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Derivation of the kinetics of devolatilisation and oxidation of pulverized biomass in a drop tube furnace: Sensitivity to volume evolution and drag-coefficient model

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Abstract

Combustion experiments of raw and torrefied pine and demolition wood particles (600-800 μ m) are performed at 800°C in a drop tube furnace. The results provide the oxygen and carbon monoxide profiles along the reactor axis. These data are then used in a numerical model, developed to determine the kinetic parameters of devolatilisation and oxidation of the pulverized biomasses. In order to simulate the gas phase reactions, the model also takes as input the composition of the volatiles of the tested fuels measured during pyrolysis experiments at 800°C in the drop tube furnace. The model adopts different scenarios of particle volume evolution and different drag coefficient models in order to test their influence on the derived kinetic parameters. One of the volume evolution scenarios is a specific sub-model obtained by optical diagnostics of the combustion of the three biomasses in a previous study. Four other volume sub-models found in literature are also tested. For each of these scenarios, the model estimates close activation energy for devolatilization with a maximum variation of 2 kJ·mol⁻¹ from one scenario to another, while the activation energy of char oxidation is more influenced, varying by 14 kJ·mol⁻¹ with different scenarios. The five scenarios show similar gas concentrations and burnout versus the distance travelled by the particle. Nevertheless, this gives rise to a noticeable difference in the particle temperature along the furnace axis ($\pm 100^\circ\text{C}$ at some positions), in addition to different particle velocity and residence time ($\sim \pm 10\%$). The influence of the drag force is also studied using enhanced non-spherical model versus a spherical model. The non-spherical model leads to 10 to 14 kJ·mol⁻¹ higher devolatilisation activation energies and 10 to 19 kJ·mol⁻¹ higher char oxidation activation energies than the spherical model, along with a better prediction of the CO levels.

Nomenclature

A	Surface area (m ²)	t	Residence time (s)
Ac	Frequency factor for heterogeneous oxidation (kg·m ² ·s ⁻¹ ·Pa ⁻¹)	T	Temperature (K)
Av	Frequency factor for devolatilization (s ⁻¹)	Ta	activation temperature (K)
C	Char content (kg of char · kg ⁻¹ of particles)	U	Unburnt fraction
C _D	Drag coefficient	v	Velocity (m·s ⁻¹)
C _p	Specific heat at constant pressure	V _p	Particle volume

D_{O_2}	Mass diffusivity of oxygen ($m^2 \cdot s^{-1}$)	V	Volatiles content (kg of volatile matter \cdot kg^{-1} of particles)
D_w	Mass diffusivity of water in the gas mixture ($m^2 \cdot s^{-1}$)	W	Moisture content (kg of water \cdot kg^{-1} of particles)
dp	Particle diameter (m)	X_w	Water fraction in the gas phase
g	Gravitational acceleration ($9.81 m \cdot s^{-2}$)	Sh	Sherwood number
E_c	Activation energy for heterogeneous oxidation ($kJ \cdot mol^{-1}$)	λ	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
E_v	Activation energy for devolatilization ($kJ \cdot mol^{-1}$)	τ	Particle relaxation time (s)
h	Coefficient of heat transfer convection	μ	Viscosity ($kg \cdot m^{-1} \cdot s^{-1}$)
H_c	Heat of heterogeneous combustion ($J \cdot kg^{-1}$)	ν_c	Stoichiometric ratio of heterogeneous oxidation ($kg O_2 \cdot kg C$)
H_w	enthalpy of vaporization of water ($J \cdot kg^{-1}$)	ν_i	Stoichiometric coefficient of oxidation reactions of volatile i (kg species i \cdot $kg^{-1} O_2$).
k_0	Frequency factor for volatiles reactions (s^{-1})	ρ	Density ($kg \cdot m^{-3}$)
k_c	Specific char oxidation rate ($kg \cdot m^{-2} \cdot s^{-1}$)	σ	Stefan–Boltzmann constant ($5.67 \times 10^{-8} W \cdot m^{-2} \cdot K^{-4}$)
kdiff	Specific oxygen diffusion rate coefficient ($kg \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$)	ϕ	Molar fraction of CO in the char oxidation reaction
K_v	Devolatilization rate (s^{-1})	ϵ	Particle emissivity
K_w	Moisture releasing rate (s^{-1})	<i>Subscripts</i>	
M	Molecular mass ($g \cdot mol^{-1}$)	exp	Experimental value
n	Apparent reaction order	calc	Calculated value
N	Number of measured points	g	Free gas stream
Nu	Nusselt number	i	Volatile species (CO, CH ₄ , H ₂)
P_{O_2}	Partial pressure of oxygen (Pa)	p	Particle
P_{sat}	Vapor saturation pressure (Pa).	r	Reactor
R	Universal gas constant ($J \cdot mol^{-1} \cdot K^{-1}$)	s	Particle surface
Re	Reynolds number	0	initial values at injection ($t = 0$)
Sc	The Schmidt number		

29 1. Introduction

30 With the increasing tendency of integrating biomass in combustion, a greater interest is given to
31 acquire a detailed knowledge of the combustion phenomenon of biomass to improve the efficiency of
32 combustion and evaluate its performance in pulverized combustion furnaces. In many ways, biomass
33 is regarded as an economical solution of energy production and waste management. Its abundance and
34 sustainability makes it a potential candidate of replacing some of the coal in the existing infrastructure.

35 Several coal power plants have been subject to cofiring projects and some even totally converted their
36 consumption to biomass-derived fuels. Recently, Thunder Bay Unit 3 in Ontario [1] and Boardman
37 power plant in Portland [2] entered service operating on 100% biomass instead of coal. Other power
38 plants around the world are following the lead. The different physical and chemical properties of
39 biomass make it difficult to project years' worth of accumulated research of coal directly on biomass.
40 Studies have shown that even biochar or coal-like biomass obeys to completely different combustion
41 behaviors than coal [3]. Therefore, it is necessary to extend our knowledge of the combustion of
42 isolated biomass particles in order to validate the theoretical concepts describing the phenomena. This
43 can provide detailed data, including kinetic parameters, to help the development of computational
44 models, which can predict the behavior of biomass particles in industrial flames.

45 The combustion of coal and biomass particles at industrial and pilot scale studies are rarely available
46 in the literature [4]–[10]. Rather, the research focuses mainly on lab-scale investigations to
47 characterize the biomass. Drop tube furnace is one of the best methods to reproduce the realistic
48 combustion conditions for isolated particles at high heating rate and short residence time. Specific
49 sensors and direct observation techniques are used to access the degradation process of the particles in
50 the hot gas stream. The data provides the combustion timeline, ignition delay, morphological evolution
51 and pyrolysis products. Lu et al. [11] reported experimental data on the effect of particle shape on
52 devolatilization of biomass in a drop tube furnace. Spherical particles lost mass slower than cylindrical
53 ones, which in turn devolatilized slower than flake like particles. The study concluded to a more
54 intense devolatilization as well as a higher degree of conversion for fine particles compared to coarser
55 particles. The pyrolysis products were measured in several studies in drop tube furnace [12]. A very
56 high gas yield is reported at high temperatures and heating rates. The main emitted species are CO₂,
57 CO, H₂, CH₄, H₂O and heavier hydrocarbons with proportions dependent on the operating conditions
58 and fuel type. CO is dominant at high temperatures, while hydrogen increases with it, and CO₂ tends
59 to stabilize beyond 800°C [13]–[15].

60 Mathematical models have also been developed in a few studies to help data analysis to extract the
61 kinetic parameters of devolatilization and char oxidation (*Table 1*), and subsequently predict other
62 combustion parameters, as in Commandre et al. [16] for petcoke. Two approaches are proposed in
63 this purpose: the model fitting approach and the 1D Lagrangian model. The first assumes that the
64 combustion process in the DTF is performed by sections, each of them having its own set of kinetic
65 parameters. Devolatilization occurs in the upper sections while char oxidation takes place in the lower
66 sections. Costa et al. [17] applied this approach to determine the activation energies of the
67 devolatilization and char oxidation of raw and torrefied pine shells ($E_v = 21.58 \text{ kJ}\cdot\text{mol}^{-1} - E_c = 129.86$
68 $\text{kJ}\cdot\text{mol}^{-1}$ and $E_v = 21.28 \text{ kJ}\cdot\text{mol}^{-1} - E_c = 89.75 \text{ kJ}\cdot\text{mol}^{-1}$ respectively). In the same study, similar
69 trends, but with much higher activation energies, were estimated for raw and torrefied olive stones.
70 Using this approach, Farrow et al. [18] also obtained apparent activation energies between 24.2

71 $\text{kJ}\cdot\text{mol}^{-1}$ and $34.7 \text{ kJ}\cdot\text{mol}^{-1}$ for the pyrolysis of pinewood sawdust. On the other hand, Ballester and
72 Jimenez [19] developed a detailed 1D Lagrangian model to perform numerical calculations on the
73 particle thermal history based on the experimental data. The model was applied originally to coal and
74 then adapted to biomass giving: $E_v = 11 \text{ kJ}\cdot\text{mol}^{-1}$ and $E_c = 63 \text{ kJ}\cdot\text{mol}^{-1}$ [20]. Wang et al. [21] also used
75 this approach to evaluate the combustion behavior of biomass waste derived fuels, pine and coal in a
76 drop tube furnace. Pereira et al. [22] applied both models to the combustion of poplar short rotation
77 coppice. In comparison, the apparent activation energies in the devolatilization zone vary from 34.1
78 $\text{kJ}\cdot\text{mol}^{-1}$ for the model-fitting approach to $12.8 \text{ kJ}\cdot\text{mol}^{-1}$ for the detailed model proposed by Jiménez et
79 al. [20], whereas in the char oxidation zone both models originate close apparent activation energies
80 ($73.2 \text{ kJ}\cdot\text{mol}^{-1}$ and $69.0 \text{ kJ}\cdot\text{mol}^{-1}$). The distinct values are attributed to the simplifications considered in
81 the model-fitting approach including the assumption of similar particle and gas temperature, which
82 explains the higher activation energy of devolatilization, and the constant oxygen pressure at the
83 particle surface along the furnace, which explains the higher activation energy of char oxidation.

<i>Study</i>	<i>Temperature (°C) – atmosphere – particle size</i>	<i>Fuel</i>	<i>Model approach</i>	<i>A_v (s^{-1})</i>	<i>E_v ($\text{kJ}\cdot\text{mol}^{-1}$)</i>	<i>A_c ($\text{g}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$)</i>	<i>E_c ($\text{kJ}\cdot\text{mol}^{-1}$)</i>
<i>Costa et al.</i> [17]	900, 950, 1000, 1050, 1100°C Air 30-1000 μm	Raw pine	Model-fitting	0.3	21.6	1670.4	129.9
		Torrefied pine		0.4	21.3	54.9	89.8
<i>Farrow et al.</i> [18]	900, 1100, 1300, 1450 °C CO ₂ and N ₂ 125-250 μm	Pinewood	Model-fitting	63.4 - 100.1	24.2-34.7	-	-
<i>Pereira et al.</i> [22]	900, 950, 1000, 1050, 1100°C Air 20-1500 μm	poplar short rotation coppice	Model-fitting	5.1×10^{-7}	34.1	0.05	73.2
			1D Lagrangian	90	12.8	0.38	69.0
<i>Jimenez and Ballester</i> [20]	1040, 1175, and 1300 °C Air 100-1000 μm	<i>Cynara cardunculus</i>	1D Lagrangian	47.17	11	0.46	63
<i>Wang et al.</i> [21]	1100°C Air 30-1128 μm	Pine braches	1D Lagrangian	15×10^3	55	1.73	93

84 *Table 1: Survey of the kinetic parameters of devolatilization and oxidation of biomass using different*
85 *model approaches*

86 In this paper, we attempt to evaluate the combustion characteristics of raw and torrefied maritime pine
87 and demolition wood in a drop tube furnace. Maritime pine is selected as a reference fuel for woody
88 biomass as it is extensively studied in literature [17], [21], [23]–[26]. Demolition wood represents a
89 resource of growing interest for energy production purposes. It is produced with large quantities in
90 construction sites with no major technology to valorize it other than incineration [27]. A detailed
91 combustion model uses the experimental data to determine the kinetic parameters of devolatilisation

92 and oxidation of these fuels. In addition, it relies on the composition of the pyrolysis gas produced in
 93 pyrolysis experiments to model the gas phase reactions. Direct time-resolved observation and
 94 characterization of the combustion of these fuels, performed by particle combustion shadowgraphy in
 95 a previous study [3] provided the main scenario of the particle volume evolution. The latter is changed
 96 in the model to study the sensitivity of the obtained kinetic parameters on the volume scenario. The
 97 sensitivity study also addresses the influence of drag coefficient modeling on the calculation of the
 98 kinetic parameters.

99 2. Experimental setup

100 2.1 Biomass fuels

101 Maritime pine obtained from the south of France is used as a reference of raw biomass in this study
 102 (referred to as *Pine*). A part of the original biomass stock was torrefied at 280 °C for 25 min to
 103 produce particles with a lower volatile content (referred to as *Pint*). Demolition wood (*DW*) obtained
 104 from a demolished construction site was also used as representative of waste fuels. All of these fuels
 105 were first milled to a size range of 0 – 2 mm. The proximate and ultimate analyses of the fuels are
 106 listed in *Table 2* (following ASTM norm) alongside with the heating value and the aspect ratio (the
 107 ratio of the maximum length to the maximum width of the particle). Pine has a high moisture content,
 108 which is largely reduced by the torrefaction process generating *pint*. Torrefaction also reduces the
 109 volatile content while increasing the fixed carbon content and improving the energy density with
 110 higher heating value. Demolition wood has a chemical composition close to that of pine but with
 111 higher ash content due to the impurities contained within. This effect lowers its heating value.

	<i>Maritime Pine (pine)</i>	<i>Torrefied pine (pint)</i>	<i>Demolition wood (DW)</i>
<i>Moisture</i>	11.46	1.93	6.32
<i>Ash (db)</i>	0.87	1.33	2.13
<i>Volatile matter (db)</i>	81.22	73.62	78.29
<i>Fixed carbon (db)</i>	18.58	25.05	19.57
<i>C (db)</i>	51.68	55.1	48.51
<i>H (db)</i>	5.93	5.68	5.63
<i>N (db)</i>	0.22	0.29	4.39
<i>O (db by difference)</i>	41.27	37.52	40.58
<i>LHV (MJ·kg⁻¹) (db)</i>	18.45	19.73	17.71
<i>Aspect ratio</i>	2.50 ± 0.70	1.67 ± 0.40	2.08 ± 0.48

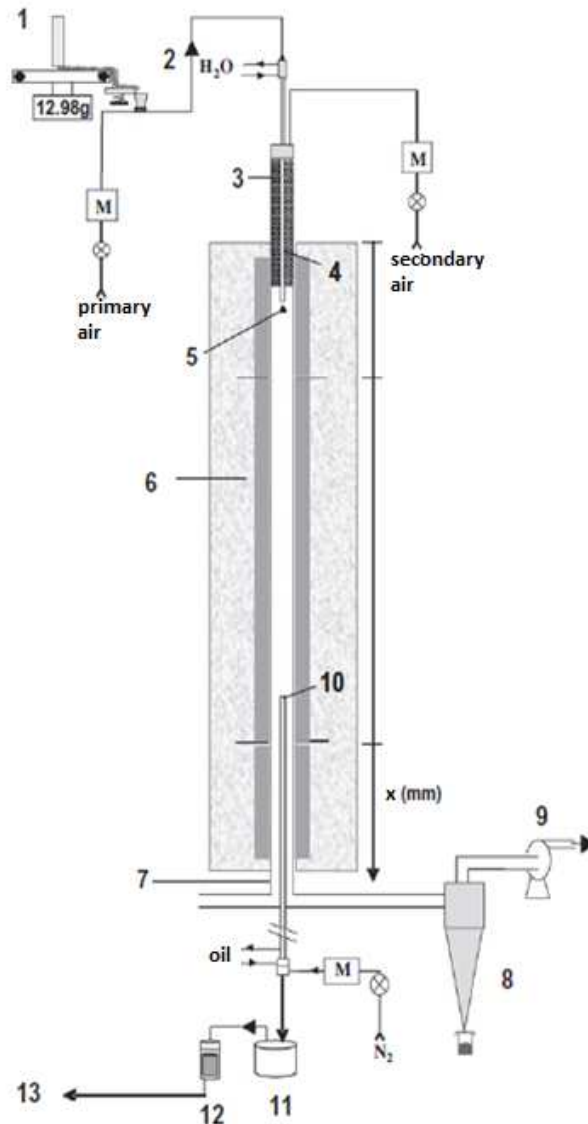
112 *Table 2: Fuels proximate and ultimate analysis and particles shape properties (db: dry basis)*

113 The pulverized fuels were thoroughly sieved to a range of 600 - 800 μm. Pine particles are mostly
 114 flake-like while torrefied pine particles are mostly cylindrical and spherical. Demolition wood
 115 particles are mostly thick flakes made of small compressed fragments of wood [3].

116 2.2 Experimental setup

117 The drop tube furnace used in the present study is a heated reactor designed to reproduce the thermal
118 conditions encountered in an industrial furnace with high heating rate. This experimental setup,
119 located in the Rapsodee laboratory of Albi, France, was reconfigured for the purpose of this study
120 (*Figure 1*). The apparatus is able to perform the study of biomass particles decomposition under
121 various atmospheres (Air, N₂, etc.) and temperatures up to 1300°C. The achievable heating rates are in
122 the order of 10⁴ °C·s⁻¹ [16]. The 1.5 m long reactor is an ø75mm alumina tube inside a three zones
123 electric furnace covered with insulation fibers, and fed with an electrically preheated laminar gas flow.
124 The solid fuel particles are injected in the reactor using the transport gas through a water-cooled
125 feeding injector. At the end thereof, a 12 mm diameter stainless steel dispersion dome is held integral
126 with the injector at a distance from the orifice of 1.2 mm. It disperses the fuel in an ideally
127 homogeneous manner over the reactor cross-section. The primary gas and the particles are then mixed
128 with the secondary gas flow inside the furnace. The thermal cycle of a particle begins at the moment it
129 leaves the injection probe and immerses in the hot gas flow.

130 A sampling probe inserted through the outlet section permits sampling the gaseous effluents and solid
131 particles at any height starting at 60 cm from the injection point. Indeed, previous temperature
132 measurements indicated that the isothermal zone starts at 30 cm from the injector [15]. The probe is
133 internally cooled by oil at 150 °C in order to quench the ongoing chemical reactions by a sudden
134 decrease in the medium temperature and prevent the tars from condensing at the same time. Two-third
135 of the total flow is sampled by the probe to ensure the collection of a representative sample.
136 Subsequently, most of solid particles are collected in a bin at the bottom of the sampling probe, and
137 the finest ones are trapped on a filter. Gases are then cooled in a condenser allowing to collect water
138 and condensable species before conveying the dry gases to the analyzer via a set of heated lines.



- 139
 140
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 142
 143
 144
- | | | | | |
|--------------------------------|-----|----------------------------------|-----|-------------------------|
| 1. Controlled weighting system | 145 | 6. Three zone electrical furnace | 150 | 11. Char pot |
| 2. Pneumatic transport | 146 | 7. 75mm i.d alumina tube reactor | 151 | 12. Filter |
| 3. Electrical preheater | 147 | 8. Cyclone collector | 152 | 13. Gas analyzer |
| 4. Water cooled feeding probe | 148 | 9. Exhaust fan | | M: Mass flow controller |
| 5. Dispersion dome | 149 | 10. Oil cooled sampling probe | 153 | |

154 *Figure 1: Scheme of the drop tube furnace*

155

156 2.3 Experimental procedures

157 In the view of the limitation set by the length of the sampling probe, the experimental conditions were
 158 chosen so that the biomass was not completely pyrolyzed upstream the first available sampling point,
 159 at 60 cm from the injection point, and reaches at the same time 80% conversion in combustion
 160 conditions at the final sampling point (150 cm). The temperature set point was the regulating
 161 parameter, since it is directly related to the conversion rate of the fuel. These conditions were achieved
 162 at a wall temperature of 800°C for biomass particles in the size range 600 to 800 µm.

163 The secondary airflow was preheated to the wall temperature before introducing it to the furnace. The
164 solid fuel feeding rate was $1 \text{ g}\cdot\text{min}^{-1}$ transported by $2 \text{ l}\cdot\text{min}^{-1}$ (at STP) of primary airflow. The
165 preheated gas flow was set to $20 \text{ l}\cdot\text{min}^{-1}$ (at STP) for all experiments. As observed from the bottom of
166 the reactor, the biomass particles were falling in a single manner. Besides, the flow was highly diluted
167 so that the particle-to-particle interactions can be neglected. In these conditions, the gas residence time
168 inside the furnace was estimated to be 3.8 sec. The particle residence time during the combustion of a
169 pine particle ($600\text{-}800 \text{ }\mu\text{m}$) was estimated to be 0.674 sec using a physical model taking into
170 consideration the size and density evolution of the particle and its slip velocity. During combustion,
171 the conversion of the fuel as a function of the residence time was determined from the partial pressure
172 of oxygen since the oxygen consumption is proportional to the burnout rate. This method is preferable
173 over the ash tracer method, which leads to high uncertainty when dealing with low ash content solid
174 fuels as explained by T. Ballantyne et al. [28], due to the uncertainty in the ash content measurement
175 and the volatility of ash at high heating rates and temperatures. The concentrations of O_2 and CO were
176 measured on line using a Testo gas analyzer model 350.

177 Moreover, experiments under pyrolysis conditions were performed in the purpose of quantifying the
178 gas composition produced during the devolatilization stage of the particle. The gas composition is
179 necessary to evaluate the gas phase reactions in the combustion model. The wall temperature was set
180 to 800°C similarly to the combustion experiments. The particles were transported with nitrogen, which
181 was also used as the secondary gas, preheated to the wall temperature. The gas was sampled at the exit
182 of the reactor using sampling bags after being filtered and dried. The bags were then analyzed by a
183 micro-GC to measure the mean concentrations of CO_2 , CO , CH_4 and H_2 produced during the
184 experiment.

185 **3. Numerical modeling of the combustion of single biomass particles**

186 A 1D Lagrangian model was coded on Matlab to perform numerical calculations on the particle
187 thermal history based on the experimental data. The model allows the determination of the kinetic
188 parameters of the physicochemical reactions that better reproduce the oxygen partial pressure obtained
189 experimentally. Similar models have been proposed in [20] and [21], using also a 1D Lagrangian
190 approach and similar kinetic formulation on thermally thin particles.

191 ***Main hypothesis***

192 Considering the dilute particle flow in the experiments, the particle-to-particle interactions were
193 neglected and the gas flow rate was considered constant at every point. Uniform temperature and
194 homogeneous concentrations of chemical species are assumed in a horizontal section of the DTF.

195 The physical properties are described through the conservation equations of mass, momentum and
 196 energy exchange between a single particle and its surrounding environment. The devolatilization
 197 reaction and heterogeneous oxidation of char are described at the particle level.

198 The particle has a simplified composition, comprising only C, H, and O species. It has a spherical
 199 shape with the initial diameter equals to the average diameter of the sample.

200 *Particle trajectory*

201 In a gas-solid flow of particles in the studied size range, the drag and body forces are known to be the
 202 dominant forces. The velocity can be calculated by integrating the second law of motion:

$$203 \quad m_p \frac{dv_p}{dt} = \frac{\pi d_p^2}{4} \cdot \frac{\rho_g}{2} \cdot C_D (v_g - v_p)^2 + m_p g - \rho_g V_p g \quad (1)$$

204 The Drag force, particle weight and Archimedes up-thrust are represented by the three terms on the
 205 right hand side. The drag coefficient C_D is expressed in the case of spherical particles by the Stokes
 206 law in terms of the Reynolds number:

$$207 \quad C_D = \frac{24}{Re_p} = \frac{24}{|v_g - v_p| \rho_g d_p / \mu} \quad (2)$$

208 Equation (1) can be rearranged in the following form:

$$209 \quad \frac{dv_p}{dt} + \frac{1}{\tau} (v_g - v_p) = \left(\frac{\rho_g}{\rho_p} - 1 \right) g \quad (3)$$

210 The right hand side is related to the buoyancy of the particle in the airflow. τ is the particle relaxation
 211 time given by the product of the particle mass and its mechanical mobility. This term characterizes the
 212 time required for the particle to adjust its velocity to a new condition of forces.

$$213 \quad \tau = \frac{\rho_p V_p d_p}{12 \mu_g A_p} \quad (4)$$

214 *Drying model*

215 The drying process of the particle is modeled using the water diffusion approach [29]. The moisture
 216 flux contained in the particle increases with the particle temperature, which increases rapidly due to
 217 the high heating rate. The vapor release to the gas is controlled by the mass transfer between the
 218 surrounding gas and the particle.

$$219 \quad \frac{dW}{dt} = 18 \cdot 10^{-2} \cdot K_w \left(\frac{P_{sat}}{RT_p} - \frac{X_w}{RT_g} \right) \quad (5)$$

220 With:

$$221 \quad P_{sat} = 1.1 \cdot 10^{-5} \cdot \exp \left[11 \cdot (T_p - 273.15)^{0.16} \right] \quad (6)$$

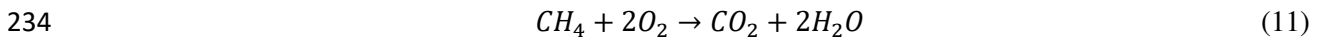
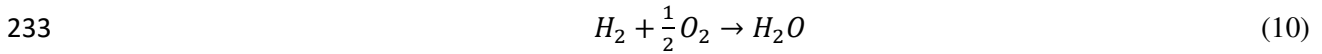
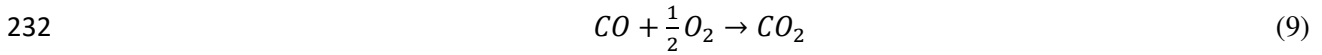
222
$$K_w = \left(2 + 0.6 \cdot Re_p^{1/2} Sc^{1/3}\right) \cdot \frac{D_w}{d_p} \quad (7)$$

223 ***Devolatilization and volatile combustion model***

224 Literature shows that two competing steps devolatilization mechanisms are suitable for high heating
 225 rate pyrolysis modeling, but are more difficult to compute. As a first approach, we assume that the
 226 release rate of volatiles follows a one-step Arrhenius mechanism where A_v and E_v are determined by
 227 iterations for the best match with experimental data.

228
$$\frac{dV}{dt} = A_v \cdot \exp\left(-\frac{E_v}{RT_p}\right) \cdot (V_0 - V) \quad (8)$$

229 The composition of the volatiles is determined by the pyrolysis experiments and it is assumed constant
 230 at all positions. The gas phase reactions are simplified to the oxidation reactions of the following
 231 combustible species: CO, H₂, and CH₄. The reactions are considered to be complete.



235 The reactions rate R_i , is formulated under the Arrhenius form where ρ_{aj} (in kmol·m⁻³) is the molar
 236 density of the species a_j . The parameters are given in *Table 3*.

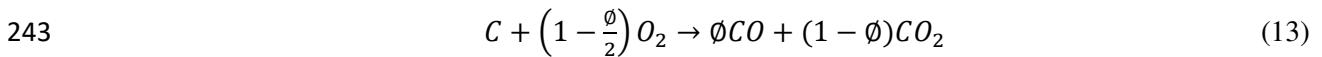
237
$$R_i = k_{0,i} \exp\left(\frac{T_{a,i}}{T}\right) \cdot T^{b_0} \rho_{a1}^{b_1} \rho_{a2}^{b_2} \rho_{a3}^{b_3} \quad (12)$$

Reaction i	$k_{0,i}$	$T_{a,i}$	b0	a1	b1	a2	b2	a3	b3
1	$1 \cdot 10^{+15}$	16000	-1.5	CO	1	O ₂	0.25	H ₂ O	0.5
2	$5.16 \cdot 10^{+13}$	3430	-1.5	H ₂	1.5	O ₂	1	-	-
3	$3.55 \cdot 10^{+12}$	15700	-1	CH ₄	1	O ₂	1	-	-

238 *Table 3: Values to be used for computations of gas-gas reaction rates [30]*

239 ***Char oxidation model***

240 The heterogeneous char oxidation starts once oxygen reaches the particle surface and reacts with
 241 carbon atoms. The reaction produces CO and CO₂ with a temperature dependent ratio ($0 < \emptyset < 1$)
 242 [14].



244
$$R_c = \frac{[CO]}{[CO_2]} = 2500 \cdot \exp\left(-\frac{51843}{RT_p}\right) = \frac{\phi}{1-\phi} \quad (14)$$

245 Therefore, the rate of the oxidation depends on the diffusion rate of oxygen and the chemical reaction
246 rate.

247
$$\frac{dC}{dt} = -A_p k_c P_{O_2,s}^n \quad (15)$$

248 k_c is the chemical reaction rate coefficient. $P_{O_2,s}$ is the oxygen partial pressure at the particle surface
249 supplied by molecular diffusion, which obeys Fick's law:

250
$$\dot{m}_{O_2} = \pi d_p Sh D_{O_2} \frac{M_{O_2}}{RT_g} (P_{O_2,g} - P_{O_2,s}) \quad (16)$$

251 Sherwood number (Sh) was set to 2 by assumption. Note that the effect of the outward flow of the
252 species is negligible and the supplied oxygen by diffusion is consumed by the heterogeneous reaction.
253 After arranging the above equations and setting n to unity [20], the carbon consumption can be
254 rewritten as follows:

255
$$\frac{dC}{dt} = -A_p \frac{1}{\frac{1}{K_{diff}} + \frac{1}{k_c}} P_{O_2,g} \quad (17)$$

256 The diffusion and chemical kinetic coefficients are calculated:

257
$$K_{diff} = Sh \cdot v_c \frac{D_{O_2} M_{O_2}}{d_p RT_g} \quad (18); \quad k_c = A_c \cdot \exp\left(-\frac{E_c}{RT_p}\right) \quad (19)$$

258 The remaining volatiles and char form the unburnt fraction U of the particle. The evolution of the
259 particle volume was obtained for each biomass in a previous study from direct observation and
260 characterization of the particle degradation by optical diagnostics in [3] assuming that particles are
261 spherical and isotropic.

262
$$d_p = d_{p_0} f(U) \quad (20)$$

263
$$U = \frac{C + (V_0 - V)}{C_0 + V_0} \quad (21)$$

264 Where $f(U)$ is a characteristic function of each fuel type in terms of the unburnt fraction. Assuming
265 spherical particles and isotropic consumption, the particle volume can be directly evaluated from its
266 projection area. In fact, the initial particle shape was fibrous and irregular for all types. The
267 irregularities tend to disappear in the remaining char, which becomes more rounded than the original
268 particle [31], [32]. The high temperatures encountered during the char combustion allow the particle
269 to deform and smooth the edges.

270 **Heat balance**

271 The particle temperature is different from the gas and wall temperatures. The small size of the particle
 272 limits the temperature gradient within the particle, so they can be considered thermally thin in our
 273 operating conditions [33] as Biot number is low. The heat balance can be converted into the following
 274 equation by assuming that mixing between atmosphere gas and transport gas is instantaneous [16]:

$$275 \quad C_{pp}m_p \frac{dT_p}{dt} = h_p A_p (T_g - T_p) + A_p \varepsilon \sigma (T_r^4 - T_p^4) - \frac{dW}{dt} \cdot H_w - \frac{dC}{dt} \cdot f_h H_c - \sum \dot{m}_i C_{pi} T_p \quad (22)$$

276 Once introduced in the furnace, the particle is exposed to convection with the surrounding gas and to
 277 radiation from the furnace wall represented by the first and second terms in the right hand side.
 278 Particle absorption of energy during drying is accounted for by the third term, while the fourth term
 279 includes the energy released during char combustion. f_h being the coefficient of heat release from char
 280 combustion due to incomplete combustion.

$$281 \quad f_h = 1 - 1.44 \cdot \left(1 - \frac{12}{32} \cdot \frac{1}{v_c}\right) \quad (23)$$

282 The particle energy balance does not include a heat exchange term between the particle and the flame.
 283 Instead, we assume that the flame heats up the surrounding gas, which in turn heats the particle. The
 284 assumption is backed experimentally by the observations made by Riaza et al. [34] in a visual free fall
 285 reactor, where a perfectly spherical flame envelops the particle at a lift-off distance. The last term of
 286 heat balance represents the heat fluxes supplied to the environment by the gases leaving the particle.
 287 During their ejection, the volatiles exchange heat with the particle, as well as with the gas phase. The
 288 ejected volatiles also exchange heat with the stream gas by convection, before liberating their energy
 289 through oxidation, causing a temperature rise in the gas phase. The energy balance of the gas phase is
 290 formulated as follows:

$$291 \quad C_{pg} \dot{m}_g \frac{dT_g}{dt} = h_p A_p (T_p - T_g) + h_r A_r (T_r - T_g) + \sum R_i \cdot H_i + \sum \dot{m}_i C_{pi} T_p \quad (24)$$

292 The terms in the right hand side include respectively: the convection heat transfer between the particle
 293 and the gas, the convection heat transfer between the furnace wall and the gas, the liberated heat from
 294 the oxidation of the volatiles, and the heat fluxes supplied to the environment by the gases leaving the
 295 particle. The Nusselt number of convection between the gas phase and the reactor inner wall is
 296 determined by Mill's model for convection in a vertical cylinder [35].

297 *Derivation of kinetic parameters*

298 Oxygen is involved in the main chemical reactions occurring in the furnace. Therefore, $P_{O_2,g}$ is not
 299 constant and its evolution should be followed to provide the input parameters for the particle
 300 consumption. A relationship is established between the partial pressure of oxygen and the consumed
 301 volatiles and char to determine its value at a given position x .

302
$$P_{O_2,x} - P_{O_2,0} = \frac{\rho_g RT_g}{M_{O_2}} \cdot \frac{Q_f}{Q_g} \cdot \left(\sum_i \frac{1}{v_i} \cdot V_i + \frac{1}{v_c} \cdot (C_0 - C) \right) \quad (25)$$

303 The first term in the right hand side sums the contribution of the oxidation reaction of each volatile
 304 species. V_i represents each species of the volatiles (CO, H₂, CH₄) and v_i is the corresponding
 305 stoichiometric coefficient of the oxidation reaction (Kg species i · Kg⁻¹ O₂). Oxygen consumed by the
 306 char is represented by the second term.

307 The prediction is compared with the measured oxygen content (%vol.) along the furnace axis. The
 308 deviation between both values is calculated:

309
$$\delta = \sum \frac{1}{N} \cdot ([O_2]_{exp} - [O_2]_{calc})^2 \quad (26)$$

310 The code runs in iterations in two rounds to spot the optimal pairs of kinetic parameters (Av, Ev) and
 311 (Ac, Ec) providing the best prediction by minimizing the deviation function δ . *Table 4* presents the
 312 scanned ranges and the increment values of each parameter.

	Av (1·s ⁻¹)	Ev (kJ·mol ⁻¹)	Ac (g·m ⁻² ·s ⁻¹ ·Pa ⁻¹)	Ec (kJ·mol ⁻¹)
First run				
Range	1-500	1-100	0.01-5	1-100
Increment	1	0.5	0.01	0.5
Second run				
Range	Av1 ± 10	Ev1 ± 0.5	Ac1 ± 0.1	Ec1 ± 0.5
Increment	1	0.1	0.01	0.1

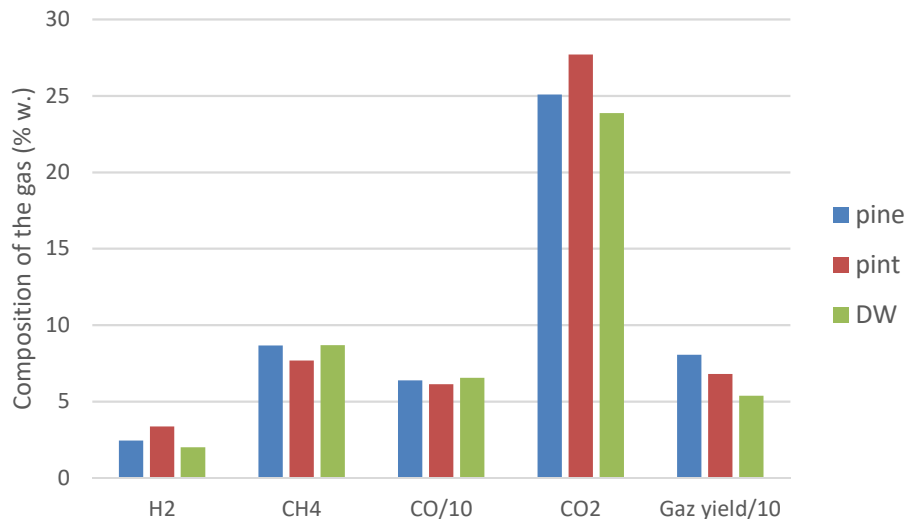
313 *Table 4: The scanned ranges of the kinetic parameters*

314 The code runs a first round in these ranges to spot (Av1, Ev1) and (Ac1, Ec1). A second run is done in
 315 a more refined range around the values spotted in the first round with a smaller increment.

316 4. Results and discussion

317 4.1 Preliminary pyrolysis experiments

318 The pyrolysis of biomass decomposes the lignocellulosic components into light gases, tar, and char.
 319 Tar eventually breaks down into light hydrocarbons. The gaseous species are mainly composed of CO,
 320 CO₂, H₂, CH₄ and a small proportion of heavier hydrocarbons such as C₂H₄, C₂H₆. The pyrolysis gas
 321 composition (% by mass) from pine, pint and DW are presented in *Figure 2*. These compositions of
 322 the pyrolysis gas of each fuel are used in the numerical model when simulating their combustion.



323
324 *Figure 2: Comparison of the pyrolysis gas composition for different biomasses at 800°C (fuel size*
325 *600-800µm)*

326 The higher moisture content in pine (11.46%) did not reduce the gas yield in front of the low moisture
327 pint. Indeed, an investigation on the fast pyrolysis of pine with different moisture content (10.7%
328 versus 0% (dried)) in [15], at 850°C for 0.9 to 1.5 s under nitrogen, concluded that the natural
329 moisture has no influence on the amount and nature of the final pyrolysis gas. While the overall gas
330 yield of pine is typical to what has been reported for the flash pyrolysis of wood in similar conditions
331 [36]–[38], demolition wood has low gas yield. This may be due to its higher density, which increases
332 its velocity and reduces the residence time in the reactor. Torrefied pine ejected less volatiles during
333 the experiment with lower CO and CH₄ yields. CO was quantified as the major fraction of the
334 produced gases followed by CO₂, CH₄ and H₂ respectively. This is in line with previous studies [39],
335 [40]. The high percentage of oxygen in the biomass favors the formation of CO. The µ-GC also
336 detected peaks corresponding to C₂H₂, C₂H₂ and C₂H₆ but they were not quantified. Heavier
337 hydrocarbons were not detected in the analysis. They may have appeared earlier in the conversion
338 pathway of volatiles, but cracked to methane, hydrogen and soot through polymerization and
339 reformation.

340 4.2 Combustion

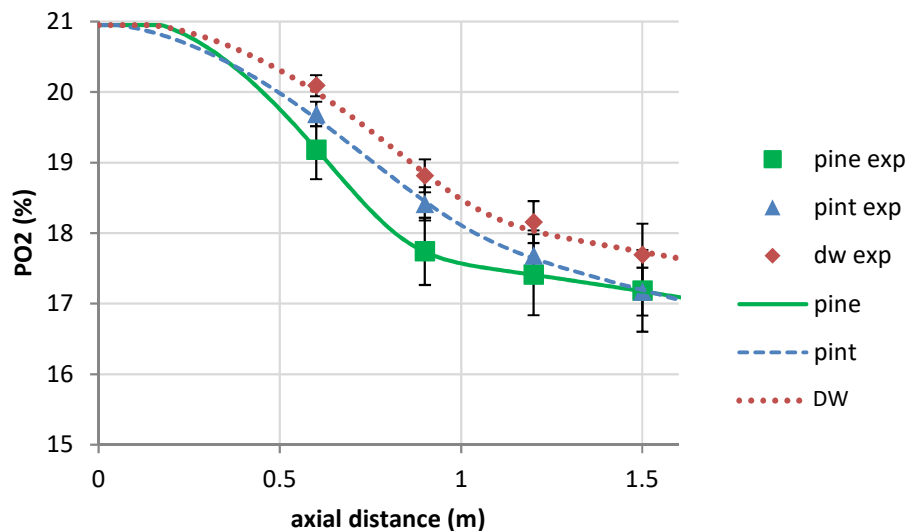
341 4.2.1 Kinetic parameters

342 The biomass fuels were injected at 800 °C with a sufficient airflow rate so that the oxygen fraction at
343 the furnace exit is at least of 16%. The model iteratively minimizes the difference between the
344 calculated and measured concentration of oxygen to determine the kinetic parameters. *Figure 3*
345 compares the predicted and the measured evolutions of the oxygen partial pressure on dry basis along
346 the reactor longitudinal axis corresponding to the three tested fuels. The algorithm successfully
347 follows the experimental points leaving a very low error margin. *Table 5* lists the kinetic parameters
348 with the corresponding deviations from the experimental points. The values are close to those reported

349 elsewhere using a similar model, for the devolatilization and char oxidation of raw and torrefied pine
 350 shell in [17] and of *Cynara cardunculus* in [20].

	A_v ($l \cdot s^{-1}$)	E_v ($kJ \cdot mol^{-1}$)	A_c ($g \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$)	E_c ($kJ \cdot mol^{-1}$)	δ eq.(26)
Pine	294	18.3	0.93	53	$1.6 \cdot 10^{-04}$
Pint	107	19.0	1.65	65	$1.7 \cdot 10^{-03}$
DW	380	21.0	3.70	53	$3.1 \cdot 10^{-03}$

351 *Table 5: Kinetic parameters obtained by the mathematical model for the tested fuels*



352
 353 *Figure 3: Evolution of %O₂ partial pressure along the tube furnace axis (600 – 800 μm particles at*
 354 *800°C with air)*

355 However, a detailed DTF-model by Wang et al. [21] similar to this study, calculated activation
 356 energies for five other biomasses, two to three times higher than the values calculated here. The
 357 difference is however compensated by a very high pre-exponential factor ($15 - 300 \cdot 10^3 s^{-1}$), but still,
 358 the model showed large discrepancies between measurements and predictions in the near injector zone
 359 where most of the devolatilization takes place. It should be noted that the experimental conditions
 360 were different in [21] (see *Table 1*), and the combustion air was injected at room temperature and
 361 consequently the particles are exposed to a different heating rate. This probably induces the different
 362 combustion kinetics. Another factor creating this difference between the models predictions is their
 363 corresponding particle volume evolution that will be discussed later. Therefore, based on this review,
 364 the activation energies in *Table 5* are in accordance to what can be found in literature using similar
 365 models and experimental conditions.

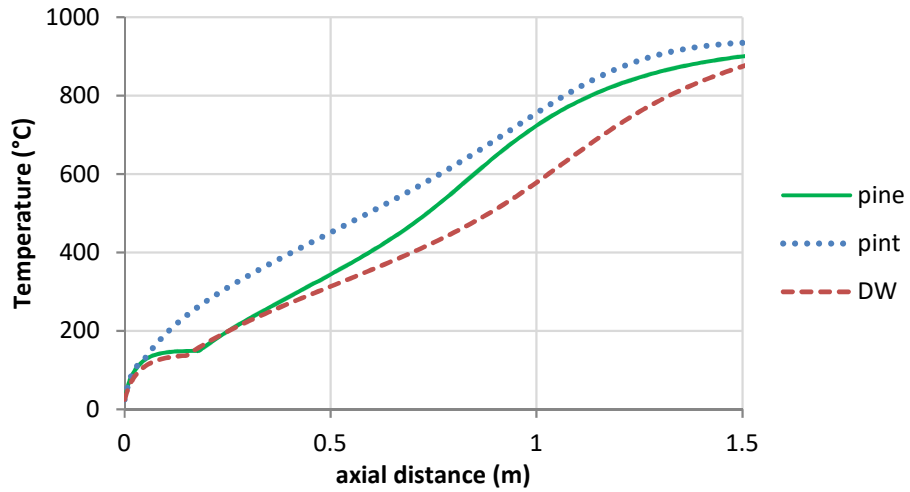
366 The results show that higher activation energies are calculated for demolition wood than pine.
 367 Moreover, torrefaction reduces the reactivity of devolatilization and char oxidation which is consistent
 368 with previous studies [41].

369 **4.2.2 Particle conversion**

370 The first sampling point at 60 cm from the injection point marks some oxygen consumption observed
371 for the three fuel types. Upstream this point, the model predicts the combustion parameters based on
372 their measured tendencies later. At this distance, the particles have already started their degradation
373 journey, which is estimated to last for 0.674 sec for pine, 0.772 sec for pint, and 0.572 sec for DW
374 inside the furnace. The heating rate is around $2000^{\circ}\text{C}\cdot\text{s}^{-1}$ as calculated by the model.

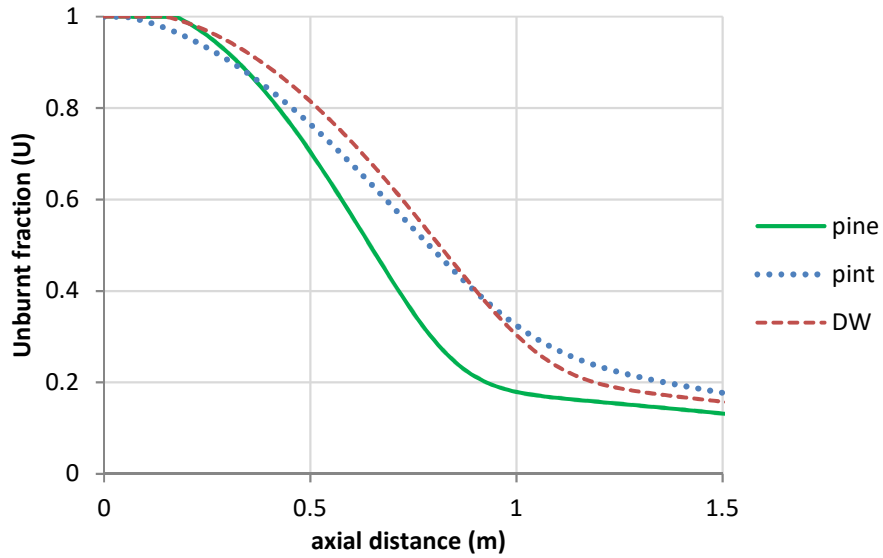
375 After injection, particle temperature increases until around 100°C during the release of moisture from
376 the particle. Most of the received energy at this stage is absorbed as latent heat for drying and thus the
377 particle temperature stabilizes for a certain time as simulated in *Figure 4*. Demolition wood and pine
378 with roughly 6 % and 11 % moisture content respectively experience a significant delay in initiation of
379 their devolatilization compared to the relatively dry particles ($\sim 2\%$ moisture) of torrefied pine. The
380 latter takes advantage for an early increase in temperature. No oxygen is consumed during the drying
381 stage. Drying is directly followed by a rapid liberation of volatiles associated with high consumption
382 rate of oxygen. Despite the late start, pine leads the consumption rate given the low activation energy
383 and the more intense devolatilization pointed out in a previous study [3]. The heavier demolition wood
384 particles acquire higher speeds than pine and pint and thus devolatilize over a longer axial distance,
385 which explains their smoother oxygen consumption as well as smoother temperature rise during this
386 phase. Oxygen consumption slows down at the end of devolatilization and the beginning of the char
387 combustion. By now, the particle temperature comes closer to the furnace temperature but does not
388 reach it yet, due to the high thermal inertia of the coarse particles. Subsequently, the particles are
389 heated by the char oxidation, and then cools down after full consumption until they reach equilibrium
390 with the ambient conditions at 800°C . Simulations with finer particles reveal faster heating to the
391 extent they overpass the furnace temperature during the flame phase.

392 The conversion profiles (*Figure 5*) are calculated using the derived optimal kinetic parameters. The
393 model indicates that most of the biomass particle journey is devoted for devolatilization due to high
394 volatile content, and the influence of char conversion is marginal on the total burnout. Given the
395 obtained data, on the basis of our previous work [3] on particle combustion shadowgraphy at 800°C in
396 air, it was also possible to calculate the overlap between the homogenous and heterogeneous
397 combustion stages. The flame extinction is assumed when 99.9 % of the initial volatile content is
398 released, whereas the heterogeneous ignition is the moment when 0.1 % of the initial FC is consumed.



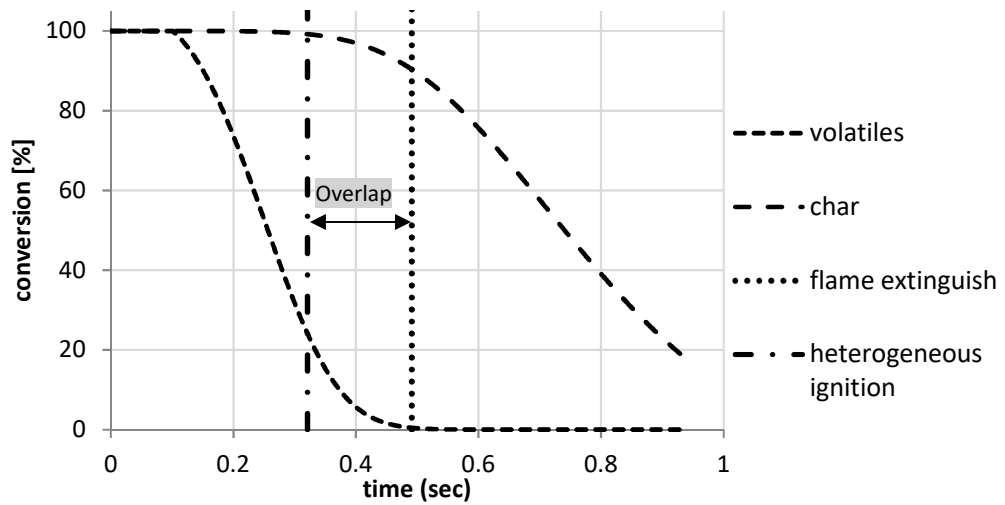
399
400
401

Figure 4: The predicted particle temperature along the furnace axis (600 – 800 μm particles at 800°C with air)



402
403
404

Figure 5: The predicted unburnt fraction of the studied fuels (600 – 800 μm particles at 800°C with air)



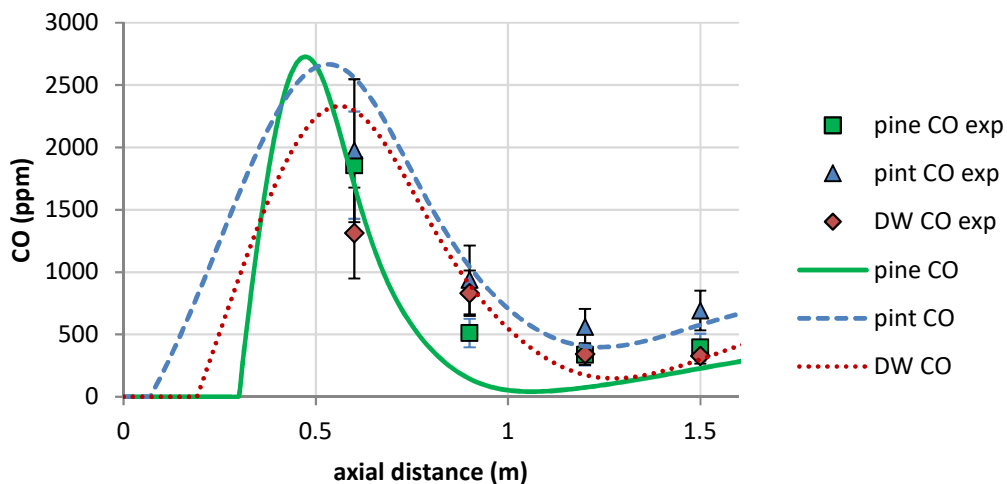
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407

Figure 6: overlap of the flame phase and char combustion phase during DW combustion (600 – 800 μm particles at 800°C with air)

408 *Figure 6* illustrates this method applied for the combustion of demolition wood. The maximum
 409 overlap was obtained for torrefied pine (0.217 sec), followed by demolition wood (0.161 sec) and the
 410 minimum overlap for pine (0.097 sec). These durations are somehow longer than the measured ones in
 411 [3] for such particle size. Nevertheless, the arrangement of the overlap durations is consistent. Given
 412 similar particle size, the overlap is mainly affected by the volatile matter content and the intensity of
 413 devolatilization, leading to pine-DW-pint series from lower to higher overlap duration.

414 4.2.3 Volatiles oxidation

415 *Figure 7* shows the prediction and the experimental data of the CO molar fraction along the reactor
 416 axis. In comparison to the experimental results, CO is overestimated during devolatilization at 60 cm
 417 but then better fits to the experimental data during char combustion. The overestimation may be
 418 related to the fact that CO was calculated based on a constant composition of volatiles that was
 419 measured during the pyrolysis experiments. The good prediction of CO validates the model, given that
 420 the CO experimental measurements were not used for the determination of the kinetic parameters.



421
 422 *Figure 7: Evolution of CO concentration along the tube furnace axis for pine, pint and DW*
 423 *combustion (600-800 μ m particles at 800°C with air)*

424 The behavior is quite similar for the three fuel types. CO is produced in high concentrations during
 425 devolatilization forming a peak before the first sampling point. This peak is directly related to the peak
 426 of devolatilisation. Despite its delayed start, pine exhibits earlier peak followed by pint and DW. The
 427 concentration then decays upon oxidation and with lower devolatilisation rate. The release of moisture
 428 promotes the early activation of the CO oxidation reaction and the earlier decay of CO, especially in
 429 the case of pine. CO decay continues to the point where char is ignited and CO emerges again as the
 430 major product of the char oxidation reaction at high temperatures. The value of the attained minimum
 431 reflects the degree of overlap between the combustion stages. In the case of pine, CO approaches zero
 432 before the second rise, while higher value of the local minimum is reached by DW and pint

433 respectively, despite the lower production in the flame phase. This also can be observed from the
 434 tendencies of the experimental points.

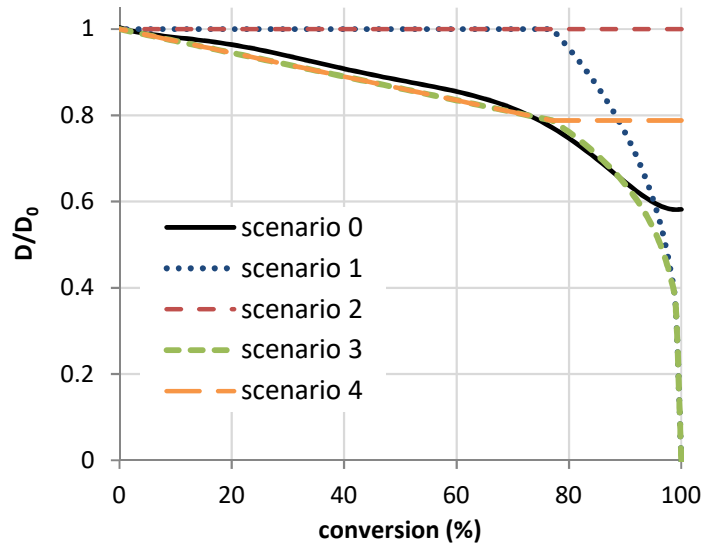
435 4.2.4 Sensitivity study

436 4.2.4.1 Influence of the volume evolution model

437 This section discusses the sensitivity of the model predictions to the volume evolution scenario of the
 438 particle. As discussed earlier, previous studies used similar approaches but employed simplified
 439 volume evolution scenarios. They are listed from # 1 to # 4 in Table 6, our proposal is labelled # 0.

Scenario	Flame phase	char combustion
#0	Experimental data from [3]	Experimental data from [3]
#1	Constant volume	Shrinking core ($\alpha=0.33$)
#2	Constant volume	Constant volume
#3	Swelling model	Shrinking core ($\alpha=0.25$)
#4	Swelling model	Constant volume

440 Table 6: Volume evolution scenarios of a biomass particle during each combustion stage

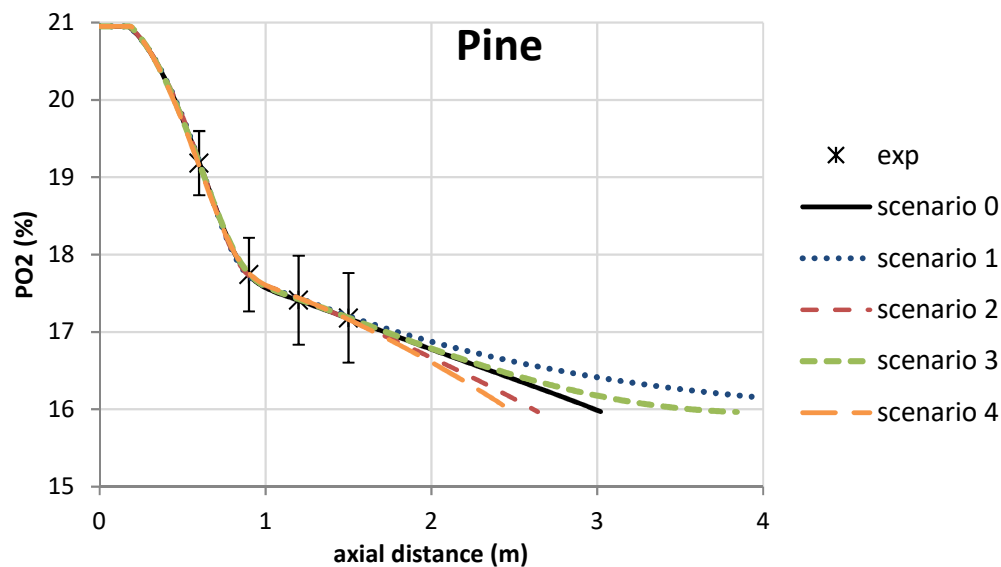


441
 442 Figure 8: Volume evolution scenarios of a biomass particle versus its conversion during combustion

443 Wang et al. model in [21] did not take into account the variation of the particle volume during
 444 devolatilization assuming constant volume, but a shrinking core was considered during char oxidation
 445 (scenario 1). On the other hand, based on experimental data, Jimenez et al. [20] assumed a constant
 446 volume for the particles in the course of their combustion (scenario 2), taking into account a density
 447 variation. This assumption is also used for coal in some studies [42]. However, many CFD studies
 448 adopt different volume evolution scenarios based on works initially developed for coal: the swelling
 449 particle model for devolatilization is often adapted to biomass by setting the swelling coefficient
 450 smaller than one. Using intrinsic model for the char oxidation part, a shrinking core model with 0.25

451 power coefficient has been found to work well for a variety of chars (scenario 3) [43]. However, most
452 CFD studies use a kinetic/diffusion char surface oxidation model with constant particle diameter
453 (scenario 4). *Figure 8* shows the five scenarios of diameter evolution during the combustion of pine.

454 A direct comparison of the parameters obtained in these studies may not be objective, considering that
455 they were applied on different fuel types and experimental conditions. The four volume evolution
456 scenarios from literature were tested here, in addition to our volume model obtained by particle
457 combustion shadowgraphy (scenario 0). The char conversion is not well established in our
458 experiments, so the simulation is extended to allow comparison until the complete burnout.



459
460 *Figure 9: Model fitting of oxygen curves to the pine experimental points using different scenarios. The*
461 *axial distance is extended beyond the furnace length to allow comparison at higher conversion.*

462 *Figure 9* shows the model fitting of oxygen partial pressure to the experimental points, using the
463 optimal parameters determined for each case. The curves agree up to the last experimental point, but
464 they diverge afterwards in the absence of experimental data at higher conversion. In order to better
465 judge and compare the results of each case, the model should have the same data input to follow until
466 the complete burnout. Therefore, the oxygen pressure calculated in scenario 0, based on the available
467 experimental points, is taken as a baseline input for the other scenarios. In this case, the model
468 optimizes the oxygen curve of each scenario to reproduce the curve determined in scenario 0.

469 Table 6 summarizes the kinetic parameters of each fuel in each volume evolution case. The kinetics of
470 scenario 0 and scenario 3 are very similar as expected, since their volume models stick together up to a
471 high conversion point. For all scenarios, the values of devolatilization kinetics are comparable
472 considering the same mathematical formulation. Moreover, the impact of shrinkage is negligible on
473 the pyrolysis time and yield in such regime [44]. The one-step reaction is not directly dependent on the
474 particle volume. The volume rather influences the velocity and temperature, which are not fully
475 established after injection.

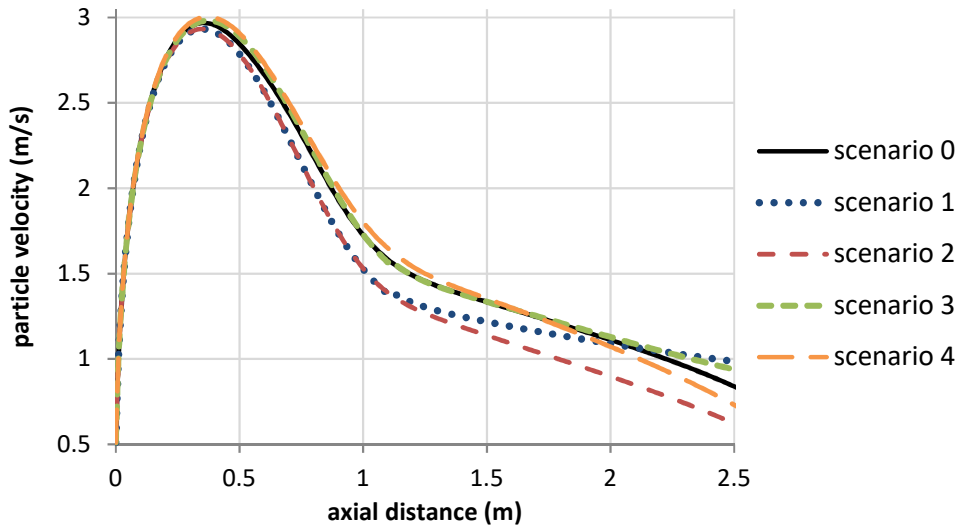
476

	A_v ($I \cdot s^{-1}$)	E_v ($kJ \cdot mol^{-1}$)	A_c ($g \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$)	E_c ($kJ \cdot mol^{-1}$)
Pine				
Scenario0 (this study)	294	18.3	0.93	53
Scenario1	220	17	1.50	67
Scenario2	230	17	0.40	60
Scenario3	290	17.8	1.4	53.4
Scenario4	290	17.2	0.51	53
Non-spherical drag (SF=0.25)	248	27.4	0.92	63.5
Pint				
Scenario0	107	19	1.65	65
Scenario1	118	20	3.30	75
Scenario2	122	20	0.78	67
Scenario3	107	19	2.10	65
Scenario4	102	18.5	0.90	61
Non-spherical drag (SF= 0.33)	250	32.4	2.11	72
DW				
Scenario0	380	21	3.70	53
Scenario1	435	22	1.20	59
Scenario2	435	22	0.84	61
Scenario3	430	21.5	2.51	53.7
Scenario4	371	20	0.53	51
Non-spherical drag (SF =0.25)	331	30	3.40	70

477 *Table 7: Comparison of the kinetic parameters due to the model sensitivity to volume evolution*

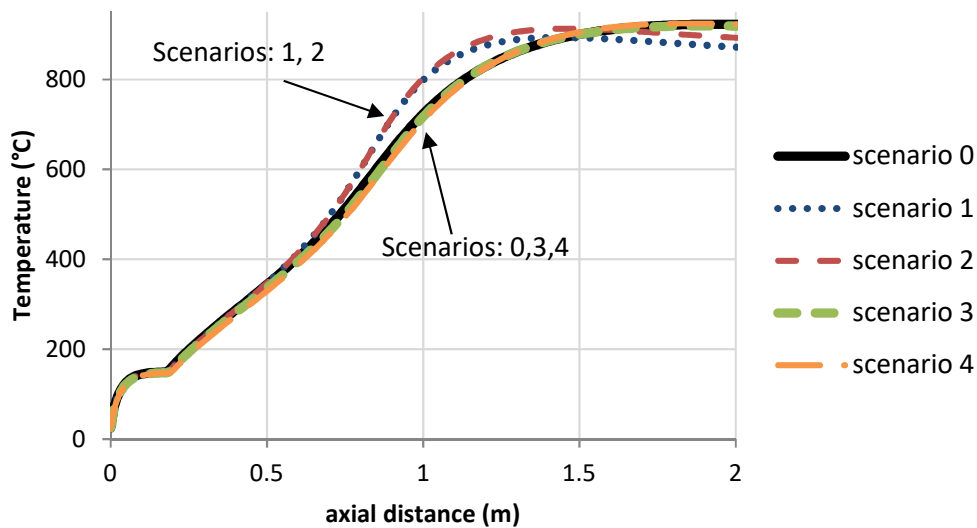
478 The difference for these entities (velocity in *Figure 10* and temperature in *Figure 11*) appears after the
479 first 50 cm where devolatilization has already started. Afterwards, a reduced volume pushes the
480 particle faster due to lower drag force. Hence, the volatiles in scenarios 0, 3 and 4 are released over a
481 wider distance so they get more diluted and their oxidation is less intense. Whereas in scenarios 1 and
482 2, the particles spend more time in intense volatile combustion region, which favors their temperature
483 rise. Ultimately, the particles have longer residence time in the furnace in these scenarios 1 and 2
484 (~+10% longer) and higher average temperature. The calculations are then performed at lower
485 temperature during the char oxidation for scenarios 0, 3 and 4 (around 100°C lower), and by following
486 the same burnout data, it means that char oxidation is activated at lower temperature, which explains
487 the lower activation energy. It is evident how the algorithm is sensitive to the evolution of the particle
488 size during this stage, because it is directly linked to the consumption rate.

489



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491
492

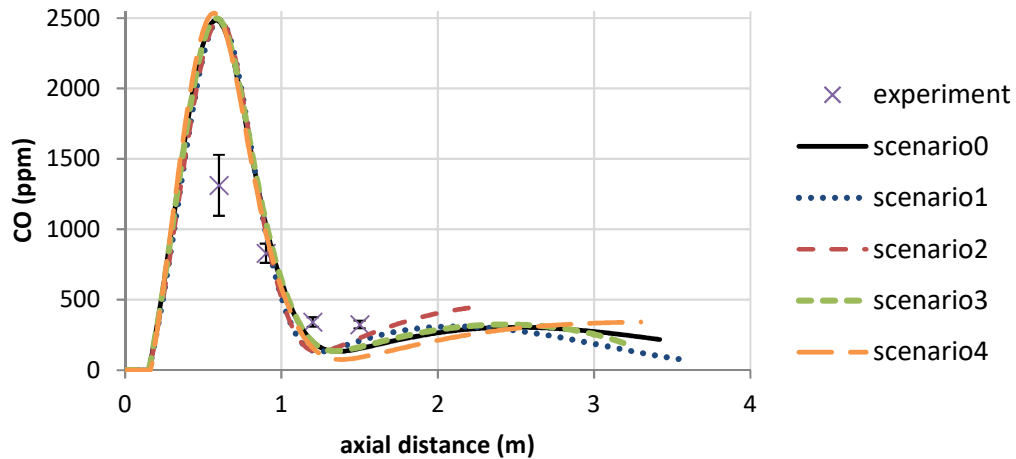
Figure 10: Sensitivity of the particle velocity to the volume evolution model (pint- (600 – 800 μm) at 800°C with air)



493
494
495

Figure 11: Sensitivity of particle temperature to the volume evolution model (pine (600 – 800 μm) at 800°C with air)

496 Changing the particle volume not only affects the chemical kinetics but also affects the diffusion of
 497 oxygen pressure to the particle surface. The diffusion kinetics is firstly controlled by the particle and
 498 gas temperature, and secondly, by the oxygen pressure in the surrounding gas. Faster particles
 499 devolatilize over a wider distance and thus oxygen consumption is slightly smoother. In this case
 500 (scenarios 0, 3 and 4), before the end of the flame where it starts to shrink back to the particle surface,
 501 the particle is surrounded by slightly higher oxygen pressure than in the other scenarios. This promotes
 502 the oxygen diffusion and consequently helps triggering the heterogeneous reaction. This also explains
 503 the longer overlap duration of homogeneous and heterogeneous reactions for scenario 0, 3 and 4 in all
 504 three fuels types resulting in the series: scenario4 > scenario0 > scenario3 > scenario1 > scenario2.



505

506 *Figure 12: CO sensitivity to the volume evolution model (DW (600 – 800 μm) at 800°C with air), The*
 507 *axial distance is extended beyond the furnace length to allow comparison at higher conversion*

508 The predictions of CO concentration (*Figure 12*) and burnout using different scenarios do not change
 509 dramatically when traced versus the axial distance; since the model in all cases follow the
 510 experimental points at a certain position which does not refer to the same residence time in every
 511 scenario. Given close apparent kinetics for devolatilization, it is normal for the profiles not to show
 512 high variations at this stage. The differences appear more pronounced during char oxidation where the
 513 consumption rate varies with the scenario. The kinetics are faster with lower activation energy and
 514 attain higher conversion within shorter residence time.

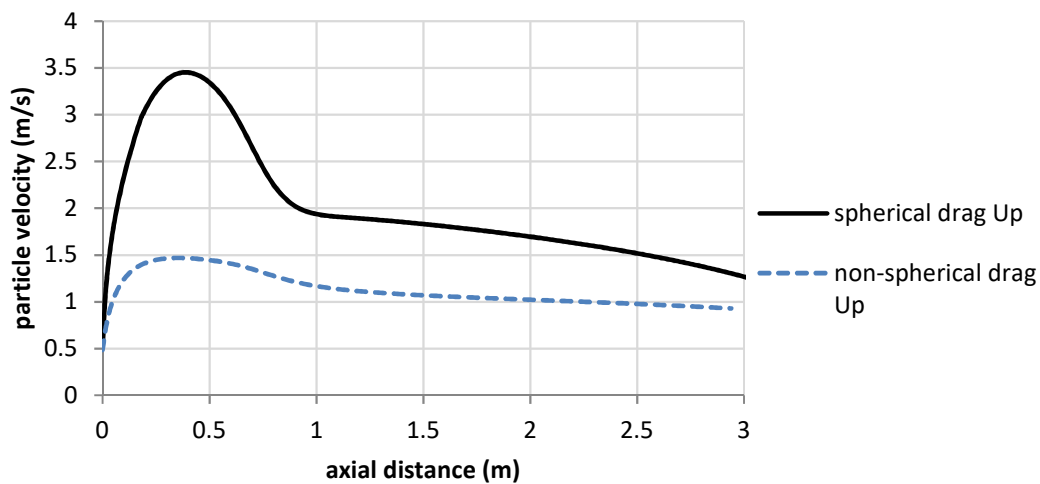
515 **4.2.4.2 Influence of the drag force model**

516 The disparity of the values of the kinetic parameters found in literature results from different used sub-
 517 models. Each has some impact on the particle trajectory and/or its thermal history. With the same
 518 given burnout data, the models are compelled towards different optimal kinetic values in order to
 519 better predict the experimental data. Modeling drag coefficient is very critical to determining the
 520 particle trajectory. Considering the uncertainty of the particle initial shape and its change during the
 521 degradation process, modeling the drag coefficient is a difficult task requiring simplified approaches.
 522 The model adopted in this study is the simplest approach as it treats particles as spherical and ignores
 523 the shape evolution in the course of their conversion. In fact, particles with arbitrary shapes are shown
 524 to be exposed to a higher drag force compared to the equivalent spherical particles [45], [46]. Several
 525 correction methods are proposed in order to include the effect of non-sphericity on the drag force.

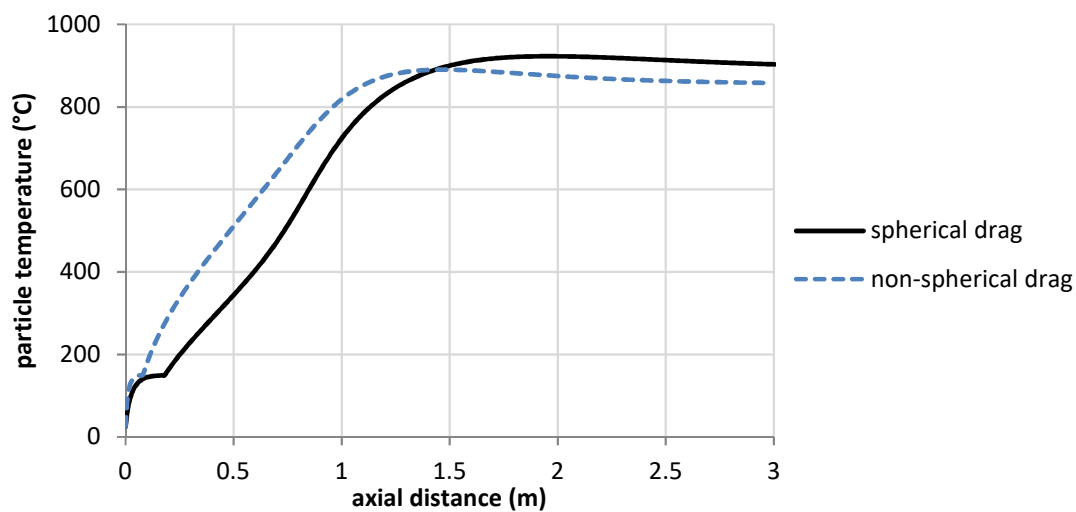
526 In the present study, the kinetic parameters are recalculated alongside the particle thermal and
 527 conversion history, using the non-spherical model proposed by Haider and Levenspiel [47]. Scenario 4
 528 is employed for the volume evolution. The model is a function of the shape factor (SF) of the particle,
 529 which is defined as the ratio of the surface area of a sphere-equivalent particle (with the same volume),
 530 to the actual surface area of the particle. *Table 6* shows the kinetic parameters of devolatilization and

531 char combustion of the three fuels using the non-spherical drag law. The chosen shape factors are used
532 as surveyed in the literature for raw and torrefied wood [45], [46], [48]–[50]. Torrefied biomass is
533 found to have higher SF due to its lower fiber content compared to raw biomass.

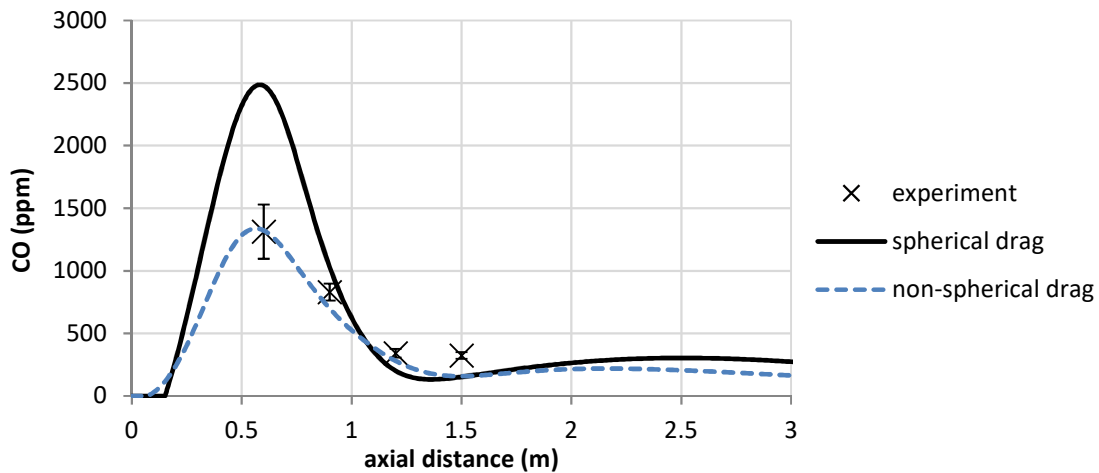
534 *Figure 13* traces the influence of the drag coefficient modeling on the particle velocity. Particles with
535 non-spherical shape are exposed to high drag effect forcing them to advance slowly in the combustion
536 chamber. This effect is true for all fuel types. The velocity peak of a spherical particle is more than
537 twice faster than the non-spherical one. Consequently, the improved interaction of the random shape
538 particle with the flow gives a faster temperature rise near the injection point (*Figure 14*). Water is
539 released in shorter distance allowing the temperature to increase further. However, the initiation of
540 devolatilization is interpolated from the same data points fed to both models. Therefore, the non-
541 spherical particles are supposed to devolatilize at higher temperature. This shift is translated to higher
542 activation energy as seen in *Table 6*.



543
544 *Figure 13: Influence of drag modeling on the particle velocity (pine (600 - 800 μm) at 800°C with air)*



545
546 *Figure 14: Influence of drag modeling on the particle temperature (pine (600 - 800 μm) at 800°C with*
547 *air)*



548
 549 *Figure 15: Influence of drag modeling on the concentration of CO along the furnace axis. (DW (600 –*
 550 *800 μm) at 800°C with air)*

551 The modified trajectory of the particle also influences the distribution of volatiles in the combustion
 552 chamber. A slow-moving particle releases its volatiles over a shorter distance. This intensifies the
 553 reaction rate of oxidation of the volatiles leaving lower concentrations of CO. *Figure 15* presents the
 554 comparison of the two drag models with the experimental measurements of CO during the combustion
 555 of demolition wood. Accounting for the non-sphericity of the particle reproduces better the
 556 experimental data of CO.

557 **5. Conclusion**

558 The combustion of raw and torrefied pine and demolition wood particles is studied in a drop tube
 559 furnace at 800°C. In order to determine the kinetic parameters of devolatilization and char oxidation of
 560 each fuel, this study proposes a numerical model using both the pyrolysis gas composition measured
 561 during preliminary pyrolysis experiments and an empirical sub-model developed specifically to
 562 describe the volume evolution of a single particle observed at 800°C [3]. The model proposed in the
 563 present study predicts well the oxygen and carbon monoxide concentrations, consistent with the
 564 literature. However, the kinetic values of char oxidation are lower than those reported in similar
 565 studies. This can be related to different experimental conditions, and is partly due to the differences in
 566 model approaches, especially considering the volume evolution and the drag coefficient of the
 567 particles. Four other scenarios of the particle volume evolution found in literature are used, to evaluate
 568 how dependent the kinetic parameters are on the volume sub-model. Our previous study using particle
 569 combustion shadowgraphy generates very close kinetics to those found using a swelling and shrinking
 570 scenario during devolatilization and char oxidation respectively. However, when assuming a constant
 571 particle volume during devolatilization, the model converges to the experimental points with higher
 572 activation energy. The four scenarios simulate similarly the gas concentrations and burnout versus the
 573 distance travelled by the particle. Nevertheless, this has to be considered with caution considering the
 574 difference in the particle temperature along the furnace axis, in addition to different particle velocities

575 and residence time. The Influence of drag coefficient model is also addressed in this study. The model
576 compares the kinetic parameters obtained using enhanced non-spherical model of drag versus those
577 obtained using a spherical model. The former model gives higher activation energies for
578 devolatilization (10 to 14 kJ·mol⁻¹ higher) and char oxidation (10 to 19 kJ·mol⁻¹ higher), and better
579 predicts the CO levels. The particle combustion model and the obtained kinetic parameters in this
580 study will be integrated in a CFD model of biomass flames in a pilot scale reactor.

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586 References

- 587 [1] "Ontario Power Generation, Canada Coal to biomass journey furnace," Ontario, Canada, 2018.
- 588 [2] U. Nowling, "Successful Torrefied Biomass Test Burn at a Coal Power Plant," 2018.
- 589 [3] H. Mohanna, J.-M. Commandre, B. Piriou, G. Vaitilingom, B. Taupin, and D. Honore, "Shadowgraphy
590 investigation of the combustion of raw and pre-treated single biomass particles: Influence of particle size
591 and volatile content," *Fuel*, vol. 258, p. 116113, Dec. 2019.
- 592 [4] R. Weber, T. Kupka, and K. Zając, "Jet flames of a refuse derived fuel," *Combust. Flame*, vol. 156, no.
593 4, pp. 922–927, Apr. 2009.
- 594 [5] R. Weber, Y. Poyraz, A. M. Beckmann, and S. Brinker, "Combustion of biomass in jet flames," *Proc.*
595 *Combust. Inst.*, vol. 35, no. 3, pp. 2749–2758, 2015.
- 596 [6] A. Elfasakhany, L. Tao, B. Espenas, J. Larfeldt, and X. S. Bai, "Pulverised wood combustion in a
597 vertical furnace: Experimental and computational analyses," *Appl. Energy*, vol. 112, pp. 454–464, Dec.
598 2013.
- 599 [7] J. Li, E. Biagini, W. Yang, L. Tognotti, and W. Blasiak, "Flame characteristics of pulverized torrefied-
600 biomass combusted with high-temperature air," *Combust. Flame*, vol. 160, no. 11, pp. 2585–2594, Nov.
601 2013.
- 602 [8] D. Ristic *et al.*, "Development of a pilot-scale flameless oxidation burner for ultra-low NO_x combustion
603 of pulverised coal," 2008.
- 604 [9] M. Weidmann *et al.*, "Experimental characterization of pulverized coal MILD flameless combustion
605 from detailed measurements in a pilot-scale facility," *Combust. Flame*, vol. 168, pp. 365–377, Jun. 2016.
- 606 [10] S. S. Daood, M. T. Javed, A. H. Rizvi, and W. Nimmo, "Combustion of Pakistani Lignite (Thar Coal) in
607 a Pilot-Scale Pulverized Fuel Down-Fired Combustion Test Facility," *Energy & Fuels*, vol. 28, no. 2, pp.
608 1541–1547, Feb. 2014.
- 609 [11] H. Lu, E. Ip, J. Scott, P. Foster, M. Vickers, and L. L. Baxter, "Effects of particle shape and size on
610 devolatilization of biomass particle," *Fuel*, vol. 89, no. 5, pp. 1156–1168, May 2010.
- 611 [12] S. Zellagui *et al.*, "Pyrolysis of coal and woody biomass under N₂ and CO₂ atmospheres using a drop
612 tube furnace - experimental study and kinetic modeling," *Fuel Process. Technol.*, vol. 148, pp. 99–109,
613 Jul. 2016.
- 614 [13] C. Dupont, J.-M. Commandré, P. Gauthier, G. Boissonnet, S. Salvador, and D. Schweich, "Biomass
615 pyrolysis experiments in an analytical entrained flow reactor between 1073K and 1273K," *Fuel*, vol. 87,
616 no. 7, pp. 1155–1164, Jun. 2008.

- 617 [14] J.-M. Commandré, "Formation des oxydes d'azote lors de la combustion de cokes de pétrole dans des
618 conditions de précalcinateur de cimenterie," L'Institut National Polytechnique de Toulouse, 2002.
- 619 [15] J.-M. Commandré, H. Lahmidi, S. Salvador, and N. Dupassieux, "Pyrolysis of wood at high temperature:
620 The influence of experimental parameters on gaseous products," *Fuel Process. Technol.*, vol. 92, no. 5,
621 pp. 837–844, May 2011.
- 622 [16] J.-M. COMMANDRÉ, S. SALVADOR, L. VAN DE STEENE, and R. GADIOU, "The Formation and
623 Reduction of NO During The Combustion of Petroluem Coke- The case of Cement Plant Precalciner
624 Condtions," *Combust. Sci. Technol.*, vol. 177, no. 3, pp. 579–611, Feb. 2005.
- 625 [17] F. F. Costa, G. Wang, and M. Costa, "Combustion Kinetics and Particle Fragmentation of Raw and
626 Torrified pine shells and olive stones in a Drop Tube Furnace," *Proc. Combust. Inst.*, vol. 35, no. 3, pp.
627 3591–3599, 2015.
- 628 [18] T. S. Farrow, C. Sun, and C. E. Snape, "Impact of CO₂ on biomass pyrolysis, nitrogen partitioning, and
629 char combustion in a drop tube furnace," *J. Anal. Appl. Pyrolysis*, vol. 113, pp. 323–331, May 2015.
- 630 [19] J. Ballester and S. Jiménez, "Kinetic parameters for the oxidation of pulverised coal as measured from
631 drop tube tests," *Combust. Flame*, vol. 142, pp. 210–222, 2005.
- 632 [20] S. Jiménez, P. Remacha, J. C. Ballesteros, A. Giménez, and J. Ballester, "Kinetics of devolatilization and
633 oxidation of a pulverized biomass in an entrained flow reactor under realistic combustion conditions,"
634 *Combust. Flame*, vol. 152, no. 4, pp. 588–603, Mar. 2008.
- 635 [21] G. Wang, R. B. Silva, J. L. T. Azevedo, S. Martins-Dias, and M. Costa, "Evaluation of the combustion
636 behaviour and ash characteristics of biomass waste derived fuels, pine and coal in a drop tube furnace,"
637 *Fuel*, vol. 117, pp. 809–824, Jan. 2014.
- 638 [22] S. Pereira, P. C. R. Martins, and M. Costa, "Kinetics of Poplar Short Rotation Coppice Obtained from
639 Thermogravimetric and Drop Tube Furnace Experiments," *Energy & Fuels*, vol. 30, no. 8, pp. 6525–
640 6536, Aug. 2016.
- 641 [23] A. Dhaundiyal and J. Gangwar, "Kinetics of the thermal decomposition of pine needles," *Acta Univ.
642 Sapientiae, Agric. Environ.*, vol. 7, no. 1, pp. 5–22, Dec. 2015.
- 643 [24] N. Gao, A. Li, C. Quan, L. Du, and Y. Duan, "TG–FTIR and Py–GC/MS analysis on pyrolysis and
644 combustion of pine sawdust," *J. Anal. Appl. Pyrolysis*, vol. 100, pp. 26–32, Mar. 2013.
- 645 [25] J. Zhao, S. Niu, Y. Li, K. Han, and C. Lu, "Thermogravimetric Analysis and Kinetics of Combustion of
646 Raw and Torrefied Pine Sawdust," *J. Chem. Eng. Japan*, vol. 48, no. 4, pp. 320–325, 2015.
- 647 [26] E. Rodriguez Alonso, C. Dupont, L. Heux, D. Da Silva Perez, J.-M. Commandre, and C. Gourdon,
648 "Study of solid chemical evolution in torrefaction of different biomasses through solid-state ¹³C cross-
649 polarization/magic angle spinning NMR (nuclear magnetic resonance) and TGA (thermogravimetric
650 analysis)," *Energy*, vol. 97, pp. 381–390, Feb. 2016.
- 651 [27] "Les quantités de déchets produits et éliminés en France en 2004," 2004.
- 652 [28] T. R. Ballantyne, P. J. Ashman, and P. J. Mullinger, "A new method for determining the conversion of
653 low-ash coals using synthetic ash as a tracer," *Fuel*, vol. 84, no. 14–15, pp. 1980–1985, Oct. 2005.
- 654 [29] D. SHIN and S. CHOI, "The Combustion of Simulated Waste Particles in a Fixed Bed," *Combust.
655 Flame*, vol. 121, pp. 167–180, 2000.
- 656 [30] M. De Souza-Santos, *Solid Fuels Combustion and Gasification Modeling, Simulation, and Equipment
657 Operations*, Second edi. New York: Taylor & Francis Group, 2010.
- 658 [31] A. Panahi, Y. A. Levendis, N. Vorobiev, and M. Schiemann, "Direct observations on the combustion
659 characteristics of Miscanthus and Beechwood biomass including fusion and spherodization," *Fuel
660 Process. Technol.*, vol. 166, pp. 41–49, Nov. 2017.
- 661 [32] C. Meesri and B. Moghtaderi, "Experimental and numerical analysis of sawdust-char combustion
662 reactivity in a drop tube reactor," *Combust. Sci. Technol.*, vol. 175, no. 4, pp. 793–823, Apr. 2003.
- 663 [33] K. M. Bryden, K. W. Ragland, and C. J. Rutland, "Modeling thermally thick pyrolysis of wood,"

- 664 *Biomass and Bioenergy*, vol. 22, no. 1, pp. 41–53, Jan. 2002.
- 665 [34] J. Rianza *et al.*, “Combustion of single biomass particles in air and in oxy-fuel conditions,” *Biomass and*
666 *Bioenergy*, vol. 64, pp. 162–174, May 2014.
- 667 [35] R. S. Subramanian, “Heat transfer in Flow Through Conduits,” 2014.
- 668 [36] J.-M. Commandré, H. Lahmidi, S. Salvador, and N. Dupassieux, “Pyrolysis of wood at high temperature:
669 The influence of experimental parameters on gaseous products,” *Fuel Process. Technol.*, vol. 92, no. 5,
670 pp. 837–844, May 2011.
- 671 [37] L. Chen, “Fast pyrolysis of millimetric wood particles between 800°C and 1000°C,” Lyon 1, 2009.
- 672 [38] L. Wei *et al.*, “Characteristics of fast pyrolysis of biomass in a free fall reactor,” *Fuel Process. Technol.*,
673 vol. 87, no. 10, pp. 863–871, Oct. 2006.
- 674 [39] D. Neves, A. Matos, L. Tarelho, H. Thunman, A. Larsson, and M. Seemann, “Volatile gases from
675 biomass pyrolysis under conditions relevant for fluidized bed gasifiers,” *J. Anal. Appl. Pyrolysis*, vol.
676 127, pp. 57–67, Sep. 2017.
- 677 [40] S. Septien, S. Valin, C. Dupont, M. Peyrot, and S. Salvador, “Effect of particle size and temperature on
678 woody biomass fast pyrolysis at high temperature (1000–1400°C),” *Fuel*, vol. 97, pp. 202–210, Jul.
679 2012.
- 680 [41] P. McNamee, L. I. Darvell, J. M. Jones, and A. Williams, “The combustion characteristics of high-
681 heating-rate chars from untreated and torrefied biomass fuels,” *Biomass and Bioenergy*, vol. 82, pp. 63–
682 72, Nov. 2015.
- 683 [42] R. Lewtak and J. Hercog, “COAL CHAR KINETICS OF OXIDATION AND GASIFICATION
684 REACTIONS,” *Chem. Process Eng.*, vol. 38, no. 1, pp. 135–145, 2017.
- 685 [43] I. W. Smith, “The kinetics of combustion of pulverized semi-anthracite in the temperature range 1400–
686 2200°K,” *Combust. Flame*, vol. 17, no. 3, pp. 421–428, Dec. 1971.
- 687 [44] K. M. Bryden and M. J. Hagge, “Modeling the combined impact of moisture and char shrinkage on the
688 pyrolysis of a biomass particle☆,” *Fuel*, vol. 82, no. 13, pp. 1633–1644, Sep. 2003.
- 689 [45] M. Mandø, L. Rosendahl, C. Yin, and H. Sørensen, “Pulverized straw combustion in a low-NO_x
690 multifuel burner: Modeling the transition from coal to straw,” *Fuel*, vol. 89, no. 10, pp. 3051–3062, Oct.
691 2010.
- 692 [46] L. Ma, J. M. Jones, M. Pourkashanian, and A. Williams, “Modelling the combustion of pulverized
693 biomass in an industrial combustion test furnace,” *Fuel*, vol. 86, no. 12–13, pp. 1959–1965, Aug. 2007.
- 694 [47] A. Haider and O. Levenspiel, “Drag coefficient and terminal velocity of spherical and nonspherical
695 particles,” *Powder Technol.*, vol. 58, no. 1, pp. 63–70, May 1989.
- 696 [48] Palo Sidwell Pokothoane, “Analysis of co-firing of biomass with South African coal in pulverised coal
697 boilers.,” University of the Witwatersrand, 2010.
- 698 [49] N. Niemelä, “Computational fluid dynamics modeling of pulverized biomass combustion using
699 optimized reactivity parameters,” Tampere University of Technology, 2015.
- 700 [50] R. C. R. Lima, R. F. B. Gonçalves, Manoel F. M. Nogueira, and Danielle R. S. Guerra, “Simulation
701 study of biomass powder combustion in cyclonic furnace,” in *23rd ABCM International Congress of*
702 *Mechanical Engineering*, 2015.
- 703