larger particles is limited by heat transfer mechanisms.
 367 In table 7 the effect of decreasing and increasing a number of parameters by

368 30 % can be seen. It can be concluded that radius, density, and gas temper-
369 ature are important parameters, when determining the devolatilization time.
370 For the first two the impact is highest for the smaller particles, whereas the
371 impact of T_g is most pronounced for the larger particles. The influence of
372 particle heat conductivity, k_p , is considerable for larger particles, whereas the
373 effect for smaller particles seems to be less pronounced in good agreement
374 with the larger particles being heat transfer controlled. To check the effect
375 of the kinetic scheme, the Arrhenius reaction rates, k_L and k_H , have both
376 simultaneously been increased and decreased by 30 %. The choice of rate
377 constants mainly influences the smaller particles' devolatilization times, as
378 they are primarily controlled by the kinetics of the devolatilization.

379 *4.2. Parameter Analysis*

380 A parameter analysis was performed to study the effect of particle prop-
381 erties and local conditions on the devolatilization time and further illustrate
382 the influence on the devolatilization process. The analysis is done for a cylin-
383 drical particle ($d_p = 1.51$ mm, AR = 5) as baseline particle. Its characteristics
384 are given in table 8. For each input parameter a low, an average and a high
385 value is chosen to cover the parameter span relevant for suspension firing.
386 The effect of changes in aspect ratio (for particles with the same radius),
387 aspect ratio (for particles with the same volume), radius (for particles with
388 the same aspect ratio), density, moisture content, and gas temperature is
389 shown in figure 10.

390 The influence of aspect ratio on devolatilization time is shown both for
391 particles with the same radius and for particles with the same volume in
392 figure 10a and figure 10b, respectively. Comparing the figures shows that

393 in the case of identical radii, the effects on devolatilization times are minor,
394 especially for $AR > 5$, whereas for particles with the same volume the effects
395 of AR on devolatilization times are greater. Thus from a modeling perspec-
396 tive, even if it is chosen to model biomass particles as spherical, using the
397 true diameter as an input parameter yields a better result with respect to
398 estimating the devolatilization time. However, this approach might lead to
399 other complications, e.g. in CFD, where a true representation of the entire
400 mass of particles is necessary, and where the drag effect would also need to
401 be accounted for.[54]

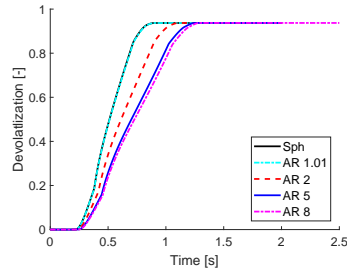
402 Comparing the effect of changes in radius in figure 10c to the model pa-
403 rameters in the remaining subfigures show that the particle size is an impor-
404 tant input parameter to specify as accurately as possible. The devolatiliza-
405 tion time varies with approximately two magnitudes within the particle size
406 interval relevant for suspension firing. The particle size influences both the
407 starting time for devolatilization, the amount of volatiles released and the
408 total devolatilization time.

409 Another parameter, which has a considerable influence, especially on the
410 onset of devolatilization, is the gas temperature as seen in figure 10d. The
411 lower the gas temperature, the longer it takes to dry out the particle and heat
412 it to a temperature where the devolatilization is initiated. The high, local
413 temperature near the burner quarl ensures a fast onset of devolatilization,
414 which improves ignition and flame stability.

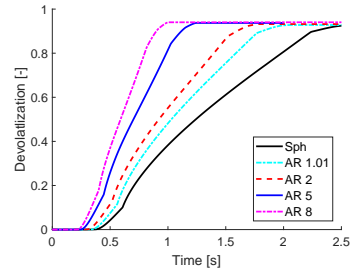
415 The influence of the particle density can be seen in figure 10e. The density
416 for the particles varies both dependent on biomass type and pelletization
417 procedure. The changes in density affects both the onset time for the de-

418 volatilization and the duration of it.

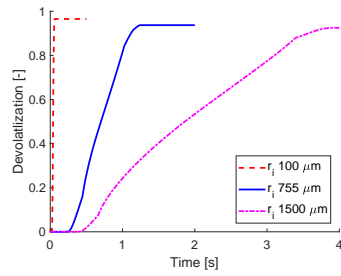
419 Compared to the other parameters, the moisture content seen in figure
420 10f has a smaller effect on total devolatilization time, but it has a strong
421 influence on the onset of volatile release, and may consequently influence
422 flame ignition. The moisture content in suspension fired units rarely exceed
423 10 wt% wb as the pelletization and milling processes result in partly dried
424 particles.



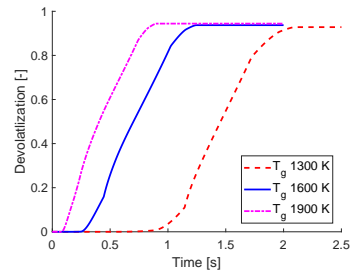
(a) Particles have identical radii.



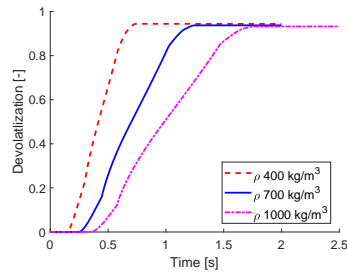
(b) Particles have identical volumes.



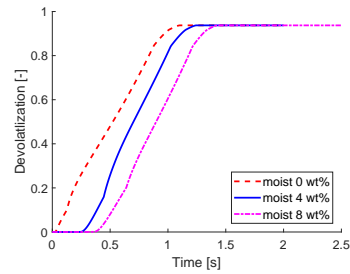
(c) Particles have identical AR.



(d)



(e)



(f)

Figure 10: Parameter analysis for relevant particle properties and boundary conditions. Baseline simulation properties include $AR = 5$, $T_g = 1600$ K, $R = 0.755$ mm, $\rho = 700$ kg/m³, moisture content = 4 wt % wb, represented by the blue solid lines.

425 5. Conclusion

426 The presented wood particle devolatilization model can describe biomass
 427 particles as both spherical and cylindrical and include end effects. The model

428 fits experimental data from the literature well for particle sizes ($d_p = 79 \mu\text{m}$
429 to 9.5 mm) and in the temperature range (1276-1667 K), which is relevant
430 for suspension firing.

431 The model results show that if a cylindrical particle should be approxi-
432 mated by the geometrically simpler sphere, the diameter of the cylinder is
433 a better approximation for a particle size than the same volume approach,
434 where the diameter is determined as the diameter of a sphere with the same
435 volume as the cylinder.

436 The model further predicts devolatilization times to vary approximately
437 two magnitudes for the particle sizes ($d_p = 0.2\text{-}3 \text{ mm}$) utilized in suspension
438 fired boilers, affecting both burnout and flame stability. Other parameters of
439 importance for devolatilization time are particle density, and local gas tem-
440 perature. Of minor importance for the final devolatilization time is moisture
441 content, within the span relevant for pelletized biomass. The moisture con-
442 tent, however, influences the onset of volatile release substantially.

443 A sensitivity analysis performed for three different particle sizes ($d_p =$
444 $79 \mu\text{m}$, $800 \mu\text{m}$, and 3.12 mm) shows that the importance of determining
445 the input parameters to the model correctly varies greatly with particle size.
446 The most significant parameters are radius, density, and T_g . E.g. for T_g the
447 devolatilization time increases with 82 % for particles with diameter $79 \mu\text{m}$,
448 whereas it only increases with 11 % for particles with radius 3.12 mm , when
449 T_g is decreased by 30 %.

450 **6. Acknowledgements**

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454 thank Henrik Ström from Chalmers University of Technology for assisting
455 with the model development.

456 **Nomenclature**

457 **Abbreviations**

458	AR	aspect ratio
459	C	center
460	CFD	Computational Fluid Dynamics
461	cyl	cylinder
462	daf	dry ash free basis
463	db	dry basis
464	S	surface
465	SFOR	single first order reaction
466	sph	sphere
467	wt	weight

468 **Greek Characters**

469	α	thermal diffusivity	[m ² /s]
470	ϵ	emissivity coefficient	[-]
471	γ	char yield	[-]
472	ω	reaction rate	[kg/s]

473 ρ density [kg/m³]

474 **Roman Characters**

475 ΔH Enthalpy [J/kg]

476 \mathcal{L} Latent heat [J/kg]

477 A Surface area [m²]

478 C_p specific heat capacity [J/(kg·K)]

479 d_p diameter [mm/ μm]

480 F Evaporation heat function []

481 h convective heat transfer coefficient [J/(s·m²·K)]

482 k reaction rate [s⁻¹]

483 k thermal conductivity [J/(s·m·K)]

484 L initial particle length [mm or μm]

485 l particle length [mm or μm]

486 m mass [kg]

487 Nu Nusselt Number

488 Q Heat flow [J/s]

489 R initial particle radius [mm or μm]

490 r particle radius [mm or μm]

491 T Temperature [K]

492 t time [s]

493 V Volume [m³]

494 Y mass fraction [-]

495 y moisture content [wt fraction db]

496 **Sub- and Superscripts**

497 *p* particle
498 *b* boundary
499 boil boiling
500 desorp desorption
501 devo devolatilization
502 *g* gas
503 *H* high
504 *j* integer
505 *L* low
506 *l* layer
507 *m* moisture
508 rxn reaction
509 *w* radiation temperature

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Table 1: Model input parameters.

Parameter	Value	Ref.
h [J/(s m ² K)]	Estimated as described by Leth-Espensen et al.	[29]
ϵ [-]	0.85	[30, 31]
\mathcal{L}_{H_2O} [J/kg]	2256 000	[32]
ΔH_{desorp} [J/kg]	3610 000	[33]
ΔH_{devo} [J/kg]	200 000	[21, 34]
A_{L1} [s ⁻¹]	$1.11 \cdot 10^{11}$	[9, 26]
$E_{a,L1}$ [J/mol]	$177 \cdot 10^3$	[9, 26]
A_{L2} [s ⁻¹]	$9.28 \cdot 10^9$	[9, 26]
$E_{a,L2}$ [J/mol]	$149 \cdot 10^3$	[9, 26]
A_{L3} [s ⁻¹]	$3.05 \cdot 10^7$	[9, 26]
$E_{a,L3}$ [J/mol]	$125 \cdot 10^3$	[9, 26]
A_H [s ⁻¹]	$18.9 \cdot 10^3$	[27]
$E_{a,H}$ [J/mol]	$21.305 \cdot 10^3$	[27]
T_{boil} [K]	373.15	
C_g [J/(kg K)]	$\left(19.50583 + 19.88705 \cdot \frac{T_g}{1000} - 8.598535 \cdot \left(\frac{T_g}{1000}\right)^2 + \dots \right. \\ \left. \dots 1.369784 \cdot \left(\frac{T_g}{1000}\right)^3 + 0.527601 \cdot \left(\frac{1000}{T_g}\right)^2 \right) \cdot \frac{1000}{28}$	[35]
$C_{p,H_2O vap}$ [J/(kg K)]	$\left(30.09200 + 6.832514 \cdot T/1000 + 6.793435 \cdot (T/1000)^2 \dots \right. \\ \left. \dots - 2.53448 \cdot (T/1000)^3 + \frac{0.082139}{(T/1000)^2} \right) \frac{1000}{18}$	[36]
$C_{p,dry w}$ [J/(kg K)]	$z1 = 380/T$ $z2 = 1800/T$ $g1 = z1^2 \cdot \exp(z1)/(exp(z1) - 1)^2$ $g2 = z2^2 \cdot \exp(z2)/(exp(z2) - 1)^2$ $C_{p,dry w} = (g1 + 2 \cdot g2) \cdot 1000 \cdot R / 7.72$	[37, 38]
$C_{p,wet w}$ [J/(kg K)]	$A = 10^3 \cdot ((0.02355T - 1.320y/(1 - y) - 6.191)y/(1 - y))$ $C_{p,wet} = C_{p,wood}(1 - y) + 4190y + A$	[39]
$C_{p,char}$ [J/(kg K)]	$C_{p,char} = (g1 + 2 \cdot g2) \cdot 1000 \cdot R / 11.3$	[37, 38]
$k_{wet wood}$ [J/(m K s)]	$1.15 \cdot \min(0.13 + 0.0003 \cdot (T - 273), 0.3)$	[28, 40, 41]
$k_{dry wood}$ [J/(m K s)]	$\min(0.13 + 0.0003 \cdot (T - 273), 0.3)$	[28, 40]
k_{char} [J/(m K s)]	$\max(0.08 - (T - 273) \cdot 10^{-8}, 0.3)$	[28, 40, 41]
Shrin. ratio drying [-]	10 % (compared to wet)	[20]
Shrin. ratio devol. [-]	50 % (compared to dry)	[20]

Table 2: Parameter intervals in which the model validation has been conducted.

Parameter	Min	Max
d_p	79 μm	9.5 mm
Moisture [wt % wb]	0	6
T_g [K]	1276	1667
ρ [kg/m ³ (dry)]	580	1000
AR [-]	1	4

Table 3: Applied model input parameters used to simulate the experiments of Johansen et al.[27] *Completely dry particles, but moisture content > 0 for mathematical reasons.**Obernberger et al.[51] ***Masche et al. [13]

Parameter	$T_g = 1405 \text{ K}$	$T_g = 1667 \text{ K}$
h_{coef} [J/(s m ² K)]	1881	2076
R [μm]	39.4	39.4
L^{***} [μm]	157.6	157.6
ρ^{**} [kg/m ³]	591	591
T_{wall} [K] (estimated value)	1205	1467
T_{gas} [K]	1405	1667
char yield [wt% daf]	4.0	6.4
ash yield [wt% db]	0.2	0.2
Moist cont* [wt % wb]	0.0001	0.0001

Table 4: Applied model input parameters used to simulate the experiments of Lu et al.[52]
 *Estimated from empirical correlation from Leth-Espensen et al.,[29] determined for $\rho = 600, 800, \text{ and } 1000 \text{ kg/m}^3$.

Parameter	Pine	Beech
h_{coef} [J/(s m ² K)]	112.0	114.2
R [mm]	1.56	1.515
T_{wall} [K] (estimated value)	1187	1187
T_{gas} [K]	1487	1487
char yield* [wt% daf]	7.6/8.1/8.5	12.8/13.6/14.2
Moist cont [wt % wb]	5.5	5.5

Table 5: Applied model input parameters used to simulate the experiments of Lu.[53]

Parameter	Cylinder	Sphere
h_{coef} [J/(s m ² K)]	54.43	54.43
R [mm]	4.75	4.75
L [mm]	38	-
ρ [kg/m ³]	580	580
T_{wall} [K] (estimated value)	1176	1176
T_{gas} [K]	1276	1276
char yield [wt% daf]	8.4	6.4
Moist cont [wt % wb]	6	6

Table 6: Parameters for sensitivity analysis.

Parameter	Value
AR [-]	2
T_g [K]	1600
ρ [kg/m ³]	700
char [wt % daf]	5
moist [wt% wb]	4
ΔH_{devo} [j/kg]	200 000
ΔH_{desorp} [j/kg]	3 610 000

Table 7: Sensitivity Analysis. Each parameter is decreased and increased by 30 %. The change in devolatilization time is marked for each particle size as a percentage of the devolatilization time for the particle with no change in input parameter. t_{devo} for each of the three baseline particles are also included in the table.

Parameter	-30 %	+30 %	-30 %	+30 %	-30 %	+30 %
R [μm]	39.4		400		1560	
t_{devo} [s]	0.0133		0.426		3.61	
k_p [J/(m K s)]	+5	-3	+12	-6	+29	-15
C_p [J/(kg K)]	-15	+14	-14	+13	-11	+11
h_{coef} [J/(s m ² K)]	+23	-14	+15	-10	+4	-3
R [μm]	-35	+38	-37	+40	-41	+47
L (R constant) [μm]	-6	+3	-7	+4	-10	+6
ρ [kg/m ³]	-23	+20	-27	+26	-30	+30
T_{gas} [K]	+82	-31	+40	-21	+11	-8
k_L, k_H	+10	-7	+4	-3	+1	0
char yield [wt% daf]	-2	0	-1	0	0	0
Moist cont [wt % wb]	-2	+2	-4	+4	-4	+4
ΔH_{devo} [J/kg]	-5	+3	-2	+2	-2	+2
ΔH_{desorp} [J/kg]	-2	+2	-3	+3	-3	+3

Table 8: Overview over input parameters for particle simulation. The following values are used when nothing else is mentioned.

Parameter	Value
AR [-]	5
T_g [K]	1600
R [mm]	0.755
ρ [kg/m ³]	700
moist [wt% wb]	4