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Modeling the influence of potassium content and heating rate on biomass pyrolysis

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Abstract

This study presents a combined kinetic and particle model that describes the effect of potassium and heating rate during the fast pyrolysis of woody and herbaceous biomass. The model calculates the mass loss rate, over a wide range of operating conditions relevant to suspension firing. The shrinking particle model considers internal and external heat transfer limitations and incorporates catalytic effects of potassium on the product yields. Modeling parameters were tuned with experimentally determined char yields at high heating rates ($> 200 \text{ K s}^{-1}$) using a wire mesh reactor, a single particle burner, and a drop tube reactor. The experimental data demonstrated that heating rate and potassium content have significant effects on the char yield. The importance of shrinkage on the devolatilization time becomes greater with increasing particle size, but showed little influence on the char yields.

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Keywords: fast pyrolysis, kinetics, metaplast, potassium, heating rate

Nomenclature

AR	Aspect ratio	K_1, K_2	Constants for the activation energy of the char formation reaction as a function of biomass potassium content
A_i	Pre-exponential factor (s^{-1})		
A_p	Particle area (m^2)		
c_p	Specific heat capacity (J (kg K)^{-1})	k_i	Reaction rate constant (s^{-1})
		L	Reactor's length (m)
d_p	Particle diameter (m)	m	Reaction order
d_{pore}	Particle pore diameter (m)	n	Dimensionality factor
D_r	Reactor diameter (m)	R	Gas constant (J (K mol)^{-1})
E_i	Activation energy (J mol^{-1})	r	Reaction rate (kg (kg s)^{-1})
f_{sh}	Shrinkage factor	R_p	Particle radius at specified interior location (m)
g	Gravity (m s^{-2})	r_p	Particle radius (m)
h	Convective heat transfer coefficient ($\text{W (m}^{-2}\text{K}^{-1})$)	T	Temperature ($^{\circ}\text{C}$)
		t	Time (s)
ΔH_{vap}	Heat of vaporization (J kg^{-1})	V_p	Particle volume (m^3)

v_p	Slip velocity between gas and particle (m s^{-1})	Ω	Correction factor for influence of potassium content on activation energy ($E_{a,3}$)
X	Conversion		
$x_{Fe,max}$	Feret maximum diameter (m)	ω	K^+ concentration (mg kg^{-1})
		ψ	Biomass fraction of solid phase
$x_{Ma,min}$	Martin minimum diameter (m)	ρ	Density (kg m^{-3})
		σ	Stefan-Boltzmann constant ($\text{J (s m}^2 \text{ K}^4)^{-1}$)
Dimensionless numbers			
Bi	Biot number	τ	Holding time (s)
Nu	Nusselt number	ε	Emissivity
Pr	Prandtl number	ξ	Void fraction occupied by the gas phase
Re	Reynolds number		
Greek symbols		Subscripts	
		0	initial
α	Particle thermal diffusivity ($\text{m}^2 \text{s}^{-1}$)	b	biomass
κ	Heating rate (K s^{-1})	c	char
λ	Thermal conductivity (W (m K)^{-1})	g	gas
		H_2O	water
μ	Viscosity (Pa s)	K	potassium

M	metaplast	pyr	pyrolysis
max	maximum	r	radiative
$mesh$	wire mesh	s	solid phase
min	minimum	$total$	overall
p	particle	w	wall

1. Introduction

1 Suspension firing of biomass is widely used for power generation. Dan-
 2 ish pulverized fuel fired power plants are undergoing a transition to 100 %
 3 biomass firing in order to reduce greenhouse gase emissions. Straw, wood
 4 pellets and wood chips are the most abundant biofuels in Denmark [1]. The
 5 annual consumption of biomass at Danish power stations is 1.2 million tones
 6 of straw and 0.2 millions of wood chips per year [2]. **The advantage of uti-**
 7 **lizing wheat straw as a renewable energy source is that it is one of**
 8 **the most readily available Danish agricultural residues, while the**
 9 **wood pellet production depends on the supply of imported wood**
 10 **residues [3, 4]. The drawback, however, is that the quality of agri-**
 11 **cultural wastes is lower than that of wood due to a higher ash**
 12 **content leading to deposition and corrosion of the boiler units. In**
 13 **pulverized biomass combustion, short residence times are required**
 14 **for biomass devolatilization, which makes it difficult to examine the**
 15 **dynamics of the process. In addition, the lignocellulosic material**
 16 **reactivity is affected by the biomass composition, namely organic**

17 **matter and minerals [5–7]. The differences in char properties gen-**
18 **erated under various pyrolysis conditions can lead to a range of**
19 **challenges in a modeling of biomass conversion.**

20 Fast pyrolysis at high temperatures and high heating rates is the initial
21 step in suspension biomass firing. Fuel particles first undergo rapid drying,
22 heating and devolatilization with the formation of char and volatiles. Despite
23 of numerous previous studies on biomass devolatilization mechanisms and
24 particle models, there is no generally accepted model that can estimate the
25 conversion rate and final char yield over a wide range of operating condi-
26 tions. Existing kinetic models [8–14] were developed with experimental data
27 using specific biomass samples and a narrow set of low temperature reaction
28 conditions. The application of lower temperatures makes extrapolation to
29 higher temperatures in combustion/gasification processes.

30 Most of the existing biomass pyrolysis models [10, 15–17] which describe
31 both the devolatilization product composition and yields (light gases, tar
32 and char) are mainly valid for low-ash fuels (hardwood, softwood); whereas
33 **considerably** less work has been carried out with herbaceous lignocellu-
34 losic materials. In addition, these mathematical models are valid for biomass
35 pyrolysis under slow heating rates ($1\text{--}50\text{ K min}^{-1}$) and long residence time
36 (1–4 h). Many kinetic models for wood pyrolysis have been reported in the
37 literature [18]. The simplest models are based on a single first order de-
38 composition reaction, and are not able to estimate the influence of heating
39 conditions on the product yields [19].



Figure 1: One-step global model [20].

Other models assume competing parallel reactions to predict the production kinetics of gas, tar and char, which is often valid only over a narrow temperature range [10, 21].

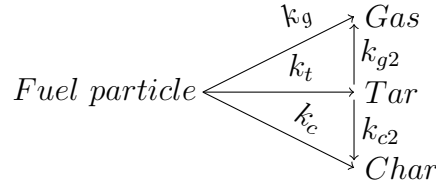


Figure 2: Competing step global model with k_g - rate constant of gas release, k_c - rate constant of char formation, k_t - rate constant of tar formation, k_{g2} - rate constant for the formation of gas from tar and k_{c2} - rate constant for the formation of char from tar [10].

Thurner and Mann [10] assumed that the activation energy for the char formation reaction is similar to the activation energy for mass loss reactions to gas and tar, and therefore, that the final residual weight (e.g. the char yield) is independent of the heating rate and heat treatment temperature. More complex models involve additional steps for tar decomposition in the gas phase [22] or an intermediate product derived from primary decomposition of biomass [15, 23, 24]. **These models can be generally applied only for a specific type of biomass. Ranzi et al. [25, 26] included the effect of holocelluloses, lignin and extractives on the product yields and composition. Previous models have not included the catalytic effect of alkali metals on biomass devolatilization, which has been shown to influence yields and product release rates sig-**

nificantly [7, 27–29]. Extrapolation kinetics fitted under low heating rate conditions to the pulverized fuel firing conditions is difficult due to the changes in devolatilization kinetics with heating rate [20]. Previous pyrolysis kinetic models have failed to extrapolate to higher temperatures because the actual particle heating rate depends on parameters which are difficult to define quantitatively [20, 30, 31].

In this study a model was developed to estimate the char yield from biomass pyrolysis at conditions relevant to suspension firing, which includes the effects of high heating rates, high heat treatment temperatures, particle size and biomass alkali content. Simulations were combined with experiments in a wire mesh reactor (WMR), a single particle burner (SPR) and a drop tube reactor (DTF) to identify the most influential fuel characteristics that explain the differences between woody and herbaceous biomass pyrolysis. **The accurate knowledge of reaction rate and solid residue yields is essential for the boiler optimal operation and design.**

2. Model development

The devolatilization model assumes non-isothermal and cylindrical biomass particles, and includes both chemical kinetics, and external and internal heat transfer. A single biomass particle enters a pre-heated gas flow and is heated up by convection and radiation from its surroundings (single particle reactor and drop tube reactor), or by conduction from the mesh (wire mesh reactor). The model assumes:

- 79 1. The fuel particle is a one-dimensional, cylindrical geometry.
- 80 2. Thermal gradients within the particle are only in the radial
- 81 direction.
- 82 3. Particle shrinkage occurs during pyrolysis.
- 83 4. Moisture content of all fuels are low (< 5 wt. %) and drying
- 84 occurs.
- 85 5. Internal and external mass transfer are fast [32], and therefore,
- 86 are not considered.
- 87 6. Only the reactor walls contribute to the radiative external
- 88 heat transfer; radiation from the flame around the particle
- 89 due to ignition of volatiles is neglected.
- 90 7. Heat transfer to the particle surface occurs through convec-
- 91 tion and radiation.
- 92 8. Heat transfer within a biomass particle occurs through con-
- 93 duction.
- 94 9. Potassium has a dominant influence on the char yield com-
- 95 pared to other ash elements.
- 96 10. Variations in plant cell wall composition (cellulose, hemicellu-
- 97 lose, lignin, extractives) are relatively small and have less in-
- 98 fluence on the biomass char yield than variations in the potas-
- 99 sium content.

100 The last two assumptions are based on previous experimental re-

101 sults obtained in a wire mesh reactor and a drop tube reactor [33,

102 34]. The proposed model includes only primary pyrolysis reactions,

103 i.e. not cracking of tar [35]. The schematic view of the proposed
 104 kinetic model is shown in Figure 3.

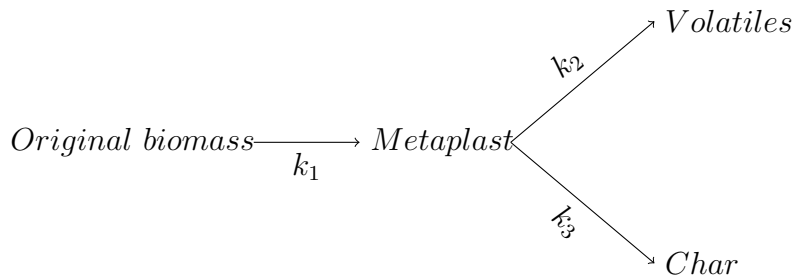


Figure 3: Three reaction model of biomass pyrolysis [12, 15, 36].

105 The shrinking particle is converted into an intermediate liquid compound
 106 (so called metaplast) which reacts further to form volatiles and char. Evi-
 107 dence of metaplast formation has been reported in the literature [23, 30, 37–
 108 40]. **The thermogravimetric results showed a change in the mass**
 109 **loss that was attributed to a high activation energy process during**
 110 **which cellulose passed from an inactive to an active form without**
 111 **sample mass loss [23]. High speed photography of hardwood lignin**
 112 **and cellulose exhibited decomposition of lignocellulosic material**
 113 **through an intermediate liquid with bursting bubbles [39]. Only**
 114 **the formation of metaplast is assumed to influence devolatiliza-**
 115 **tion whereas the fractional split between volatiles and char is de-**
 116 **termined by the heating rate and alkali content. The pyrolysis**
 117 **reactions are assumed to be irreversible and first order with an**
 118 **Arrhenius type of rate expression. One fixed set of kinetic param-**
 119 **eters (activation energy and pre-exponential factor) for each of the**
 120 **three reactions for a generic biomass was obtained by fitting the**

121 model to the char yields obtained in the wire mesh and entrained
 122 flow reactors. The catalytic effect of potassium on the char yield
 123 was accounted for by decreasing the activation energy required for
 124 the reaction from metaplast to char (E_3), thereby leading to higher
 125 char yields. The particle model was solved with the initial condi-
 126 tions:

$$\rho_b(r_p, 0) = 1$$

$$\rho_M(r_p, 0) = 0$$

$$\rho_c(r_p, 0) = 0$$

127 The radial concentrations of biomass, metaplast and char are calculated from:

$$\frac{d\rho_b}{dt} = -k_1 \cdot \rho_b \tag{1}$$

$$\frac{d\rho_M}{dt} = k_1 \cdot \rho_b - (k_2 \cdot \rho_M + k_3(\omega_K) \cdot \rho_M) \tag{2}$$

$$\frac{d\rho_c}{dt} = k_3(\omega_K) \cdot \rho_M \tag{3}$$

$$k_i = A_i \cdot \exp\left(-\frac{E_{a,i}}{R \cdot T}\right) \tag{4}$$

$$E_{a,3,max} = \Omega_K(\omega_K) \cdot E_{a,i} \tag{5}$$

$$\Omega_K(\omega_K) = 1 - K_1 \cdot \left(1 - \exp\left(-\frac{\omega_K}{K_2}\right)^2\right) \tag{6}$$

128 The correction factor for the potassium content (Ω_K) becomes
 129 $\Omega_K(\omega_K = 0) = 1$ and the activation energy $E_{a,3}$ is equal to the max-
 130 imum activation energy $E_{a,3,max}$ when there is no potassium in the
 131 sample. Ω_K approaches the minimum value and the activation en-
 132 ergy $E_{a,3}$ is equal to the minimum activation energy $E_{a,3,min}$ when

133 the biomass contains high amounts of potassium. The K_1 param-
134 eter is a constant and describes a range of activation energy; the
135 K_2 parameter is a constant for the exponential adjustment of the
136 potassium content (ω_K in mg kg^{-1}). Various expressions of Ω_K to
137 describe the influence of potassium content were tested, and equa-
138 tion 6 was found to fit the char yield data best.

139 The results of the fitting showed that the kinetic parameters
140 (A_i and $E_{a,i}$) for the metaplast formation and volatiles release are
141 similar. The char yields were calculated in the model by keep-
142 ing the kinetic parameters (k_1 and k_2) of other reactions constant,
143 whereas the activation energy $E_{a,3}$ required for the reaction from
144 metaplast to char was calculated according to equation 5. The mod-
145 eling parameters were fitted by minimizing the sum of squares of
146 the residuals using `fmincon` in Matlab (version 8.6, MathWorks
147 Inc.).

148 2.1. Shrinking

149 The model calculates the radial shrinkage of the particle at
150 radius r_p , which is divided into R_p grid points numbered from $i=0$
151 to $i=R_p$, where 0 is the center of the particle, generating a number
152 of discrete volumes. The density distribution along the particle radius
153 is calculated using a linear approximation between two neighboring points
154 which form a discrete volume as shown in Figure 4.

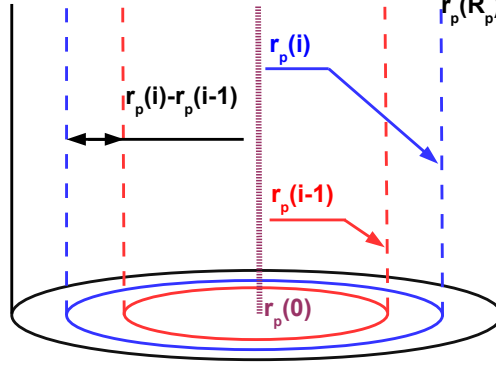


Figure 4: **Representation of a shrinking cylindrical biomass particle.**

155 The size of the control volume at a given time is calculated according to
 156 equation 7:

$$dV_i = 2 \cdot \pi \cdot R_p \cdot AR \cdot (r_{p(i)}^2 - r_{p(i-1)}^2) \quad (7)$$

157 The initial size of control volume is given by equation 8:

$$dV_{i,0} = 2 \cdot \pi \cdot R_p \cdot AR \cdot (r_{p(i,0)}^2 - r_{p(i-1,0)}^2) \quad (8)$$

158 In the shrinking particle model, the volume occupied by the solid structure of
 159 the particle is assumed to decrease proportionally with the conversion. The
 160 current size of the control volume is related to the initial size of the control
 161 volume through a shrinkage factor in equation 9, and further implemented in
 162 heat transfer equation 11:

$$f_{sh} = \frac{dV_i}{dV_{i,0}} = \frac{r_{p(i)}^2 - r_{p(i-1)}^2}{r_{p(i,0)}^2 - r_{p(i-1,0)}^2} \quad (9)$$

163 The shrinkage factor is calculated from the density change of a fuel particle
 164 which is affected by the original biomass, metaplast and char fractions in

equation 10:

$$f_{Sh} = 1 - f_{Sh,min} \cdot \left(1 - \frac{\rho_b + \rho_M + \rho_c}{\rho_{b,0}} \right) \quad (10)$$

The shrinkage factor varies from 1 for the untreated biomass particle, to a minimum value $f_{Sh,min}$, when a particle is converted to volatiles and char. Here, the minimum shrinkage factor was varied from 0 to 0.5 according to previous experimental observations from fast pyrolysis of smaller wood particles (0.2-0.4 mm) [34], larger wood particles (3-5 mm) [41], and modeling results from Anca-Couce et al. [42].

2.2. *Conservation of energy*

The unsteady energy equation for the particle describes internal heat transfer using Fourier's Law in cylindrical coordinates:

$$c_{p,s} \cdot \frac{dT_p}{dt} = \frac{1}{\rho_s \cdot f_{sh}} \cdot \frac{1}{r_p^n} \cdot \frac{\partial}{\partial r_p} \left(r_p^n \lambda_{eff} \frac{\partial T_p}{\partial r_p} \right) + \sum_{j=1}^3 r_{pyr,j} \cdot (-\Delta H_{reac,j}) + r_{H_2O} \cdot (-\Delta H_{vap}) \quad (11)$$

$$r_{pyr,j} = -A_{pyr,j} \cdot \exp \left(-\frac{E_{pyr,j}}{RT} \right) \cdot \left(\frac{\rho_b}{\rho_{b,0}} \right)^m \quad (12)$$

$$r_{H_2O} = -A_{H_2O} \cdot T_p^{1/2} \cdot \exp \left(-\frac{E_{H_2O}}{RT} \right) \cdot \left(\frac{\rho_w}{\rho_{b,0}} \right)^m \quad (13)$$

The overall reaction enthalpy includes the heat of reaction ($\Delta H_{reac,j}$) multiplied by the pyrolysis reaction rate ($r_{pyr,j}$) for each reaction product: metaplast (j=1), char (j=2), and volatiles (j=3). The reactions from metaplast to gas or to char are competitive. **The metaplast formation was assumed to be as thermally neutral [43, 44], gas formation as endothermic, and char formation as exothermic [45, 46].** This approach resulted in the dependence of overall heat of reaction depending on the char yield [47],

182 which is consistent with experimental results [48, 49]. Thus the overall reac-
 183 tion enthalpy changes with the char yield, similar to the modeling approach
 184 of Haseli et al. [47]. The presence of potassium in fuels catalyzes pyrolysis
 185 reactions favoring the formation of char. Therefore, the endothermic heat
 186 of pyrolysis decreases with increasing char yield, and eventually shifts to an
 187 exothermic process, similar to results of Rath et al. [49] and Mack et al. [48].
 188 Exothermic and endothermic heat of reaction ($\Delta H_{reac,2} = -255000 \text{ J kg}^{-1}$;
 189 $\Delta H_{reac,3} = 20000 \text{ J kg}^{-1}$) were proposed by Koufopoulos et al. [45].

190 The rates of mass loss during drying and devolatilization were described
 191 by equations 1-3 [50]. A first order reaction model ($m=1$) was chosen to
 192 describe the experimental results [51]. The heat of vaporization was assumed
 193 to be $\Delta H_{vap} = 2440000 \text{ J kg}^{-1}$ [52, 53]. The initial condition is given by the
 194 ambient temperature:

$$T_p(r_p, 0) = T_{amb} \quad (14)$$

195 The boundary conditions specify that the particle center line is adiabatic
 196 due to symmetry shown in equation 15 and that convection and radiation
 197 entering at the particle surface is conducted into the particle as shown the
 198 equation 16 or given by the temperature of the mesh in equation 17:

$$\lambda_{eff} \frac{dT_p}{dr_p} \Big|_{r_p=0} = 0 \quad (15)$$

$$\lambda_{eff} \frac{dT_p}{dr_p} \Big|_{r_p=R_p} = h \cdot (T_g - T_p|_{r_p=R_p}) + \epsilon \cdot \sigma \cdot (T_w^4 - T_p^4|_{r_p=R_p}) \text{ drop tube reactor} \quad (16)$$

$$T_p|_{r_p=R_p} = T_{mesh}(t) \text{ wire mesh reactor} \quad (17)$$

199 When the biomass sample is heated up in the wire mesh reactor, it is assumed
 200 that the particle surface temperature is equivalent to that of the mesh. The
 201 effective thermal conductivity (λ_{eff}) inside the particle is approximated by
 202 equation 18 [16, 17]:

$$\lambda_{eff} = \xi \cdot \lambda_g + \lambda_b \cdot \psi \cdot (1 - \xi) + \lambda_c \cdot (1 - \psi) \cdot (1 - \xi) + \lambda_r \cdot (1 - \xi) \quad (18)$$

$$\lambda_r = \frac{4 \cdot \xi}{(1 - \xi)} \cdot \epsilon \cdot \sigma \cdot d_{pore} \cdot T_p^3 \quad (19)$$

$$\rho_{c,0} = \frac{\rho_{b,0} \cdot Y_c}{f_{sh,min}} \quad (20)$$

$$\psi = \frac{\rho_b + \rho_M}{\rho_b + \rho_M + \rho_{c,0}} \quad (21)$$

203 where λ_r is the thermal conductivity induced by radiation through pores,
 204 correlated from previous investigations [16, 17], λ_g , λ_b and λ_c are the thermal
 205 conductivities of gas, unconverted biomass and char, respectively, ξ is the
 206 void fraction occupied by the gas phase and ψ is the biomass fraction of the
 207 solid phase which varies 0 to 1. **ρ_b and $\rho_{b,0}$ are the original (reacting)**
 208 **biomass particle density and initial (unreacted) biomass particle**
 209 **density. The thermal conductivity of metaplast is assumed to be**
 210 **equal to the thermal conductivity of original biomass. The convec-**
 211 **tion coefficient of the gas in the drop tube reactor is described in**
 212 **equation 22 [54]:**

$$h = \frac{Nu \cdot \lambda_g}{d_p} \quad (22)$$

213 The particle Reynolds, Prandtl and Nusselt numbers are defined in equa-

214 tions 23-25 [54]:

$$Re = \frac{d_p \cdot (v_p - v_g) \cdot \rho_g}{\mu_g} \quad (23)$$

$$Pr = \frac{c_{p,g} \cdot \mu_g}{\lambda_g} \quad (24)$$

$$Nu = 0.3 + \frac{0.62 \cdot Re^{1/2} \cdot Pr^{1/3}}{(1 + (\frac{0.4}{Pr})^{2/3})^{1/4}} \cdot \left(1 + \left(\frac{Re}{282000}\right)^{5/8}\right)^{4/5} \quad RePr > 0.2 \quad (25)$$

215 The terminal velocity of the biomass particle is calculated from correlations
 216 for Stokes regime, steady separated and unsteady separated flows in equa-
 217 tions 26-28 [55]:

$$v_p = \frac{d_p^2 \cdot g \cdot (\rho_s - \rho_g)}{18 \cdot \mu_g} \quad Re < 2 \quad (26)$$

$$v_p = 0.153 \left[\frac{(\rho_s - \rho_g) \cdot d_p^{1.6} \cdot g}{\mu_g^{0.6} \cdot \rho_g^{0.4}} \right]^{0.714} \quad 2 < Re < 400 \quad (27)$$

$$v_p = 1.74 \cdot \sqrt{\frac{d_p \cdot (\rho_s - \rho_g) \cdot g}{\rho_g}} \quad 400 < Re < 200000 \quad (28)$$

218 Stokes Law was used for small fuel particles, steady separated flow was used
 219 for intermediate fuel particles, and turbulent flow was used for large fuel
 220 particles.

221 2.3. Method of lines

222 Most of the pyrolysis models [15, 17, 56–59] involve solution schemes
 223 based on the method of lines (finite difference method) to solve the heat
 224 transfer equations. The heat transfer equation is discretized using a central
 225 difference scheme:

$$c_{p,s,i} \cdot \frac{dT_i}{dt} = \left(\frac{\lambda_{eff,i}}{\rho_{s,i} \cdot f_{sh}} \cdot \left(\frac{T_{i-1} - 2 \cdot T_i + T_{i+1}}{\Delta r_p^2} + \frac{n}{r_{p,i}} \cdot \frac{T_{i+1} - T_{i-1}}{2 \cdot \Delta r_p} \right) \right) + \sum_{j=1}^3 r_{pyr,i,j} \cdot (-\Delta H_{reac,i,j}) + r_{H_2O,i} \cdot (-\Delta H_{vap,i}) \quad (29)$$

226 In the present model, the ode15s method in MatLab was chosen as an ODE
227 solver. The ode15s function based on the Backward Differentiation Formula
228 (BDF) is recommended for the solution of stiff problems [60]. **Calculations**
229 **were performed to verify the convergence of the adopted numerical**
230 **procedure with grids having 51, 101 and 201 mesh points. Since the**
231 **results showed that sufficient accuracy is attained using a grid with**
232 **101 mesh points for different biomass particle sizes, the number of**
233 **mesh points was set to 101 with an error tolerance of 10^{-10} in time**
234 **integration.**

235 *2.4. Fuel characterization*

236 **Pinewood, beechwood, Danish wheat straw, leached Danish**
237 **wheat straw, alfalfa straw and rice husk were used in this work**
238 **to represent softwood, hardwood and agricultural residues. The**
239 **low-ash containing wood (pinewood, beechwood) and grass sam-**
240 **ples (wheat straw, alfalfa straw), which are rich in potassium, were**
241 **selected to investigate the effect of differences in potassium compo-**
242 **sition on the char yields. The fuels were milled on a Retsch rotor**
243 **mill ZM200 and sieved to particle size fractions of 0.02-0.4 mm and**
244 **0.85-1 mm.**

Table 1: Proximate and ultimate analysis of fuels (on % dry basis) and ash analysis (on mg/kg dry basis).

Fuel	Pine- wood	Beech- wood	Wheat straw	Leached wheat straw	Alfalfa straw
Proximate and ultimate analysis (% db)					
Moisture ^a	5.1	4.5	5.5	4.3	5.2
Ash (550 °C)	0.3	1.4	4.1	2	7.4
Volatiles	86.6	79.4	77.5	84.2	75.9
HHV ^b	21.6	20.2	18.8	18.7	19.7
LHV ^b	20.2	19	17.5	17.4	16.9
C	50.5	46.7	42.4	45.7	42.5
H	6.8	6.3	6.3	6.6	6.1
N	0.1	0.3	1	0.3	3.3
S	<0.01	0.02	0.1	0.02	0.03
Cl	0.01	0.02	0.1	0.01	0.5
Ash compositional analysis (mg/kg db)					
Al	10	10	150	100	600
Ca	600	2000	2500	1300	12900
Fe	20	10	200	350	-
K	200	3600	11000	1300	28000
Mg	100	600	750	350	1400
Na	30	100	150	50	1000
P	6	150	550	80	1900
Si	50	200	8500	6200	2000
Ti	2	<8	10	10	30

^a wt. % (ar) ^b in MJ/kg

2.5. Biomass particle properties

Biomass samples were analyzed with a 2D dynamic imaging instrument by using different size measures (width and length). The diameters $x_{Ma,min}$ and $x_{Fe,max}$ were chosen to represent the biomass particle's width and length. Diameter $x_{Fe,max}$ is the largest diameter to fulfill the assumption that the

length of a particle is larger than its width. Diameter $x_{Ma,min}$ is an area
bisector representing the shortest distance to the particle's opposite edges. **A
biomass particle was represented as a plate, a cylinder and a sphere
in planar (n=0), cylindrical (n=1), and spherical (n=2) coordinates
under the assumption of similar volume to surface ratios using a
different characteristic length:**

$$d_p = x_{Ma,min} \quad (cylinder) \quad (30)$$

$$d_p = \frac{1}{2} \cdot x_{Ma,min} \quad (plate) \quad (31)$$

$$d_p = \frac{3}{2} \cdot x_{Ma,min} \quad (sphere) \quad (32)$$

Biomass particles were described as infinite cylinders, corresponding to
n=1 in equation 11 with a particle size equal to $R_p/2$, where R_p is represented
by $x_{Ma,min}$. The thermo-physical parameters used in the devolatilization
model are listed in Table 2.

Table 2: Thermophysical properties used in the devolatilization model and geometrical parameters of the drop tube reactor.

Symbol	Unit	Description	Expression	
ϵ		Emissivity	0.85	[61]
σ	$\text{J}\cdot(\text{s}\cdot\text{m}^2\cdot\text{K}^4)^{-1}$	Stefan-Boltzmann	$5.67\cdot 10^{-8}$	[61]
ξ		Void fraction	$1 - \frac{(\rho_b + \rho_M + \rho_{c,0})}{1500}$	[58]
$\rho_{b,0}$	$\text{kg}\cdot\text{m}^{-3}$	Raw biomass density	650 (wood) and 700 (straw)	[62, 63]
ρ_g	$\text{kg}\cdot\text{m}^{-3}$	Gas density (N_2)	$362.65\cdot T_g^{-1}$	[64]
d_{pore}	m	Pore diameter	$3.2\cdot 10^{-6}$	[61]
$d_{pore,c}$	m	Char pore diameter	$2\cdot 10^{-4}$	[65]
$c_{p,b}$	$\text{J}\cdot(\text{kg}\cdot\text{K})^{-1}$	Raw biomass specific heat capacity	$1500 + T_p$	[16]
$c_{p,c}$	$\text{J}\cdot(\text{kg}\cdot\text{K})^{-1}$	Char specific heat capacity	$420 + 2.09\cdot T_p + 6.85\cdot T_p^2$	[16]
$c_{p,g}$	$\text{J}\cdot(\text{kg}\cdot\text{K})^{-1}$	Gas specific heat capacity	$770 + 0.629\cdot T_g + 1.91\cdot 10^{-4}\cdot T_g^2$	[17]
λ_g	$\text{W}\cdot(\text{m}\cdot\text{K})^{-1}$	Gas thermal conductivity	0.026	[66]
λ_b	$\text{W}\cdot(\text{m}\cdot\text{K})^{-1}$	Raw biomass thermal conductivity	0.35	[16]
λ_c	$\text{W}\cdot(\text{m}\cdot\text{K})^{-1}$	Char thermal conductivity	0.1	[16]
μ_g	Pa·s	Gas phase dynamic viscosity	$4.847\cdot 10^{-7}\cdot T_g^{0.64487}$	[58]
$\Delta H_{\text{reac},1}$	$\text{J}\cdot\text{kg}^{-1}$	Heat of reaction from biomass to metaplast	0	[43, 44]
$-\Delta H_{\text{reac},2}$	$\text{J}\cdot\text{kg}^{-1}$	Heat of reaction from metaplast to char	-255000	[45]
$\Delta H_{\text{reac},3}$	$\text{J}\cdot\text{kg}^{-1}$	Heat of reaction from metaplast to gas	20000	[45]
ΔH_{vap}	$\text{J}\cdot\text{kg}^{-1}$	Heat of vaporization	2440000	[53]
A_{H_2O}	$\text{s}^{-1}\text{K}^{-0.5}$	Pre-exponential factor	$5.1\cdot 10^{10}$	[58]
E_{H_2O}	$\text{J}\cdot\text{mol}^{-1}$	Activation energy	88000	[58]
L	m	Drop tube reactor's length	2.3	
D_r	m	Drop tube reactor's diameter	0.054	

2.6. Experimental

2.6.1. Small and intermediate size particles (0.2 and 1 mm)

The model was validated against data from three high-temperature reactors. The char yields of 0.2 and 1 mm pinewood particles were determined

264 in separate pyrolysis experiments performed at an intermediate heating rate
265 ($10\text{-}10^3\text{ K s}^{-1}$) in the wire mesh reactor and at a high heating rate of (10^4 K
266 s^{-1}) in the drop tube reactor.

267 The wire mesh reactor at TU Munich was previously described by Tru-
268 betskaya et al. [33]. Tests on the wire mesh reactor were conducted at 350-
269 1400°C , with 1 s holding time on the mesh at atmospheric pressure. The
270 DTF setup was described in detail by Trubetskaya et al. [34]. The experi-
271 ments were conducted by feeding $\approx 5\text{ g}$ of biomass at a rate for 0.2 g min^{-1} .
272 The residence time for 0.2 mm and 1 mm pinewood particles was estimated
273 to be about 1 s, taking into account density changes during pyrolysis [29].
274 Biomass was rapidly heated and reacted as it fell through the reactor at
275 temperatures of $1000\text{-}1400^\circ\text{C}$. Reaction products were separated into coarse
276 particles (mainly char and fly ashes), fine particles (mainly soot and ash
277 aerosols), and permanent gases.

278 **The heating rate in the wire mesh reactor was set to 1000 K s^{-1} .**
279 **In the drop tube reactor, the heating rate was calculated by the**
280 **model using dimensions and operating parameters of the reactor**
281 **shown in Table 2. Char yields of wood and herbaceous biomass in**
282 **the wire mesh reactor and drop tube reactor are shown on dry ash**
283 **free basis (daf) excluding ash content of original biomass and char.**

284 *2.6.2. Large size particles (3-5 mm)*

285 The devolatilization time and char yield of 3, 4 and 5 mm pinewood
286 particles in a temperature range of $1350\text{-}1450^\circ\text{C}$ were determined by Jepsen
287 in a single particle reactor (SPR) located at the DTU Chemical Engineering

288 Department [41]. The SPR was designed for oxidation and pyrolysis studies
 289 on fuel particles $> 2\text{ mm}$ at temperatures up to 1500°C at high heating
 290 rates. **The setup consists of the reactor, a flat flame burner with 94**
 291 **injection nozzles, a gas supply system and gas analyzers as shown**
 292 **in Figure 5.**

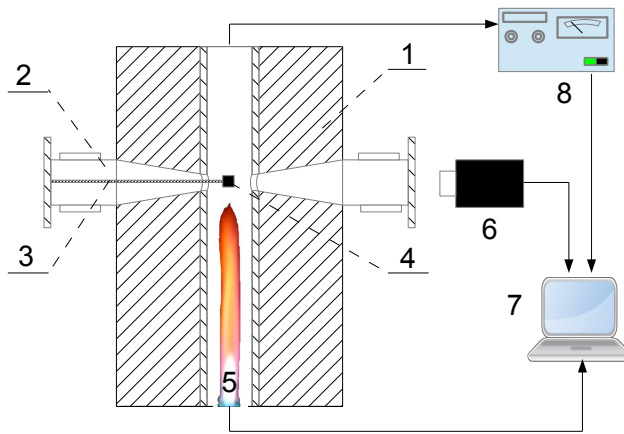


Figure 5: Schematic view of a single particle reactor at DTU: 1. Reactor corpus; 2. insertion ports with a water-cooled chamber; 3. particle holder; 4. sample particle; 5. 94 injection nozzles; 6. High-speed camera; 7. Computer; 8. Gas analyzers.

293 The formation of a soot cloud in the single particle reactor is associated
 294 with pyrolysis initiation. Soot formation occurs under reducing conditions.
 295 The oxygen level was kept very low ($< 0.2\text{ vol.}\%$) during the experiments to
 296 eliminate char and soot oxidation. Devolatilization time is defined as the
 297 time from the soot cloud is seen until it extinguishes and char conversion
 298 begins due to gasification with steam and the remaining oxygen. The char
 299 yield is defined as the solid fraction of the reacted biomass, remaining on the
 300 platinum wire after an experiment.

301 3. Results

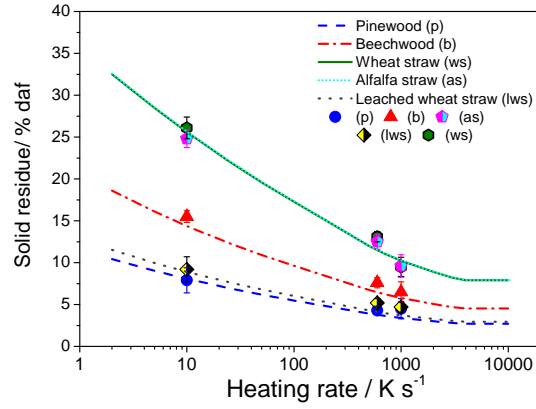
302 3.1. Kinetic parameters

303 The results of fitting of the rate constants, including the influence of
304 potassium are shown in Table 3.

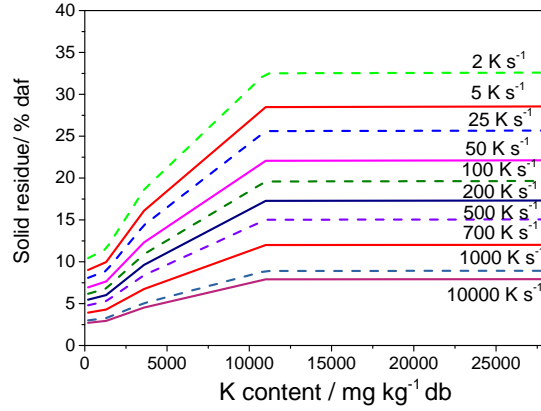
Table 3: The best fit values of the kinetic parameters. In the model, the constants $K_1 = 0.068$ and $K_2 = 4500$ (mg kg^{-1}) were fitted.

Metaplast		Volatiles		Char	
$E_{a,1}$	A_1	$E_{a,2}$	A_2	$E_{a,3}$	A_3
J mol^{-1}	s^{-1}	J mol^{-1}	s^{-1}	J mol^{-1}	s^{-1}
228000	$3.2 \cdot 10^{14}$	174100	$3.6 \cdot 10^{12}$	$132500 \cdot \Omega_K$	$5.6 \cdot 10^8$

305 Figure 6 illustrates that the char yield increases with increasing potas-
306 sium content in the lignocellulosic material and decreases with the higher
307 heating rate. The activation energy of the char forming reaction decreases
308 with increasing potassium content, and thus, the influence of potassium be-
309 comes smaller at higher heating rates. In Figure 6(b), the model estimates
310 that char yield increases from 2.6 % to 32.5 % when the heating rates decrease
311 from 10^4 to 2 K s^{-1} .



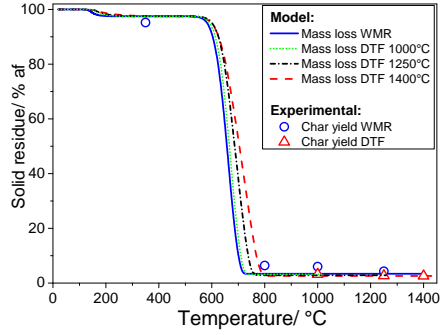
6(a): Heating rate effect on the char yield



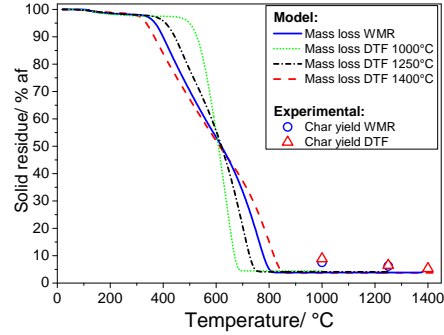
6(b): Char yields versus potassium content in the fuel

Figure 6: (a) Comparison of simulated and experimental data for the influence of heating rate on the char yield of pinewood, beechwood, wheat straw, leached wheat straw and alfalfa straw in the wire mesh reactor, and (b) Simulated char yields versus potassium content in the original fuel (heat treatment temperature: 1400°C, holding time: 1 s, particle size: 0.2 mm).

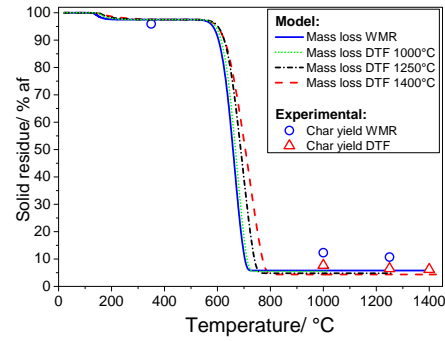
312 Estimated biomass particle mass as a function of mean particle temper-
 313 ature is shown in Figure 7.



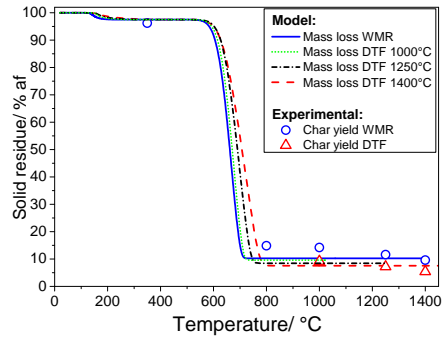
7(a): Pinewood 0.2 mm



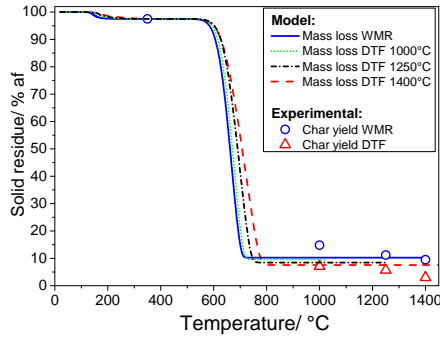
7(b): Pinewood 1 mm



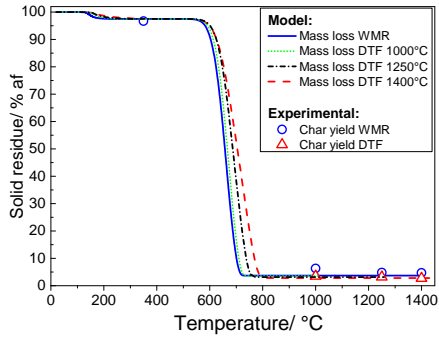
7(c): Beechwood 0.2 mm



7(d): Alfalfa straw 0.2 mm



7(e): Wheat straw 0.2 mm

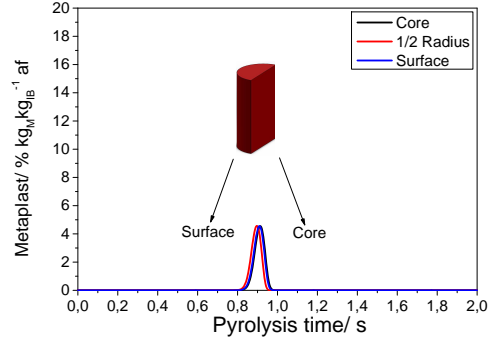
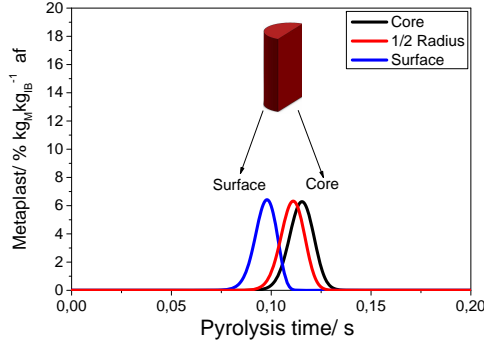


7(f): Leached wheat straw 0.2 mm

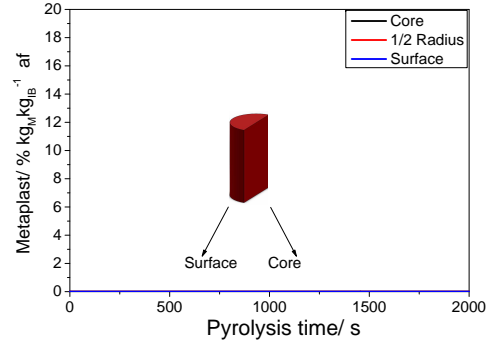
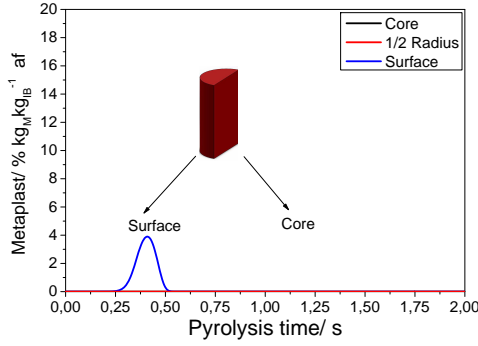
Figure 7: Simulated mass loss over the **mean particle temperature** (% af) of pinewood, beechwood, wheat straw, alfalfa straw, leached wheat straw at 1000, 1250 and 1400°C in the DTF and at 1400°C in the WMR, and comparison with the char yields determined experimentally in the wire mesh reactor at (heat treatment temperature: 350, 800, 1000, 1250 and 1400°C; heating rate: 1000 K s⁻¹; holding time: 1 s) and drop tube reactor at 1000, 1250 and 1400°C as determined by Trubetskaya et al. [33, 34].

314 The mass loss of smaller particles is shown only at 1400°C in the wire-
315 mesh reactor, since pyrolysis is complete at temperatures below 800°C. The
316 simulation results show that char yields from pyrolysis of wood and leached
317 wheat straw in the drop tube reactor were similar over a temperature range
318 of 1000-1400°C, whereas the char yield of wheat and alfalfa straw decreased
319 slightly from 10.3 % to 7.6 % by weight. The present results show that the
320 model accurately estimates the char yield for smaller (0.2 mm) biomass par-
321 ticles. The char yield from pyrolysis of 1 mm pinewood particles is also
322 estimated well and is **about 3 %** lower relative to the experimentally deter-
323 mined char yields in the drop tube reactor. The experimental data obtained
324 in the wire mesh reactor agree with the mass loss estimated by the model.
325 **The lower WMR heating rate caused the reaction to take place**
326 **at lower temperatures for an extended period compared to fast**
327 **pyrolysis conditions in the drop tube reactor.**

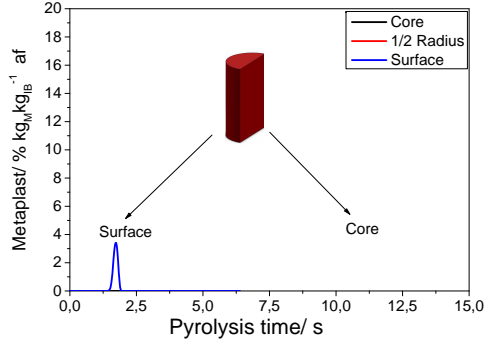
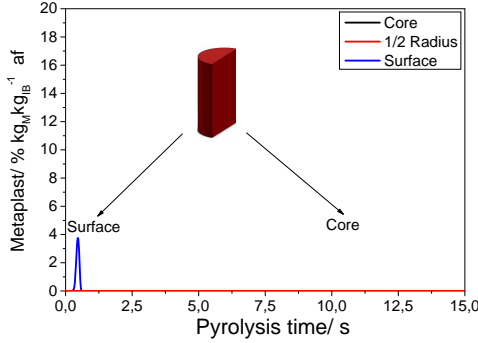
328 Figure 8 illustrates the mass fraction of metaplast formed at the surface,
329 middle and center of the particle as a function of time. The simulation results
330 show that both heating rate and particle size influence metaplast formation.
331 In general, high heating rates promote the formation of metaplast. Due to
332 negligible temperature gradients, high heating rates cause small particles first
333 to become fluid and form a molten sphere, then solidify into char [6, 7, 33].
334 For large particles, significant formation of metaplast at high heating rates
335 is only observed at the surface.



8(a): 0.2 mm, heated by 10^4 K s^{-1} gas flow 8(b): 0.2 mm, heated by 10^3 K s^{-1} gas flow



8(c): 3 mm, heated by 10^4 K s^{-1} gas flow 8(d): 3 mm, heated by 10 K min^{-1} gas flow



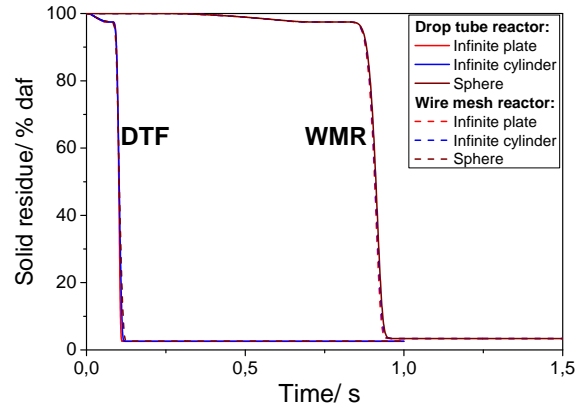
8(e): 10 mm, heated by 10^4 K s^{-1} gas flow 8(f): 10 mm, heated by 10^3 K s^{-1} gas flow

Figure 8: Simulated metaplast formation (% af) from pyrolysis of 0.2, 3 and 10 mm pinewood particles at slow heating rate in the thermogravimetric instrument (10 K min^{-1}), at intermediate heating rate (10^3 K s^{-1}) in the wire mesh reactor and at high heating rates in the drop tube reactor. The metaplast formation ($\text{kg}_M \text{ kg}_{IB}^{-1}$) is showed over the pyrolysis time.

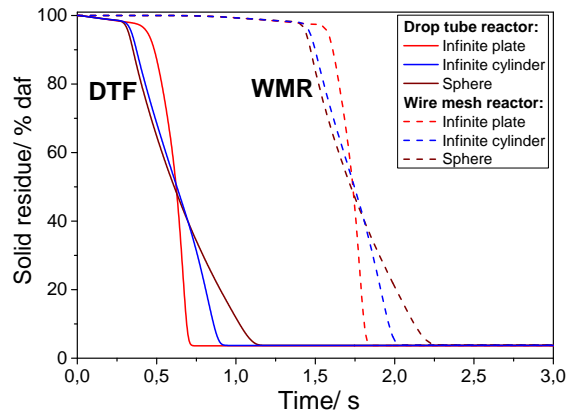
336 This means that the particle surface melts during pyrolysis, whereas the
337 interior retains the original biomass structure [33]. The rate of metaplast
338 formation was slower than formation of volatiles and char at lower temper-
339 atures. Thus, metaplast was formed faster than it was consumed at higher
340 temperatures. At low heating rates, the particle was nearly isothermal, indi-
341 cating only small differences in metaplast formation as function of position
342 within the particle. Thus, the relatively low heating rate for the particle core
343 increased the time for the three reactions, leading to lower metaplast yields.

344 3.2. *Influence of assumed particle geometry*

345 Figure 9 illustrates the mass loss of 0.2, 1 and 5 mm pinewood
346 particles. Devolatilization time decreased with the higher heating
347 rate in the drop tube reactor compared to the wire mesh reactor.
348 The representation of the 0.2 mm particles using different charac-
349 teristics lengths does not give large deviations with respect to char
350 yield and devolatilization time among the three particle geometries
351 as shown in Figure 9(a).



9(a): Pinewood 0.2 mm



9(b): Pinewood 1 mm

Figure 9: Mass loss histories of pinewood particles (0.2 and 1 mm) with the similar volume to surface ratio and different characteristic lengths which were calculated in plate-like ($n=0$), cylindrical ($n=1$) and spherical ($n=2$) geometries at the final temperature of 1400°C during pyrolysis in the wire mesh and drop tube reactors.

creasing particle size due to the larger internal temperature gradients as shown in Figure 9(b). The relative influence of heating rate on devolatilization time of 1 mm pinewood was less compared that for smaller particles. This is because of the predominance of internal heat transfer control within the large particles.

3.3. *Influence of volumetric shrinkage on devolatilization time*

In the model, the shrinkage front moves from the surface towards the center. At high heating rates, the outer layers initially shrink while the inner layers remain unaffected. Later, the fuel particle shrinks due to devolatilization. During slow pyrolysis, internal thermal gradients are small, and therefore, drying followed by devolatilization takes place over throughout the particle. Particle shrinkage takes place after the original biomass is converted into metaplast. The rate of volatiles formation determines the rate at which the particle shrinks.

Figure 10(a) shows that the particle size of 5 mm particle was reduced by 27 % during pyrolysis at high heating rates. A 26 % reduction in a particle size was measured during devolatilization of 3 mm pinewood particle in a temperature range of 1180-1440°C in the single particle reactor [41].

Figure 10(c) shows that shrinkage has a negligible influence on the devolatilization time of smaller particles, which are practically isothermal. For the large particles, the inclusion of shrinkage increases the devolatilization rate and thereby decreases the devolatilization time. Internal temperature gradients in larger particles becomes smaller as the particle shrinks which enhances the devolatilization rate. The shrinkage of 5 mm pine particle leads to the decrease of devolatilization time by 19 % during pyrolysis in the WMR

378 and DTF.

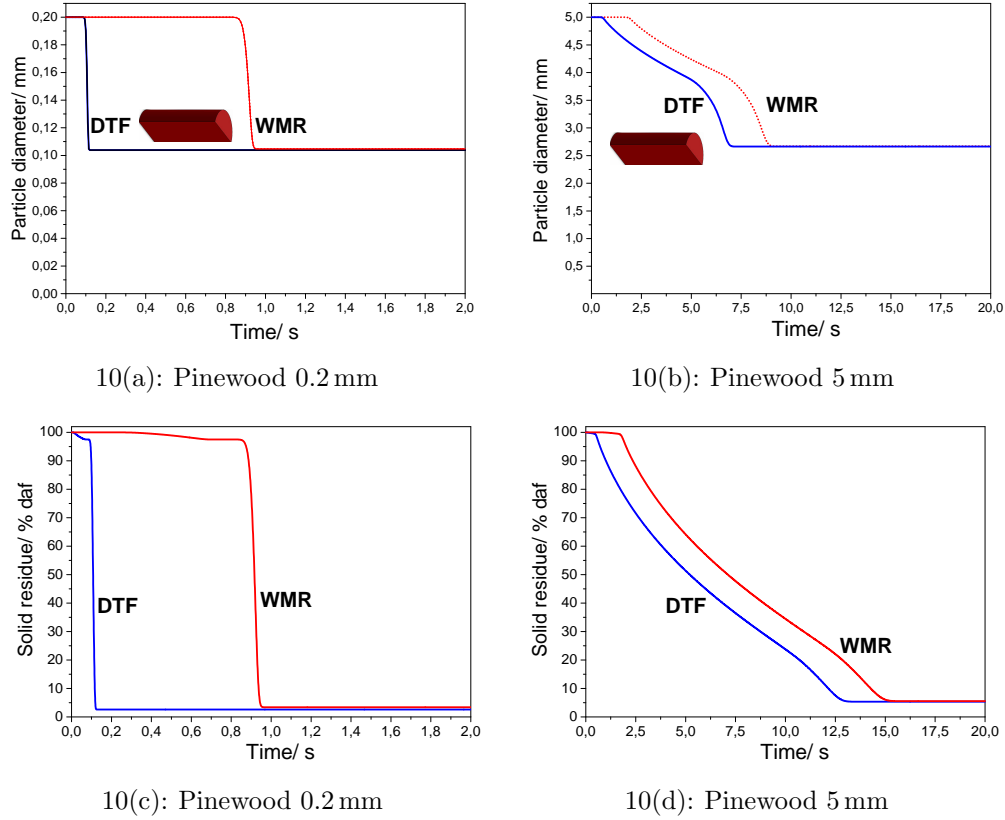


Figure 10: (a)-(b) Simulated pinewood particle shrinking (0.2 and 5 mm) and (c)-(d) Simulated mass loss of shrinking pinewood particles in the wire mesh and drop tube reactors.

379 3.4. *Influence of particle size on devolatilization time*

380 Figure 11 compares the times required for complete devolatilization of
 381 3, 4 and 5 mm pinewood particles in the single particle reactor to those
 382 estimated by the model for particles from 0.01 to 10 mm. **In the model,**
 383 **the complete devolatilization time is defined as the time when 95 %**

384 of the volatile matter in the original pinewood particle has been
385 released [67].

386 Figure 11 shows that under fast heating particles with mean di-
387 ameters < 0.25 mm may be considered as thermally thin based on
388 the modeling results with 0.1 s deviation, while the intra-particle
389 heat conduction in larger particles plays a key role in biomass de-
390 volatilization. The diameter of 3, 4 and 5 mm pinewood cubes was recalcu-
391 lated for corresponding cylinders under the assumption of a similar volume to
392 surface ratio (3, 4 and 5 mm). A comparison of experimental and estimated
393 devolatilization times showed that the model estimates the devolatilization
394 time of pinewood particles well. In addition, the results showed that the 1 mm
395 pinewood particles require more than 1 s in the WMR and DTF for complete
396 conversion. The estimated devolatilization time by the model showed a sim-
397 ilar trend for the experiments in the drop tube reactor.

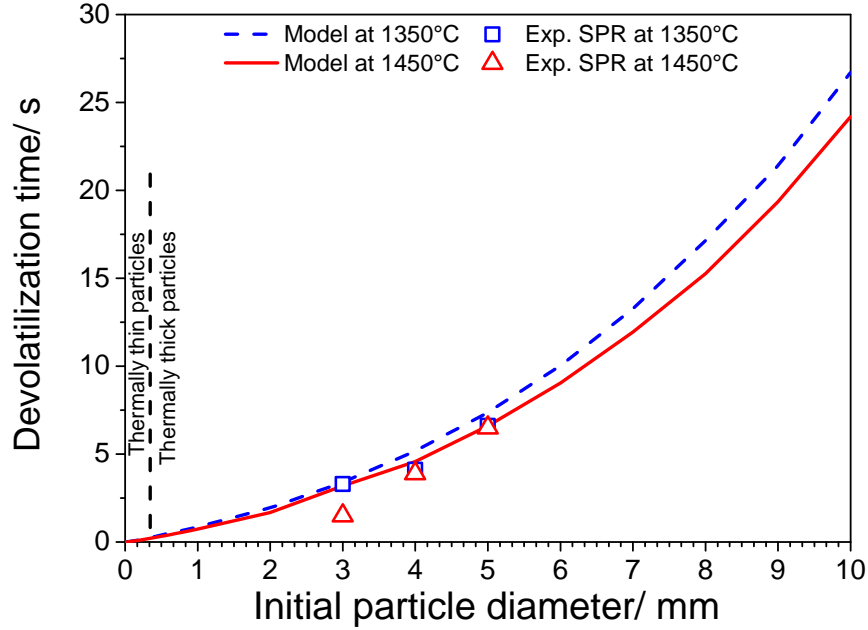


Figure 11: **Simulated devolatilization time of shrinking pinewood particles (from 0.01 mm to 10 mm) at 1000, 1250 and 1400°C, and compared with the experimental results obtained in the SPR for 3, 4 and 5 mm particles at 1350 and 1450°C. Experimental data was taken from the investigations of Jepsen [41]. The black dashed line separates the thermally thin regime ($Bi < 0.1$) from the thermally thick ($Bi > 0.1$).**

398 4. Discussion

399 The present pyrolysis model describes the char yield at high tempera-
 400 tures (up to 1500°C) and high heating rates $> 200 \text{ K s}^{-1}$. In the model, an
 401 intermediate liquid (so called metaplast) is formed from the decomposition
 402 of biomass which reacts further to char and gas. It was assumed that the ki-
 403 netics for metaplast formation does not depend on the biomass type and that

404 reaction of metaplast to char and gas is influenced by the biomass potassium
 405 content.

406 The impact of heating rate on the maximum metaplast formation and
 407 subsequent reaction to char and gas shown in Figure 12.

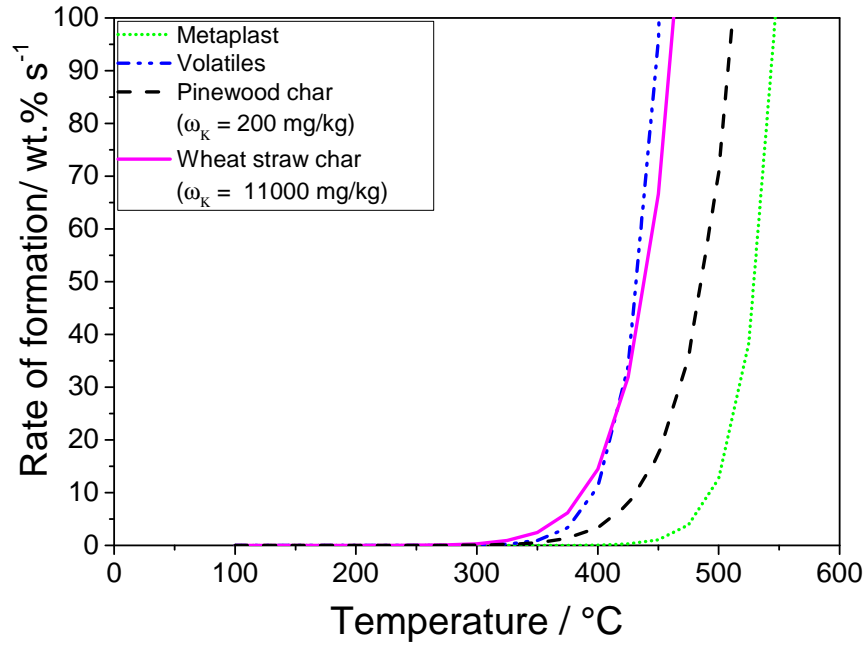


Figure 12: Simulated reaction rates (wt.% s⁻¹) of metaplast, char and volatile formation during fast pyrolysis of 0.2 mm pinewood ($\omega_K = 200 \text{ mg kg}^{-1}$, dry basis) and wheat straw ($\omega_K = 11000 \text{ mg kg}^{-1}$, dry basis) particles in the wire mesh reactor (1000 K s^{-1}).

408 **Figure 12 demonstrates that the rate of metaplast formation is**
 409 **slower than formation of volatiles and char at temperatures below**
 410 **350°C. Thus, lower concentrations of metaplast are formed at lower**
 411 **heating rates. The particle temperature was nearly uniform over**

the particle diameter, and therefore, only small differences in metaplast formation were observed. At higher temperatures, the rate of char formation was lower than the rate of metaplast formation, in agreement with experimental results from Koufopoulos [15, 45]. Higher temperatures result in greater metaplast accumulation because its formation rate is faster than its rate of consumption. At high heating rates, such as in the wire mesh and drop tube reactors, lower mass fractions of metaplast were formed in the particle core compared to the particle surface. This could be due to the lower heating rates at the core compared to at the surface. At high heating rates, formation of metaplast is initially fast relative to reaction from metaplast to char and gas, so a high concentration of metaplast is obtained. With a high fraction of metaplast, the particle may become molten (locally or throughout the whole particle), thereby leading to structural changes of the particle [33].

Particle size demonstrates a greater influence on metaplast, volatile and char formation in the drop tube reactor (10^{-4} K s^{-1}) than in the wire mesh reactor (10 K s^{-1}). The larger internal temperature gradients led to slower pyrolysis of 3 and 10 mm pinewood particles compared to 0.2 mm particles. For large particles the formation of metaplast mainly takes place at the particle surface at high heating rates, whereas the lower heating rates result in high metaplast concentrations in the interior. At low heating rates, both small and large particles were nearly isothermal, leading to smaller local differences in metaplast formation. Differences in local mass

437 fractions of metaplast became larger with increasing particle size
438 and increasing heating rates because of the predominance of inter-
439 nal heat transfer control within the large particles.

440 Char yield has been experimentally shown to increase with
441 potassium content in the original biomass [33, 34]. This effect was
442 accounted for in the model by modifying the activation energy for
443 the char formation reaction as a function of the potassium content.
444 The influence of potassium on char formation became stronger with
445 decreasing heating rate, which corresponds to the experimental
446 observations from the wire mesh and drop tube reactors. Cal-
447 culations suggested that pyrolysis was completed at temperatures
448 below 800°C, and thus, the char yields for woody and herbaceous
449 biomass remain unchanged. The experimental data showed that
450 the biomass char yields decreased with the increasing tempera-
451 ture due to the dehydrogenation and cross-linking reactions [68],
452 which are not considered in the present simulation. The simu-
453 lated char yield from wheat straw pyrolysis was slightly lower than
454 the char yield from the wire mesh and drop tube reactor experi-
455 ments. The ash compositional analysis of char from the pyrolysis
456 in the drop tube reactor showed that close to 70 % potassium in
457 the wheat straw has been released in a temperature range of 1000-
458 1500°C [69]. The remaining potassium in herbaceous biomass sam-
459 ples is still present in a larger amount than in woody chars. The
460 large differences in herbaceous char yields between the model and
461 experimental data might be attributed to the interactions between

462 potassium, other remaining alkali metals and carbonaceous char
463 matrix which were not considered during the model development.

464 Moreover, the char yield of larger particles is underestimated
465 by the model. It was hypothesized that tar inside larger particles
466 may undergo secondary reactions, leading to higher char yields [36].
467 At high heat treatment temperatures of 750-1100°C, secondary re-
468 actions occurring in larger particles strongly decrease tar release
469 and increase char formation during pyrolysis. Tar decomposition
470 occurs by secondary reactions (i.e. cracking and polymerization),
471 and tar release to ambient by mass transfer [35]. The evolutionary
472 profiles of the temperatures at the pinewood particle surface and
473 the particle center as a function of time are shown in the supple-
474 mental material. Due to the fast heat transfer in 0.2 mm particles,
475 the differences between surface and core temperatures are small
476 and thus, tar release remains unchanged at 1100°C. The differences
477 between surface and core temperatures become more pronounced
478 with the increasing particle size. Tar formation from pyrolysis of
479 larger pinewood particles was stronger, whereas the soot yield was
480 half lower compared to smaller particles [70]. The lower soot yields
481 were related to the less formed PAH precursors. Tar inside larger
482 particles underwent secondary reactions due to the lower heat flux,
483 leading to a slower pyrolysis and thereby higher char yields and less
484 soot, corresponding to investigations of Miller and Bellan [36]. This
485 effect was not included in the model and could be the reason why
486 the model slightly underpredicts the char yield for large particles.

487 5. Conclusion

488 The novelty of this work relies on the description of both low
489 and high temperature kinetics for wood and herbaceous biomass
490 using one set of kinetic parameters. The actual particle heating
491 rate of biomass particles was quantitatively defined in wire mesh
492 and drop tube reactors. The results presented in this work empha-
493 size a stronger catalytic effect of potassium on char yield at low
494 and intermediate heating rates compared to high heating rates.
495 The potassium content and heating rate affected the char yield
496 more than other operational parameters.

497 An innovative approach was used to implement the influence
498 of potassium on the char yield in the model by reduction in the
499 activation energy of char formation with increasing potassium con-
500 tent, and fitted to the experimental results. The simulation results
501 showed that particle size has a more significant influence on meta-
502 plast formation and reaction to char and gas at high heating rates
503 (10^4 K s^{-1}) compared to pyrolysis at low heating rates (10 K s^{-1}).

504 In addition, the model showed that the impact of shrinkage on
505 devolatilization time increases with increasing particle size, but it
506 has negligible influence on char yields. Results from the 1D model
507 are in agreement with experimental data, and emphasize a key role
508 of intra-particle heat conduction in biomass particle $> 0.25 \text{ mm}$.

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Modeling the influence of potassium content and heating rate on biomass pyrolysis

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Abstract

This study presents a combined kinetic and particle model that describes the effect of potassium and heating rate during the fast pyrolysis of woody and herbaceous biomass. The model calculates the mass loss rate, over a wide range of operating conditions relevant to suspension firing. The shrinking particle model considers internal and external heat transfer limitations and incorporates catalytic effects of potassium on the product yields. Modeling parameters were tuned with experimentally determined char yields at high heating rates ($> 200 \text{ K s}^{-1}$) using a wire mesh reactor, a single particle burner, and a drop tube reactor. The experimental data demonstrated that heating rate and potassium content have significant effects on the char yield. The importance of shrinkage on the devolatilization time becomes greater with increasing particle size, but showed little influence on the char yields.

Keywords: fast pyrolysis, kinetics, metaplast, potassium, heating rate

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Nomenclature

AR	Aspect ratio		tion reaction as a function of biomass potassium content
A_i	Pre-exponential factor (s^{-1})		
A_p	Particle area (m^2)	k_i	Reaction rate constant (s^{-1})
c_p	Specific heat capacity (J (kg K)^{-1})	L	Reactor's length (m)
		m	Reaction order
d_p	Particle diameter (m)	n	Dimensionality factor
d_{pore}	Particle pore diameter (m)	R	Gas constant (J (K mol)^{-1})
D_r	Reactor diameter (m)	r	Reaction rate (kg (kg s)^{-1})
E_i	Activation energy (J mol^{-1})	R_p	Particle radius at specified interior location (m)
f_{sh}	Shrinkage factor		
g	Gravity (m s^{-2})	r_p	Particle radius (m)
h	Convective heat transfer coefficient ($\text{W (m}^{-2}\text{K}^{-1})$)	T	Temperature ($^{\circ}\text{C}$)
		t	Time (s)
ΔH_{vap}	Heat of vaporization (J kg^{-1})	V_p	Particle volume (m^3)
K_1, K_2	Constants for the activation energy of the char forma-	v_p	Slip velocity between gas and particle (m s^{-1})

X	Conversion	ω	K ⁺ concentration (mg kg ⁻¹)
$x_{Fe,max}$	Feret maximum diameter (m)	ψ	Biomass fraction of solid phase
$x_{Ma,min}$	Martin minimum diameter (m)	ρ	Density (kg m ⁻³)
		σ	Stefan-Boltzmann constant (J (s m ² K ⁴) ⁻¹)
Dimensionless numbers		τ	Holding time (s)
Bi	Biot number	ε	Emissivity
Nu	Nusselt number	ξ	Void fraction occupied by the gas phase
Pr	Prandlt number		
Re	Reynolds number	Subscripts	
Greek symbols		0	initial
α	Particle thermal diffusivity (m ² s ⁻¹)	b	biomass
		c	char
κ	Heating rate (K s ⁻¹)	g	gas
λ	Thermal conductivity (W (m K) ⁻¹)	H_2O	water
		K	potassium
μ	Viscosity (Pa s)	M	metaplast
Ω	Correction factor for influence of potassium content on acti- vation energy (E _{a,3})	max	maximum
		$mesh$	wire mesh

<i>min</i>	minimum	<i>s</i>	solid phase
<i>p</i>	particle		
		<i>total</i>	overall
<i>pyr</i>	pyrolysis		
<i>r</i>	radiative	<i>w</i>	wall

1. Introduction

Suspension firing of biomass is widely used for power generation. Danish pulverized fuel fired power plants are undergoing a transition to 100 % biomass firing in order to reduce greenhouse gas emissions. Straw, wood pellets and wood chips are the most abundant biofuels in Denmark [1]. The annual consumption of biomass at Danish power stations is 1.2 million tones of straw and 0.2 millions of wood chips per year [2]. The advantage of utilizing wheat straw as a renewable energy source is that it is one of the most readily available Danish agricultural residues, while the wood pellet production depends on the supply of imported wood residues [3, 4]. The drawback, however, is that the quality of agricultural wastes is lower than that of wood due to a higher ash content leading to deposition and corrosion of the boiler units. In pulverized biomass combustion, short residence times are required for biomass devolatilization, which makes it difficult to examine the dynamics of the process. In addition, the lignocellulosic material reactivity is affected by the biomass composition, namely organic matter and minerals [5–7]. The differences in char properties generated under various pyrolysis conditions can lead to a range of challenges in a modeling of biomass conversion.

Fast pyrolysis at high temperatures and high heating rates is the initial

step in suspension biomass firing. Fuel particles first undergo rapid drying, heating and devolatilization with the formation of char and volatiles. Despite of numerous previous studies on biomass devolatilization mechanisms and particle models, there is no generally accepted model that can estimate the conversion rate and final char yield over a wide range of operating conditions. Existing kinetic models [8–14] were developed with experimental data using specific biomass samples and a narrow set of low temperature reaction conditions. The application of lower temperatures makes extrapolation to higher temperatures in combustion/gasification processes.

Most of the existing biomass pyrolysis models [10, 15–17] which describe both the devolatilization product composition and yields (light gases, tar and char) are mainly valid for low-ash fuels (hardwood, softwood); whereas considerably less work has been carried out with herbaceous lignocellulosic materials. In addition, these mathematical models are valid for biomass pyrolysis under slow heating rates ($1\text{--}50\text{ K min}^{-1}$) and long residence time (1–4 h). Many kinetic models for wood pyrolysis have been reported in the literature [18]. The simplest models are based on a single first order decomposition reaction, and are not able to estimate the influence of heating conditions on the product yields [19].



Figure 1: One-step global model [20].

Other models assume competing parallel reactions to predict the production kinetics of gas, tar and char, which is often valid only over a narrow temperature range [10, 21].

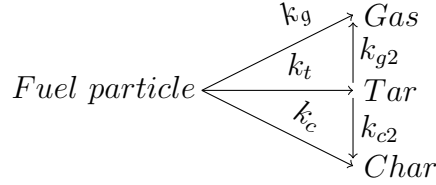


Figure 2: Competing step global model with k_g - rate constant of gas release, k_c - rate constant of char formation, k_t - rate constant of tar formation, k_{g2} - rate constant for the formation of gas from tar and k_{c2} - rate constant for the formation of char from tar [10].

Turner and Mann [10] assumed that the activation energy for the char formation reaction is similar to the activation energy for mass loss reactions to gas and tar, and therefore, that the final residual weight (e.g. the char yield) is independent of the heating rate and heat treatment temperature. More complex models involve additional steps for tar decomposition in the gas phase [22] or an intermediate product derived from primary decomposition of biomass [15, 23, 24]. These models can be generally applied only for a specific type of biomass. Ranzi et al. [25, 26] included the effect of holocelluloses, lignin and extractives on the product yields and composition. Previous models have not included the catalytic effect of alkali metals on biomass devolatilization, which has been shown to influence yields and product release rates significantly [7, 27–29]. Extrapolation kinetics fitted under low heating rate conditions to the pulverized fuel firing conditions is difficult due to the changes in devolatilization kinetics with heating rate [20]. Previous pyrolysis kinetic models have failed to extrapolate to higher temperatures because the actual particle heating rate depends on parameters which are difficult to define quantitatively [20, 30, 31].

In this study a model was developed to estimate the char yield from

biomass pyrolysis at conditions relevant to suspension firing, which includes the effects of high heating rates, high heat treatment temperatures, particle size and biomass alkali content. Simulations were combined with experiments in a wire mesh reactor (WMR), a single particle burner (SPR) and a drop tube reactor (DTF) to identify the most influential fuel characteristics that explain the differences between woody and herbaceous biomass pyrolysis. The accurate knowledge of reaction rate and solid residue yields is essential for the boiler optimal operation and design.

2. Model development

The devolatilization model assumes non-isothermal and cylindrical biomass particles, and includes both chemical kinetics, and external and internal heat transfer. A single biomass particle enters a pre-heated gas flow and is heated up by convection and radiation from its surroundings (single particle reactor and drop tube reactor), or by conduction from the mesh (wire mesh reactor). The model assumes:

1. The fuel particle is a one-dimensional, cylindrical geometry.
2. Thermal gradients within the particle are only in the radial direction.
3. Particle shrinkage occurs during pyrolysis.
4. Moisture content of all fuels are low (< 5 wt. %) and drying occurs.
5. Internal and external mass transfer are fast [32], and therefore, are not considered.
6. Only the reactor walls contribute to the radiative external heat transfer; radiation from the flame around the particle due to ignition of volatiles is neglected.

7. Heat transfer to the particle surface occurs through convection and radiation.
8. Heat transfer within a biomass particle occurs through conduction.
9. Potassium has a dominant influence on the char yield compared to other ash elements.
10. Variations in plant cell wall composition (cellulose, hemicellulose, lignin, extractives) are relatively small and have less influence on the biomass char yield than variations in the potassium content.

The last two assumptions are based on previous experimental results obtained in a wire mesh reactor and a drop tube reactor [33, 34]. The proposed model includes only primary pyrolysis reactions, i.e. not cracking of tar [35]. The schematic view of the proposed kinetic model is shown in Figure 3.

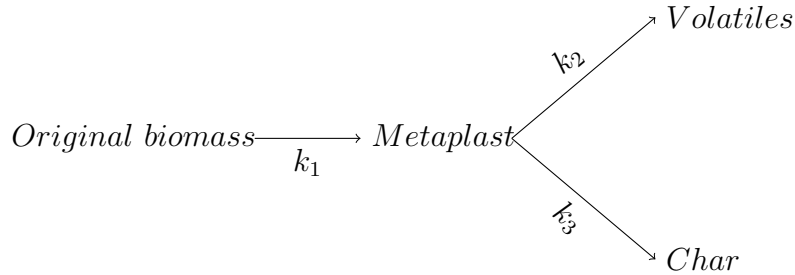


Figure 3: Three reaction model of biomass pyrolysis [12, 15, 36].

The shrinking particle is converted into an intermediate liquid compound (so called metaplast) which reacts further to form volatiles and char. Evidence of metaplast formation has been reported in the literature [23, 30, 37–40]. The thermogravimetric results showed a change in the mass loss that was attributed to a high activation energy process during which cellulose

passed from an inactive to an active form without sample mass loss [23]. High speed photography of hardwood lignin and cellulose exhibited decomposition of lignocellulosic material through an intermediate liquid with bursting bubbles [39]. Only the formation of metaplast is assumed to influence devolatilization whereas the fractional split between volatiles and char is determined by the heating rate and alkali content. The pyrolysis reactions are assumed to be irreversible and first order with an Arrhenius type of rate expression. One fixed set of kinetic parameters (activation energy and pre-exponential factor) for each of the three reactions for a generic biomass was obtained by fitting the model to the char yields obtained in the wire mesh and entrained flow reactors. The catalytic effect of potassium on the char yield was accounted for by decreasing the activation energy required for the reaction from metaplast to char (E_3), thereby leading to higher char yields. The particle model was solved with the initial conditions:

$$\rho_b(r_p, 0) = 1$$

$$\rho_M(r_p, 0) = 0$$

$$\rho_c(r_p, 0) = 0$$

The radial concentrations of biomass, metaplast and char are calculated from:

$$\frac{d\rho_b}{dt} = -k_1 \cdot \rho_b \quad (1)$$

$$\frac{d\rho_M}{dt} = k_1 \cdot \rho_b - (k_2 \cdot \rho_M + k_3(\omega_K) \cdot \rho_M) \quad (2)$$

$$\frac{d\rho_c}{dt} = k_3(\omega_K) \cdot \rho_M \quad (3)$$

$$k_i = A_i \cdot \exp\left(-\frac{E_{a,i}}{R \cdot T}\right) \quad (4)$$

$$E_{a,3,max} = \Omega_K(\omega_K) \cdot E_{a,i} \quad (5)$$

$$\Omega_K(\omega_K) = 1 - K_1 \cdot \left(1 - \exp\left(-\frac{\omega_K}{K_2}\right)^2\right) \quad (6)$$

The correction factor for the potassium content (Ω_K) becomes $\Omega_K(\omega_K = 0) = 1$ and the activation energy $E_{a,3}$ is equal to the maximum activation energy $E_{a,3,max}$ when there is no potassium in the sample. Ω_K approaches the minimum value and the activation energy $E_{a,3}$ is equal to the minimum activation energy $E_{a,3,min}$ when the biomass contains high amounts of potassium. The K_1 parameter is a constant and describes a range of activation energy; the K_2 parameter is a constant for the exponential adjustment of the potassium content (ω_K in mg kg⁻¹). Various expressions of Ω_K to describe the influence of potassium content were tested, and equation 6 was found to fit the char yield data best.

The results of the fitting showed that the kinetic parameters (A_i and $E_{a,i}$) for the metaplast formation and volatiles release are similar. The char yields were calculated in the model by keeping the kinetic parameters (k_1 and k_2) of other reactions constant, whereas the activation energy $E_{a,3}$ required for the reaction from metaplast to char was calculated according to equation 5. The modeling parameters were fitted by minimizing the sum of squares of

the residuals using fmincon in Matlab (version 8.6, MathWorks Inc.).

2.1. Shrinking

The model calculates the radial shrinkage of the particle at radius r_p , which is divided into R_p grid points numbered from $i=0$ to $i=R_p$, where 0 is the center of the particle, generating a number of discrete volumes. The density distribution along the particle radius is calculated using a linear approximation between two neighboring points which form a discrete volume as shown in Figure 4.

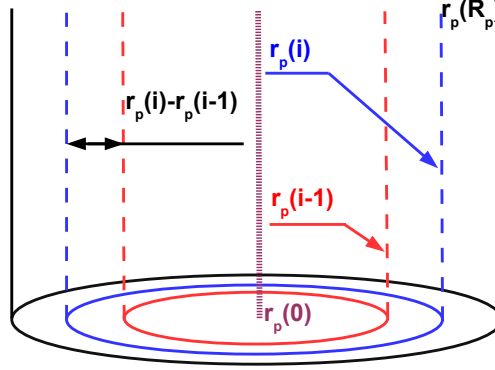


Figure 4: Representation of a shrinking cylindrical biomass particle.

The size of the control volume at a given time is calculated according to equation 7:

$$dV_i = 2 \cdot \pi \cdot R_p \cdot AR \cdot (r_{p(i)}^2 - r_{p(i-1)}^2) \quad (7)$$

The initial size of control volume is given by equation 8:

$$dV_{i,0} = 2 \cdot \pi \cdot R_p \cdot AR \cdot (r_{p(i,0)}^2 - r_{p(i-1,0)}^2) \quad (8)$$

In the shrinking particle model, the volume occupied by the solid structure of the particle is assumed to decrease proportionally with the conversion. The current size of the control volume is related to the initial size of the control volume through a shrinkage factor in equation 9, and further implemented in heat transfer equation 11:

$$f_{Sh} = \frac{dV_i}{dV_{i,0}} = \frac{r_{p(i)}^2 - r_{p(i-1)}^2}{r_{p(i,0)}^2 - r_{p(i-1,0)}^2} \quad (9)$$

The shrinkage factor is calculated from the density change of a fuel particle which is affected by the original biomass, metaplast and char fractions in equation 10:

$$f_{Sh} = 1 - f_{Sh,min} \cdot \left(1 - \frac{\rho_b + \rho_M + \rho_c}{\rho_{b,0}} \right) \quad (10)$$

The shrinkage factor varies from 1 for the untreated biomass particle, to a minimum value $f_{Sh,min}$, when a particle is converted to volatiles and char. Here, the minimum shrinkage factor was varied from 0 to 0.5 according to previous experimental observations from fast pyrolysis of smaller wood particles (0.2-0.4 mm) [34], larger wood particles (3-5 mm) [41], and modeling results from Anca-Couce et al. [42].

2.2. Conservation of energy

The unsteady energy equation for the particle describes internal heat transfer using Fourier's Law in cylindrical coordinates:

$$c_{p,s} \cdot \frac{dT_p}{dt} = \frac{1}{\rho_s \cdot f_{sh}} \cdot \frac{1}{r_p^n} \cdot \frac{\partial}{\partial r_p} \left(r_p^n \lambda_{eff} \frac{\partial T_p}{\partial r_p} \right) + \sum_{j=1}^3 r_{pyr,j} \cdot (-\Delta H_{reac,j}) + r_{H_2O} \cdot (-\Delta H_{vap}) \quad (11)$$

$$r_{pyr,j} = -A_{pyr,j} \cdot \exp \left(-\frac{E_{pyr,j}}{RT} \right) \cdot \left(\frac{\rho_b}{\rho_{b,0}} \right)^m \quad (12)$$

$$r_{H_2O} = -A_{H_2O} \cdot T_p^{1/2} \cdot \exp \left(-\frac{E_{H_2O}}{RT} \right) \cdot \left(\frac{\rho_w}{\rho_{b,0}} \right)^m \quad (13)$$

The overall reaction enthalpy includes the heat of reaction ($\Delta H_{reac,j}$) multiplied by the pyrolysis reaction rate ($r_{pyr,j}$) for each reaction product: metaplast (j=1), char (j=2), and volatiles (j=3). The reactions from metaplast to gas or to char are competitive. The metaplast formation was assumed to be as thermally neutral [43, 44], gas formation as endothermic, and char formation as exothermic [45, 46]. This approach resulted in the dependence of overall heat of reaction depending on the char yield [47], which is consistent with experimental results [48, 49]. Thus the overall reaction enthalpy changes with the char yield, similar to the modeling approach of Haseli et al. [47]. The presence of potassium in fuels catalyzes pyrolysis reactions favoring the formation of char. Therefore, the endothermic heat of pyrolysis decreases with increasing char yield, and eventually shifts to an exothermic process, similar to results of Rath et al. [49] and Mack et al. [48]. Exothermic and endothermic heat of reaction ($\Delta H_{reac,2} = -255000 \text{ J kg}^{-1}$; $\Delta H_{reac,3} = 20000 \text{ J kg}^{-1}$) were proposed by Koufopoulos et al. [45].

The rates of mass loss during drying and devolatilization were described

by equations 1-3 [50]. A first order reaction model ($m=1$) was chosen to describe the experimental results [51]. The heat of vaporization was assumed to be $\Delta H_{vap} = 2440000 \text{ J kg}^{-1}$ [52, 53]. The initial condition is given by the ambient temperature:

$$T_p(r_p, 0) = T_{amb} \quad (14)$$

The boundary conditions specify that the particle center line is adiabatic due to symmetry shown in equation 15 and that convection and radiation entering at the particle surface is conducted into the particle as shown the equation 16 or given by the temperature of the mesh in equation 17:

$$\lambda_{eff} \frac{dT_p}{dr_p} \Big|_{r_p=0} = 0 \quad (15)$$

$$\lambda_{eff} \frac{dT_p}{dr_p} \Big|_{r_p=R_p} = h \cdot (T_g - T_p|_{r_p=R_p}) + \epsilon \cdot \sigma \cdot (T_w^4 - T_p^4|_{r_p=R_p}) \quad \text{drop tube reactor} \quad (16)$$

$$T_p|_{r_p=R_p} = T_{mesh}(t) \quad \text{wire mesh reactor} \quad (17)$$

When the biomass sample is heated up in the wire mesh reactor, it is assumed that the particle surface temperature is equivalent to that of the mesh. The effective thermal conductivity (λ_{eff}) inside the particle is approximated by equation 18 [16, 17]:

$$\lambda_{eff} = \xi \cdot \lambda_g + \lambda_b \cdot \psi \cdot (1 - \xi) + \lambda_c \cdot (1 - \psi) \cdot (1 - \xi) + \lambda_r \cdot (1 - \xi) \quad (18)$$

$$\lambda_r = \frac{4 \cdot \xi}{(1 - \xi)} \cdot \epsilon \cdot \sigma \cdot d_{pore} \cdot T_p^3 \quad (19)$$

$$\rho_{c,0} = \frac{\rho_{b,0} \cdot Y_c}{f_{sh,min}} \quad (20)$$

$$\psi = \frac{\rho_b + \rho_M}{\rho_b + \rho_M + \rho_{c,0}} \quad (21)$$

where λ_r is the thermal conductivity induced by radiation through pores, correlated from previous investigations [16, 17], λ_g , λ_b and λ_c are the thermal conductivities of gas, unconverted biomass and char, respectively, ξ is the void fraction occupied by the gas phase and ψ is the biomass fraction of the solid phase which varies 0 to 1. ρ_b and $\rho_{b,0}$ are the original (reacting) biomass particle density and initial (unreacted) biomass particle density. The thermal conductivity of metaplast is assumed to be equal to the thermal conductivity of original biomass. The convection coefficient of the gas in the drop tube reactor is described in equation 22 [54]:

$$h = \frac{Nu \cdot \lambda_g}{d_p} \quad (22)$$

The particle Reynolds, Prandtl and Nusselt numbers are defined in equations 23-25 [54]:

$$Re = \frac{d_p \cdot (v_p - v_g) \cdot \rho_g}{\mu_g} \quad (23)$$

$$Pr = \frac{c_{p,g} \cdot \mu_g}{\lambda_g} \quad (24)$$

$$Nu = 0.3 + \frac{0.62 \cdot Re^{1/2} \cdot Pr^{1/3}}{(1 + (\frac{0.4}{Pr})^{2/3})^{1/4}} \cdot \left(1 + \left(\frac{Re}{282000}\right)^{5/8}\right)^{4/5} \quad RePr > 0.2 \quad (25)$$

The terminal velocity of the biomass particle is calculated from correlations for Stokes regime, steady separated and unsteady separated flows in equations 26-28 [55]:

$$v_p = \frac{d_p^2 \cdot g \cdot (\rho_s - \rho_g)}{18 \cdot \mu_g} \quad Re < 2 \quad (26)$$

$$v_p = 0.153 \left[\frac{(\rho_s - \rho_g) \cdot d_p^{1.6} \cdot g}{\mu_g^{0.6} \cdot \rho_g^{0.4}} \right]^{0.714} \quad 2 < Re < 400 \quad (27)$$

$$v_p = 1.74 \cdot \sqrt{\frac{d_p \cdot (\rho_s - \rho_g) \cdot g}{\rho_g}} \quad 400 < Re < 200000 \quad (28)$$

Stokes Law was used for small fuel particles, steady separated flow was used for intermediate fuel particles, and turbulent flow was used for large fuel particles.

2.3. Method of lines

Most of the pyrolysis models [15, 17, 56–59] involve solution schemes based on the method of lines (finite difference method) to solve the heat transfer equations. The heat transfer equation is discretized using a central difference scheme:

$$c_{p,s,i} \cdot \frac{dT_i}{dt} = \left(\frac{\lambda_{eff,i}}{\rho_{s,i} \cdot f_{sh}} \cdot \left(\frac{T_{i-1} - 2 \cdot T_i + T_{i+1}}{\Delta r_p^2} + \frac{n}{r_{p,i}} \cdot \frac{T_{i+1} - T_{i-1}}{2 \cdot \Delta r_p} \right) \right) + \sum_{j=1}^3 r_{pyr,i,j} \cdot (-\Delta H_{reac,i,j}) + r_{H_2O,i} \cdot (-\Delta H_{vap,i}) \quad (29)$$

In the present model, the ode15s method in MatLab was chosen as an ODE solver. The ode15s function based on the Backward Differentiation Formula (BDF) is recommended for the solution of stiff problems [60]. Calculations were performed to verify the convergence of the adopted numerical procedure with grids having 51, 101 and 201 mesh points. Since the results showed that sufficient accuracy is attained using a grid with 101 mesh points for different biomass particle sizes, the number of mesh points was set to 101 with an error tolerance of 10^{-10} in time integration.

2.4. Fuel characterization

Pinewood, beechwood, Danish wheat straw, leached Danish wheat straw, alfalfa straw and rice husk were used in this work to represent softwood, hardwood and agricultural residues. The low-ash containing wood (pinewood,

beechnwood) and grass samples (wheat straw, alfalfa straw), which are rich in potassium, were selected to investigate the effect of differences in potassium composition on the char yields. The fuels were milled on a Retsch rotor mill ZM200 and sieved to particle size fractions of 0.02-0.4 mm and 0.85-1 mm.

Table 1: Proximate and ultimate analysis of fuels (on % dry basis) and ash analysis (on mg/kg dry basis).

Fuel	Pine- wood	Beech- wood	Wheat straw	Leached wheat straw	Alfalfa straw
Proximate and ultimate analysis (% db)					
Moisture ^a	5.1	4.5	5.5	4.3	5.2
Ash (550 °C)	0.3	1.4	4.1	2	7.4
Volatiles	86.6	79.4	77.5	84.2	75.9
HHV ^b	21.6	20.2	18.8	18.7	19.7
LHV ^b	20.2	19	17.5	17.4	16.9
C	50.5	46.7	42.4	45.7	42.5
H	6.8	6.3	6.3	6.6	6.1
N	0.1	0.3	1	0.3	3.3
S	<0.01	0.02	0.1	0.02	0.03
Cl	0.01	0.02	0.1	0.01	0.5
Ash compositional analysis (mg/kg db)					
Al	10	10	150	100	600
Ca	600	2000	2500	1300	12900
Fe	20	10	200	350	-
K	200	3600	11000	1300	28000
Mg	100	600	750	350	1400
Na	30	100	150	50	1000
P	6	150	550	80	1900
Si	50	200	8500	6200	2000
Ti	2	<8	10	10	30

^a wt. % (ar) ^b in MJ/kg

2.5. Biomass particle properties

Biomass samples were analyzed with a 2D dynamic imaging instrument by using different size measures (width and length). The diameters $x_{Ma,min}$ and $x_{Fe,max}$ were chosen to represent the biomass particle's width and length. Diameter $x_{Fe,max}$ is the largest diameter to fulfill the assumption that the length of a particle is larger than its width. Diameter $x_{Ma,min}$ is an area bisector representing the shortest distance to the particle's opposite edges. A biomass particle was represented as a plate, a cylinder and a sphere in planar (n=0), cylindrical (n=1), and spherical (n=2) coordinates under the assumption of similar volume to surface ratios using a different characteristic length:

$$d_p = x_{Ma,min} \quad (cylinder) \quad (30)$$

$$d_p = \frac{1}{2} \cdot x_{Ma,min} \quad (plate) \quad (31)$$

$$d_p = \frac{3}{2} \cdot x_{Ma,min} \quad (sphere) \quad (32)$$

Biomass particles were described as infinite cylinders, corresponding to n=1 in equation 11 with a particle size equal to $R_p/2$, where R_p is represented by $x_{Ma,min}$. The thermo-physical parameters used in the devolatilization model are listed in Table 2.

Table 2: Thermophysical properties used in the devolatilization model and geometrical parameters of the drop tube reactor.

Symbol	Unit	Description	Expression	
ϵ		Emissivity	0.85	[61]
σ	$\text{J}\cdot(\text{s}\cdot\text{m}^2\cdot\text{K}^4)^{-1}$	Stefan-Boltzmann	$5.67\cdot 10^{-8}$	[61]
ξ		Void fraction	$1 - \frac{(\rho_b + \rho_M + \rho_{c,0})}{1500}$	[58]
$\rho_{b,0}$	$\text{kg}\cdot\text{m}^{-3}$	Raw biomass density	650 (wood) and 700 (straw)	[62, 63]
ρ_g	$\text{kg}\cdot\text{m}^{-3}$	Gas density (N_2)	$362.65\cdot T_g^{-1}$	[64]
d_{pore}	m	Pore diameter	$3.2\cdot 10^{-6}$	[61]
$d_{pore,c}$	m	Char pore diameter	$2\cdot 10^{-4}$	[65]
$c_{p,b}$	$\text{J}\cdot(\text{kg}\cdot\text{K})^{-1}$	Raw biomass specific heat capacity	$1500 + T_p$	[16]
$c_{p,c}$	$\text{J}\cdot(\text{kg}\cdot\text{K})^{-1}$	Char specific heat capacity	$420 + 2.09\cdot T_p + 6.85\cdot T_p^2$	[16]
$c_{p,g}$	$\text{J}\cdot(\text{kg}\cdot\text{K})^{-1}$	Gas specific heat capacity	$770 + 0.629\cdot T_g + 1.91\cdot 10^{-4}\cdot T_g^2$	[17]
λ_g	$\text{W}\cdot(\text{m}\cdot\text{K})^{-1}$	Gas thermal conductivity	0.026	[66]
λ_b	$\text{W}\cdot(\text{m}\cdot\text{K})^{-1}$	Raw biomass thermal conductivity	0.35	[16]
λ_c	$\text{W}\cdot(\text{m}\cdot\text{K})^{-1}$	Char thermal conductivity	0.1	[16]
μ_g	Pa·s	Gas phase dynamic viscosity	$4.847\cdot 10^{-7}\cdot T_g^{0.64487}$	[58]
$\Delta H_{reac,1}$	$\text{J}\cdot\text{kg}^{-1}$	Heat of reaction from biomass to metaplast	0	[43, 44]
$-\Delta H_{reac,2}$	$\text{J}\cdot\text{kg}^{-1}$	Heat of reaction from metaplast to char	-255000	[45]
$\Delta H_{reac,3}$	$\text{J}\cdot\text{kg}^{-1}$	Heat of reaction from metaplast to gas	20000	[45]
ΔH_{vap}	$\text{J}\cdot\text{kg}^{-1}$	Heat of vaporization	2440000	[53]
A_{H_2O}	$\text{s}^{-1}\text{K}^{-0.5}$	Pre-exponential factor	$5.1\cdot 10^{10}$	[58]
E_{H_2O}	$\text{J}\cdot\text{mol}^{-1}$	Activation energy	88000	[58]
L	m	Drop tube reactor's length	2.3	
D_r	m	Drop tube reactor's diameter	0.054	

2.6. Experimental

2.6.1. Small and intermediate size particles (0.2 and 1 mm)

The model was validated against data from three high-temperature reactors. The char yields of 0.2 and 1 mm pinewood particles were determined

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9 in separate pyrolysis experiments performed at an intermediate heating rate
10 (10-10³ K s⁻¹) in the wire mesh reactor and at a high heating rate of (10⁴ K
11 s⁻¹) in the drop tube reactor.
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15 The wire mesh reactor at TU Munich was previously described by Tru-
16 betskaya et al. [33]. Tests on the wire mesh reactor were conducted at 350-
17 1400°C, with 1 s holding time on the mesh at atmospheric pressure. The
18 DTF setup was described in detail by Trubetskaya et al. [34]. The experi-
19 ments were conducted by feeding ≈ 5 g of biomass at a rate for 0.2 g min⁻¹.
20 The residence time for 0.2 mm and 1 mm pinewood particles was estimated
21 to be about 1 s, taking into account density changes during pyrolysis [29].
22 Biomass was rapidly heated and reacted as it fell through the reactor at
23 temperatures of 1000-1400°C. Reaction products were separated into coarse
24 particles (mainly char and fly ashes), fine particles (mainly soot and ash
25 aerosols), and permanent gases.
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36 The heating rate in the wire mesh reactor was set to 1000 K s⁻¹. In
37 the drop tube reactor, the heating rate was calculated by the model using
38 dimensions and operating parameters of the reactor shown in Table 2. Char
39 yields of wood and herbaceous biomass in the wire mesh reactor and drop
40 tube reactor are shown on dry ash free basis (daf) excluding ash content of
41 original biomass and char.
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48 *2.6.2. Large size particles (3-5 mm)*

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50 The devolatilization time and char yield of 3, 4 and 5 mm pinewood
51 particles in a temperature range of 1350-1450°C were determined by Jepsen
52 in a single particle reactor (SPR) located at the DTU Chemical Engineering
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Department [41]. The SPR was designed for oxidation and pyrolysis studies on fuel particles $> 2\text{ mm}$ at temperatures up to 1500°C at high heating rates. The setup consists of the reactor, a flat flame burner with 94 injection nozzles, a gas supply system and gas analyzers as shown in Figure 5.

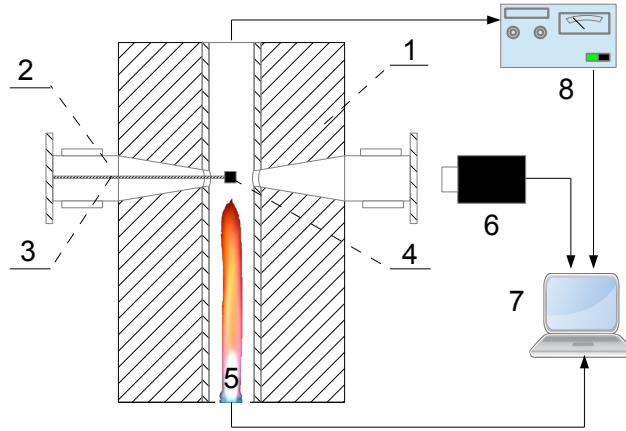


Figure 5: Schematic view of a single particle reactor at DTU: 1. Reactor corpus; 2. insertion ports with a water-cooled chamber; 3. particle holder; 4. sample particle; 5. 94 injection nozzles; 6. High-speed camera; 7. Computer; 8. Gas analyzers.

The formation of a soot cloud in the single particle reactor is associated with pyrolysis initiation. Soot formation occurs under reducing conditions. The oxygen level was kept very low ($< 0.2\text{ vol.}\%$) during the experiments to eliminate char and soot oxidation. Devolatilization time is defined as the time from the soot cloud is seen until it extinguishes and char conversion begins due to gasification with steam and the remaining oxygen. The char yield is defined as the solid fraction of the reacted biomass, remaining on the platinum wire after an experiment.

3. Results

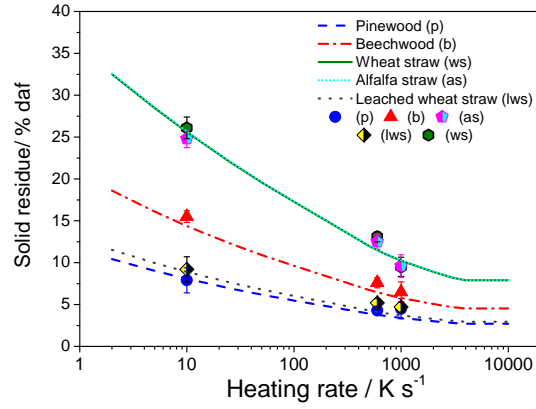
3.1. Kinetic parameters

The results of fitting of the rate constants, including the influence of potassium are shown in Table 3.

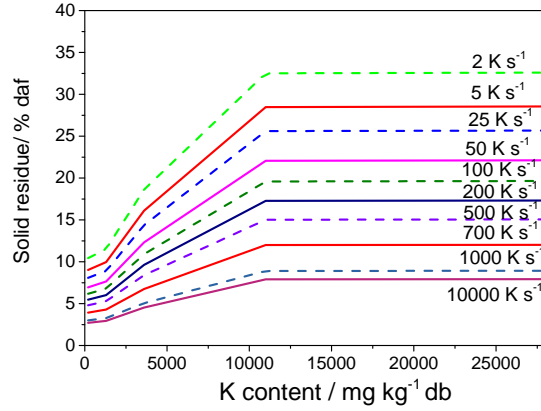
Table 3: The best fit values of the kinetic parameters. In the model, the constants $K_1 = 0.068$ and $K_2 = 4500$ (mg kg⁻¹) were fitted.

Metaplast		Volatiles		Char	
$E_{a,1}$	A_1	$E_{a,2}$	A_2	$E_{a,3}$	A_3
J mol ⁻¹	s ⁻¹	J mol ⁻¹	s ⁻¹	J mol ⁻¹	s ⁻¹
228000	$3.2 \cdot 10^{14}$	174100	$3.6 \cdot 10^{12}$	$132500 \cdot \Omega_K$	$5.6 \cdot 10^8$

Figure 6 illustrates that the char yield increases with increasing potassium content in the lignocellulosic material and decreases with the higher heating rate. The activation energy of the char forming reaction decreases with increasing potassium content, and thus, the influence of potassium becomes smaller at higher heating rates. In Figure 6(b), the model estimates that char yield increases from 2.6 % to 32.5 % when the heating rates decrease from 10^4 to 2 K s^{-1} .



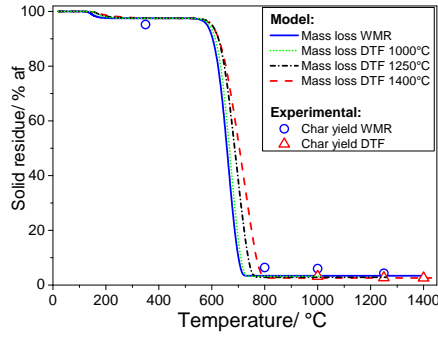
6(a): Heating rate effect on the char yield



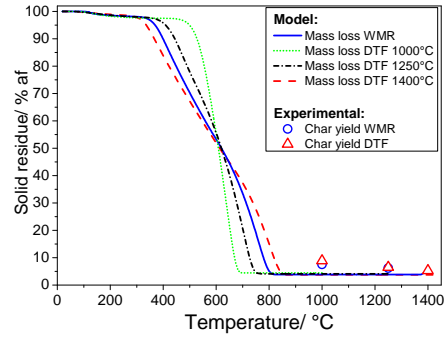
6(b): Char yields versus potassium content in the fuel

Figure 6: (a) Comparison of simulated and experimental data for the influence of heating rate on the char yield of pinewood, beechwood, wheat straw, leached wheat straw and alfalfa straw in the wire mesh reactor, and (b) Simulated char yields versus potassium content in the original fuel (heat treatment temperature: 1400°C, holding time: 1 s, particle size: 0.2 mm).

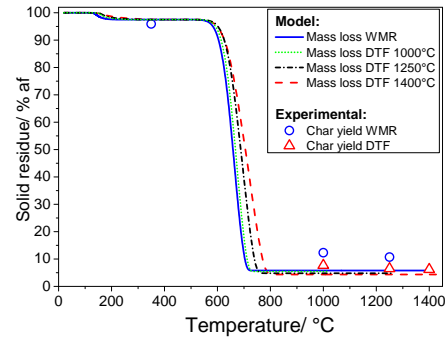
Estimated biomass particle mass as a function of mean particle temperature is shown in Figure 7.



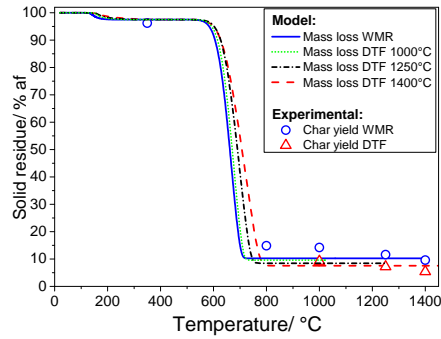
7(a): Pinewood 0.2 mm



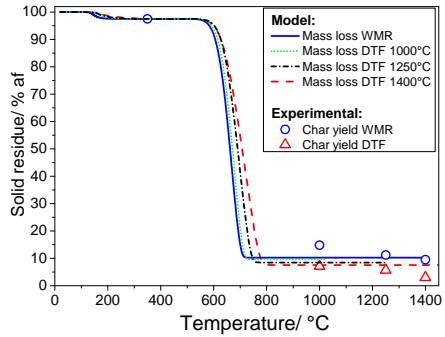
7(b): Pinewood 1 mm



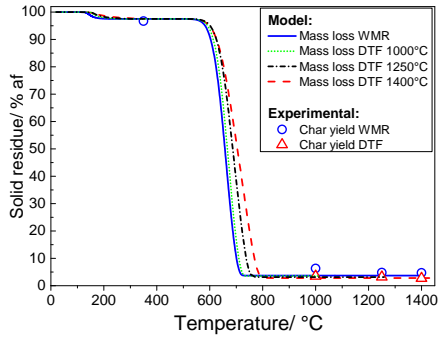
7(c): Beechwood 0.2 mm



7(d): Alfalfa straw 0.2 mm



7(e): Wheat straw 0.2 mm

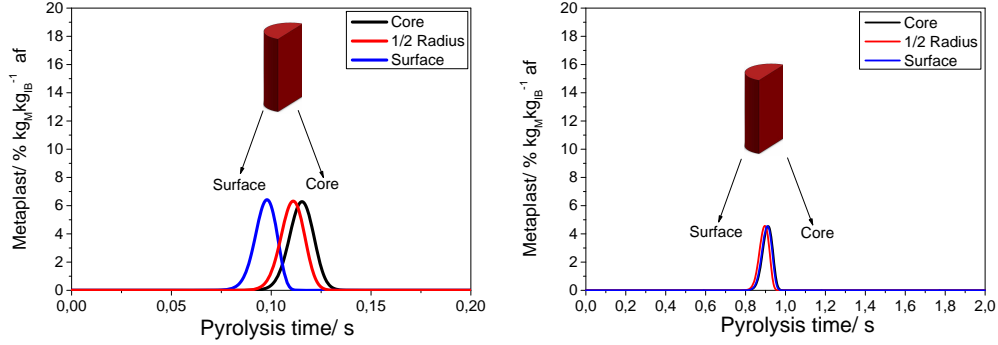


7(f): Leached wheat straw 0.2 mm

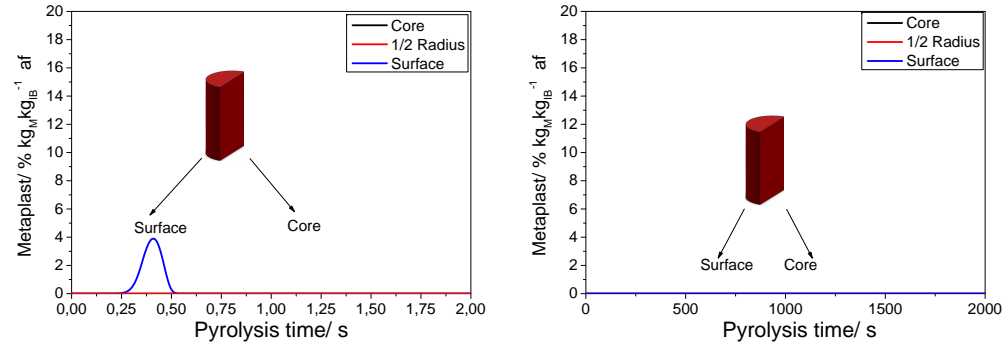
Figure 7: Simulated mass loss over the mean particle temperature (% af) of pinewood, beechwood, wheat straw, alfalfa straw and leached wheat straw at 1000, 1250 and 1400°C in the DTF and at 1400°C in the WMR, and comparison with the char yields determined experimentally in the wire mesh reactor at (heat treatment temperature: 350, 800, 1000, 1250 and 1400°C; heating rate: 1000 K s⁻¹; holding time: 1 s) and drop tube reactor at 1000, 1250 and 1400°C as determined by Trubetskaya et al. [33, 34].

The mass loss of smaller particles is shown only at 1400°C in the wire-mesh reactor, since pyrolysis is complete at temperatures below 800°C. The simulation results show that char yields from pyrolysis of wood and leached wheat straw in the drop tube reactor were similar over a temperature range of 1000-1400°C, whereas the char yield of wheat and alfalfa straw decreased slightly from 10.3 % to 7.6 % by weight. The present results show that the model accurately estimates the char yield for smaller (0.2 mm) biomass particles. The char yield from pyrolysis of 1 mm pinewood particles is also estimated well and is about 3 % lower relative to the experimentally determined char yields in the drop tube reactor. The experimental data obtained in the wire mesh reactor agree with the mass loss estimated by the model. The lower WMR heating rate caused the reaction to take place at lower temperatures for an extended period compared to fast pyrolysis conditions in the drop tube reactor.

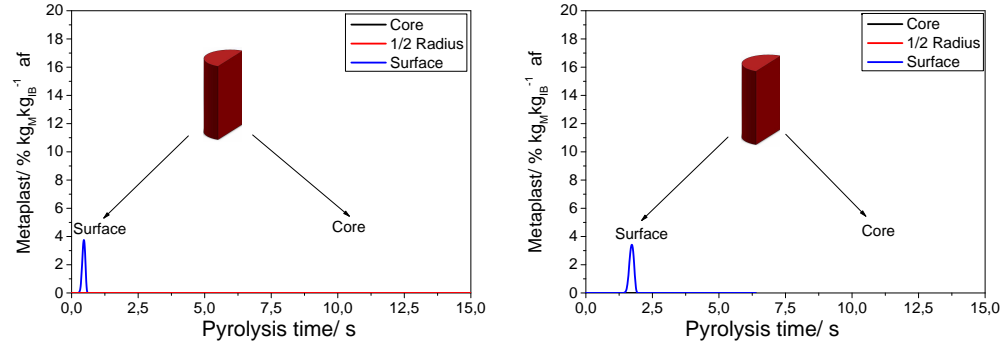
Figure 8 illustrates the mass fraction of metaplast formed at the surface, middle and center of the particle as a function of time. The simulation results show that both heating rate and particle size influence metaplast formation. In general, high heating rates promote the formation of metaplast. Due to negligible temperature gradients, high heating rates cause small particles first to become fluid and form a molten sphere, then solidify into char [6, 7, 33]. For large particles, significant formation of metaplast at high heating rates is only observed at the surface.



8(a): 0.2 mm, heated by 10^4 K s^{-1} gas flow 8(b): 0.2 mm, heated by 10^3 K s^{-1} gas flow



8(c): 3 mm, heated by 10^4 K s^{-1} gas flow 8(d): 3 mm, heated by 10 K min^{-1} gas flow



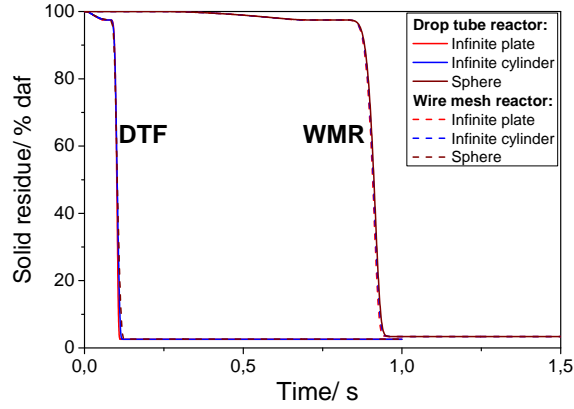
8(e): 10 mm, heated by 10^4 K s^{-1} gas flow 8(f): 10 mm, heated by 10^3 K s^{-1} gas flow

Figure 8: Simulated metaplast formation (% af) from pyrolysis of 0.2, 3 and 10 mm pinewood particles at slow heating rate in the thermogravimetric instrument (10 K min^{-1}), at intermediate heating rate (10^3 K s^{-1}) in the wire mesh reactor and at high heating rates in the drop tube reactor. The metaplast formation ($\text{kg}_M \text{ kg}_{IB}^{-1}$) is showed over the pyrolysis time.

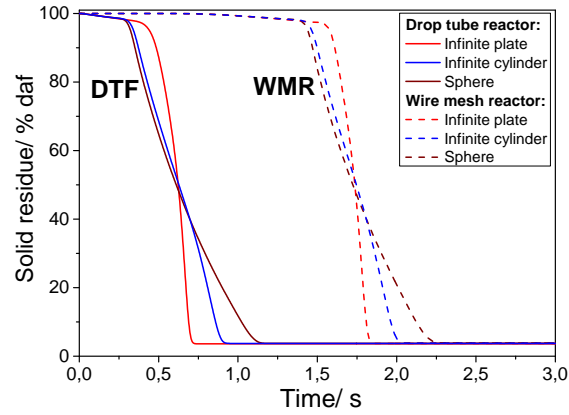
This means that the particle surface melts during pyrolysis, whereas the interior retains the original biomass structure [33]. The rate of metaplast formation was slower than formation of volatiles and char at lower temperatures. Thus, metaplast was formed faster than it was consumed at higher temperatures. At low heating rates, the particle was nearly isothermal, indicating only small differences in metaplast formation as function of position within the particle. Thus, the relatively low heating rate for the particle core increased the time for the three reactions, leading to lower metaplast yields.

3.2. Influence of assumed particle geometry

Figure 9 illustrates the mass loss of 0.2, 1 and 5 mm pinewood particles. Devolatilization time decreased with the higher heating rate in the drop tube reactor compared to the wire mesh reactor. The representation of the 0.2 mm particles using different characteristics lengths does not give large deviations with respect to char yield and devolatilization time among the three particle geometries as shown in Figure 9(a).



9(a): Pinewood 0.2 mm



9(b): Pinewood 1 mm

Figure 9: Mass loss histories of pinewood particles (0.2 and 1 mm) with the similar volume to surface ratio and different characteristic lengths which were calculated in plate-like ($n=0$), cylindrical ($n=1$) and spherical ($n=2$) geometries at the final temperature of 1400°C during pyrolysis in the wire mesh and drop tube reactors.

The influence of particle shape becomes more important with the increasing particle size due to the larger internal temperature gradients as

shown in Figure 9(b). The relative influence of heating rate on devolatilization time of 1 mm pinewood was less compared that for smaller particles. This is because of the predominance of internal heat transfer control within the large particles.

3.3. Influence of volumetric shrinkage on devolatilization time

In the model, the shrinkage front moves from the surface towards the center. At high heating rates, the outer layers initially shrink while the inner layers remain unaffected. Later, the fuel particle shrinks due to devolatilization. During slow pyrolysis, internal thermal gradients are small, and therefore, drying followed by devolatilization takes place over throughout the particle. Particle shrinkage takes place after the original biomass is converted into metaplast. The rate of volatiles formation determines the rate at which the particle shrinks.

Figure 10(a) shows that the particle size of 5 mm particle was reduced by 27 % during pyrolysis at high heating rates. A 26 % reduction in a particle size was measured during devolatilization of 3 mm pinewood particle in a temperature range of 1180-1440°C in the single particle reactor [41].

Figure 10(c) shows that shrinkage has a negligible influence on the devolatilization time of smaller particles, which are practically isothermal. For the large particles, the inclusion of shrinkage increases the devolatilization rate and thereby decreases the devolatilization time. Internal temperature gradients in larger particles becomes smaller as the particle shrinks which enhances the devolatilization rate. The shrinkage of 5 mm pine particle leads to the decrease of devolatilization time by 19 % during pyrolysis in the WMR and DTF.

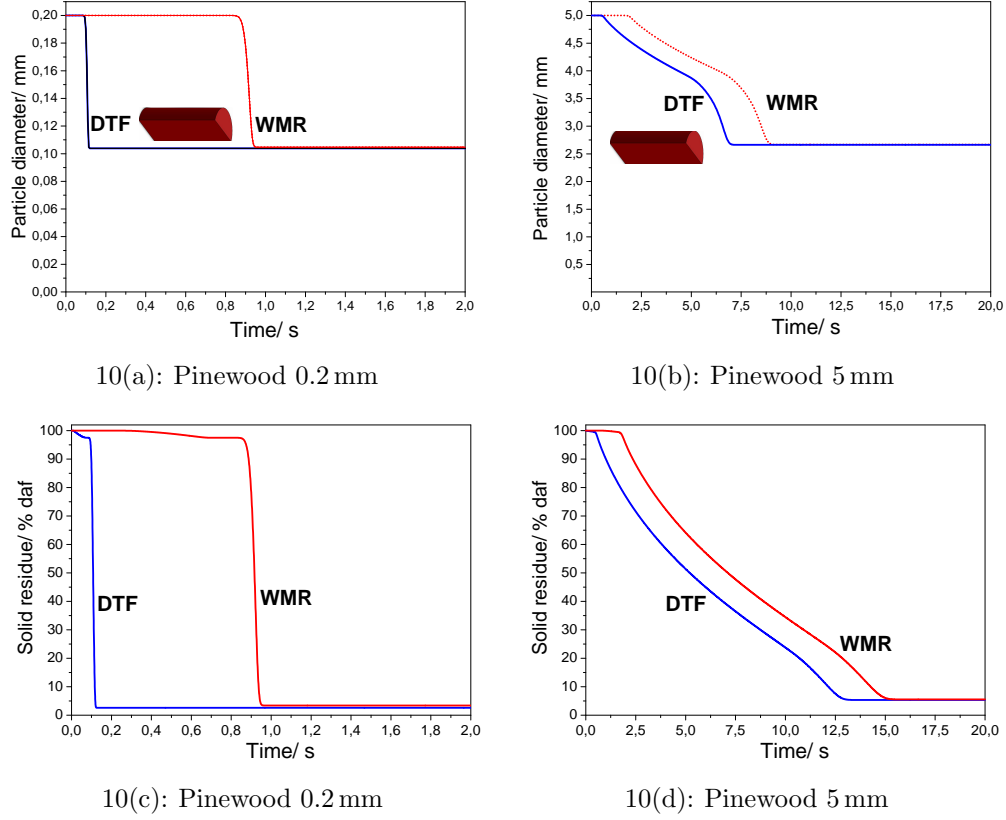


Figure 10: (a)-(b) Simulated pinewood particle shrinking (0.2 and 5 mm) and (c)-(d) Simulated mass loss of shrinking pinewood particles in the wire mesh and drop tube reactors.

3.4. Influence of particle size on devolatilization time

Figure 11 compares the times required for complete devolatilization of 3, 4 and 5 mm pinewood particles in the single particle reactor to those estimated by the model for particles from 0.01 to 10 mm. In the model, the complete devolatilization time is defined as the time when 95 % of the volatile matter in the original pinewood particle has been released [67].

Figure 11 shows that under fast heating particles with mean diameters < 0.25 mm may be considered as thermally thin based on the modeling results with 0.1 s deviation, while the intra-particle heat conduction in larger particles plays a key role in biomass devolatilization. The diameter of 3, 4 and 5 mm pinewood cubes was recalculated for corresponding cylinders under the assumption of a similar volume to surface ratio (3, 4 and 5 mm). A comparison of experimental and estimated devolatilization times showed that the model estimates the devolatilization time of pinewood particles well. In addition, the results showed that the 1 mm pinewood particles require more than 1 s in the WMR and DTF for complete conversion. The estimated devolatilization time by the model showed a similar trend for the experiments in the drop tube reactor.

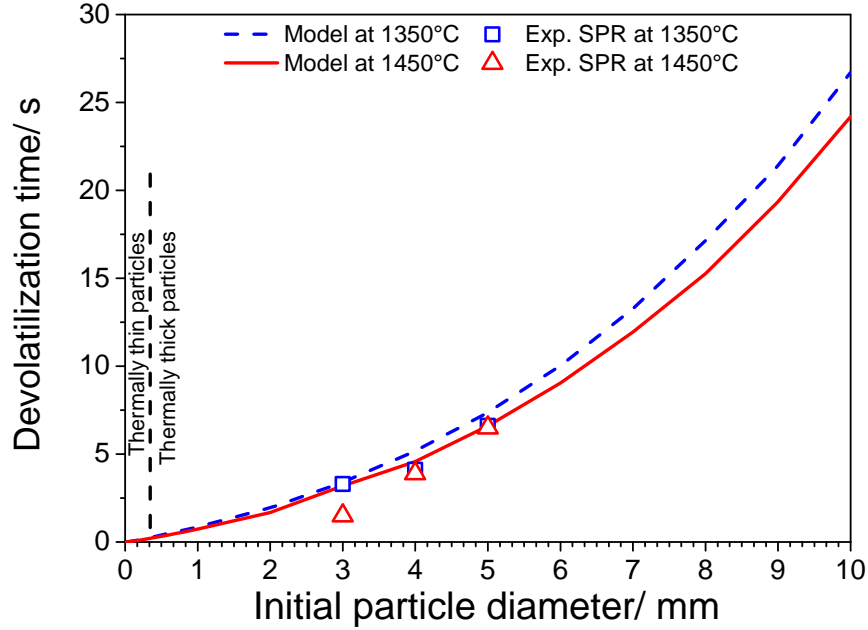


Figure 11: Simulated devolatilization time of shrinking pinewood particles (from 0.01 mm to 10 mm) at 1000, 1250 and 1400°C, and compared with the experimental results obtained in the SPR for 3, 4 and 5 mm particles at 1350 and 1450°C. Experimental data was taken from the investigations of Jepsen [41]. The black dashed line separates the thermally thin regime ($Bi < 0.1$) from the thermally thick ($Bi > 0.1$).

4. Discussion

The present pyrolysis model describes the char yield at high temperatures (up to 1500°C) and high heating rates $> 200 \text{ K s}^{-1}$. In the model, an intermediate liquid (so called metaplast) is formed from the decomposition of biomass which reacts further to char and gas. It was assumed that the kinetics for metaplast formation does not depend on the biomass type and that

reaction of metaplast to char and gas is influenced by the biomass potassium content.

The impact of heating rate on the maximum metaplast formation and subsequent reaction to char and gas shown in Figure 12.

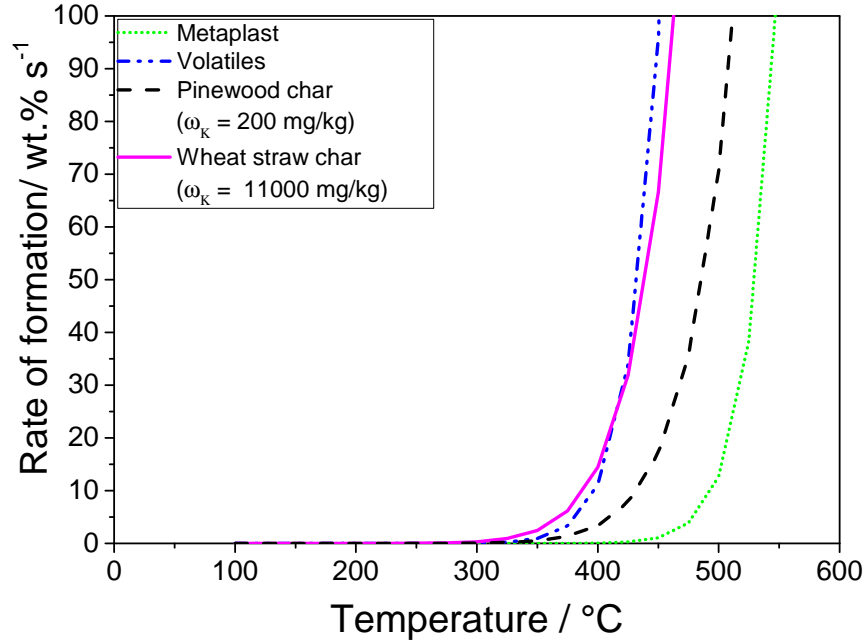


Figure 12: Simulated reaction rates (wt.% s⁻¹) of metaplast, char and volatile formation during fast pyrolysis of 0.2 mm pinewood ($\omega_K = 200 \text{ mg kg}^{-1}$, dry basis) and wheat straw ($\omega_K = 11000 \text{ mg kg}^{-1}$, dry basis) particles in the wire mesh reactor (1000 K s⁻¹).

Figure 12 demonstrates that the rate of metaplast formation is slower than formation of volatiles and char at temperatures below 350°C. Thus, lower concentrations of metaplast are formed at lower heating rates. The particle temperature was nearly uniform over the particle diameter, and therefore,

only small differences in metaplast formation were observed. At higher temperatures, the rate of char formation was lower than the rate of metaplast formation, in agreement with experimental results from Koufopoulos [15, 45]. Higher temperatures result in greater metaplast accumulation because its formation rate is faster than its rate of consumption. At high heating rates, such as in the wire mesh and drop tube reactors, lower mass fractions of metaplast were formed in the particle core compared to the particle surface. This could be due to the lower heating rates at the core compared to at the surface. At high heating rates, formation of metaplast is initially fast relative to reaction from metaplast to char and gas, so a high concentration of metaplast is obtained. With a high fraction of metaplast, the particle may become molten (locally or throughout the whole particle), thereby leading to structural changes of the particle [33].

Particle size demonstrates a greater influence on metaplast, volatile and char formation in the drop tube reactor (10^{-4} K s^{-1}) than in the wire mesh reactor (10 K s^{-1}). The larger internal temperature gradients led to slower pyrolysis of 3 and 10 mm pinewood particles compared to 0.2 mm particles. For large particles the formation of metaplast mainly takes place at the particle surface at high heating rates, whereas the lower heating rates result in high metaplast concentrations in the interior. At low heating rates, both small and large particles were nearly isothermal, leading to smaller local differences in metaplast formation. Differences in local mass fractions of metaplast became larger with increasing particle size and increasing heating rates because of the predominance of internal heat transfer control within the large particles.

Char yield has been experimentally shown to increase with potassium content in the original biomass [33, 34]. This effect was accounted for in the model by modifying the activation energy for the char formation reaction as a function of the potassium content. The influence of potassium on char formation became stronger with decreasing heating rate, which corresponds to the experimental observations from the wire mesh and drop tube reactors. Calculations suggested that pyrolysis was completed at temperatures below 800°C, and thus, the char yields for woody and herbaceous biomass remain unchanged. The experimental data showed that the biomass char yields decreased with the increasing temperature due to the dehydrogenation and cross-linking reactions [68], which are not considered in the present simulation. The simulated char yield from wheat straw pyrolysis was slightly lower than the char yield from the wire mesh and drop tube reactor experiments. The ash compositional analysis of char from the pyrolysis in the drop tube reactor showed that close to 70 % potassium in the wheat straw has been released in a temperature range of 1000-1500°C [69]. The remaining potassium in herbaceous biomass samples is still present in a larger amount than in woody chars. The large differences in herbaceous char yields between the model and experimental data might be attributed to the interactions between potassium, other remaining alkali metals and carbonaceous char matrix which were not considered during the model development.

Moreover, the char yield of larger particles is underestimated by the model. It was hypothesized that tar inside larger particles may undergo secondary reactions, leading to higher char yields [36]. At high heat treatment temperatures of 750-1100°C, secondary reactions occurring in larger

particles strongly decrease tar release and increase char formation during pyrolysis. Tar decomposition occurs by secondary reactions (i.e. cracking and polymerization), and tar release to ambient by mass transfer [35]. The evolutionary profiles of the temperatures at the pinewood particle surface and the particle center as a function of time are shown in the supplemental material. Due to the fast heat transfer in 0.2 mm particles, the differences between surface and core temperatures are small and thus, tar release remains unchanged at 1100°C. The differences between surface and core temperatures become more pronounced with the increasing particle size. Tar formation from pyrolysis of larger pinewood particles was stronger, whereas the soot yield was half lower compared to smaller particles [70]. The lower soot yields were related to the less formed PAH precursors. Tar inside larger particles underwent secondary reactions due to the lower heat flux, leading to a slower pyrolysis and thereby higher char yields and less soot, corresponding to investigations of Miller and Bellan [36]. This effect was not included in the model and could be the reason why the model slightly underpredicts the char yield for large particles.

5. Conclusion

The novelty of this work relies on the description of both low and high temperature kinetics for wood and herbaceous biomass using one set of kinetic parameters. The actual particle heating rate of biomass particles was quantitatively defined in wire mesh and drop tube reactors. The results presented in this work emphasize a stronger catalytic effect of potassium on char yield at low and intermediate heating rates compared to high heating rates.

The potassium content and heating rate affected the char yield more than other operational parameters.

An innovative approach was used to implement the influence of potassium on the char yield in the model by reduction in the activation energy of char formation with increasing potassium content, and fitted to the experimental results. The simulation results showed that particle size has a more significant influence on metaplast formation and reaction to char and gas at high heating rates (10^4 K s^{-1}) compared to pyrolysis at low heating rates (10 K s^{-1}).

In addition, the model showed that the impact of shrinkage on devolatilization time increases with increasing particle size, but it has negligible influence on char yields. Results from the 1D model are in agreement with experimental data, and emphasize a key role of intra-particle heat conduction in biomass particle $> 0.25 \text{ mm}$.

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Supplemental material

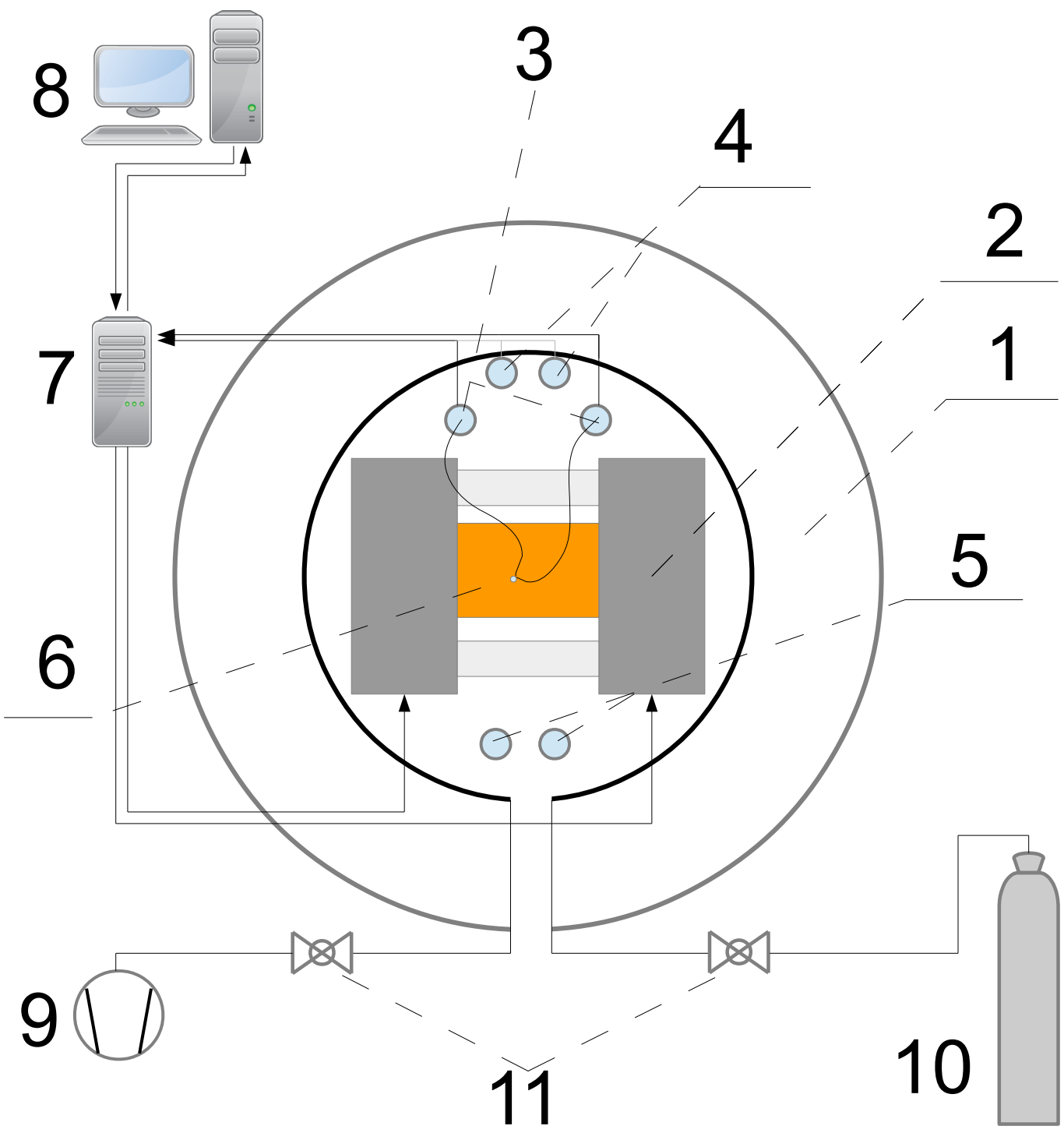
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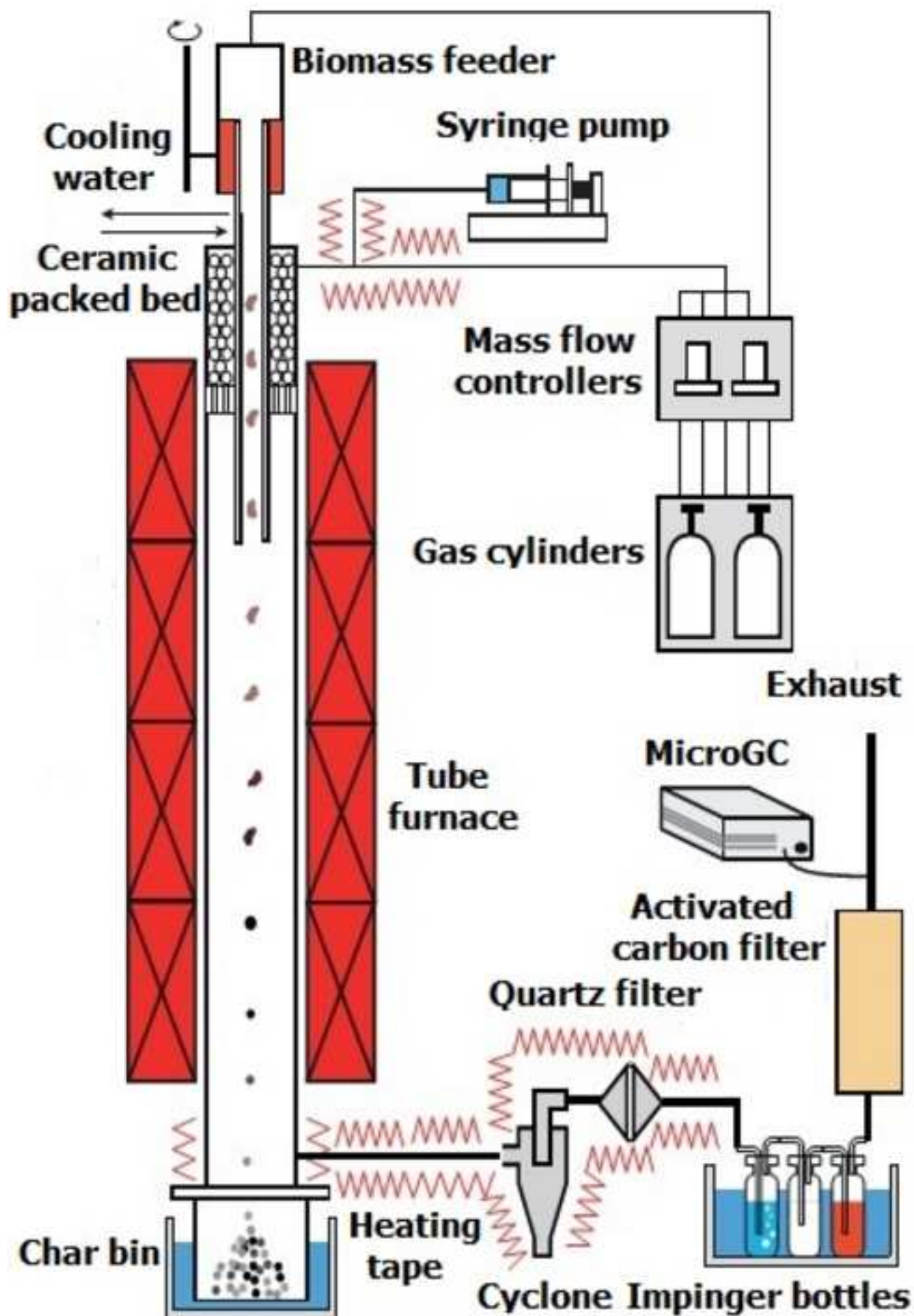
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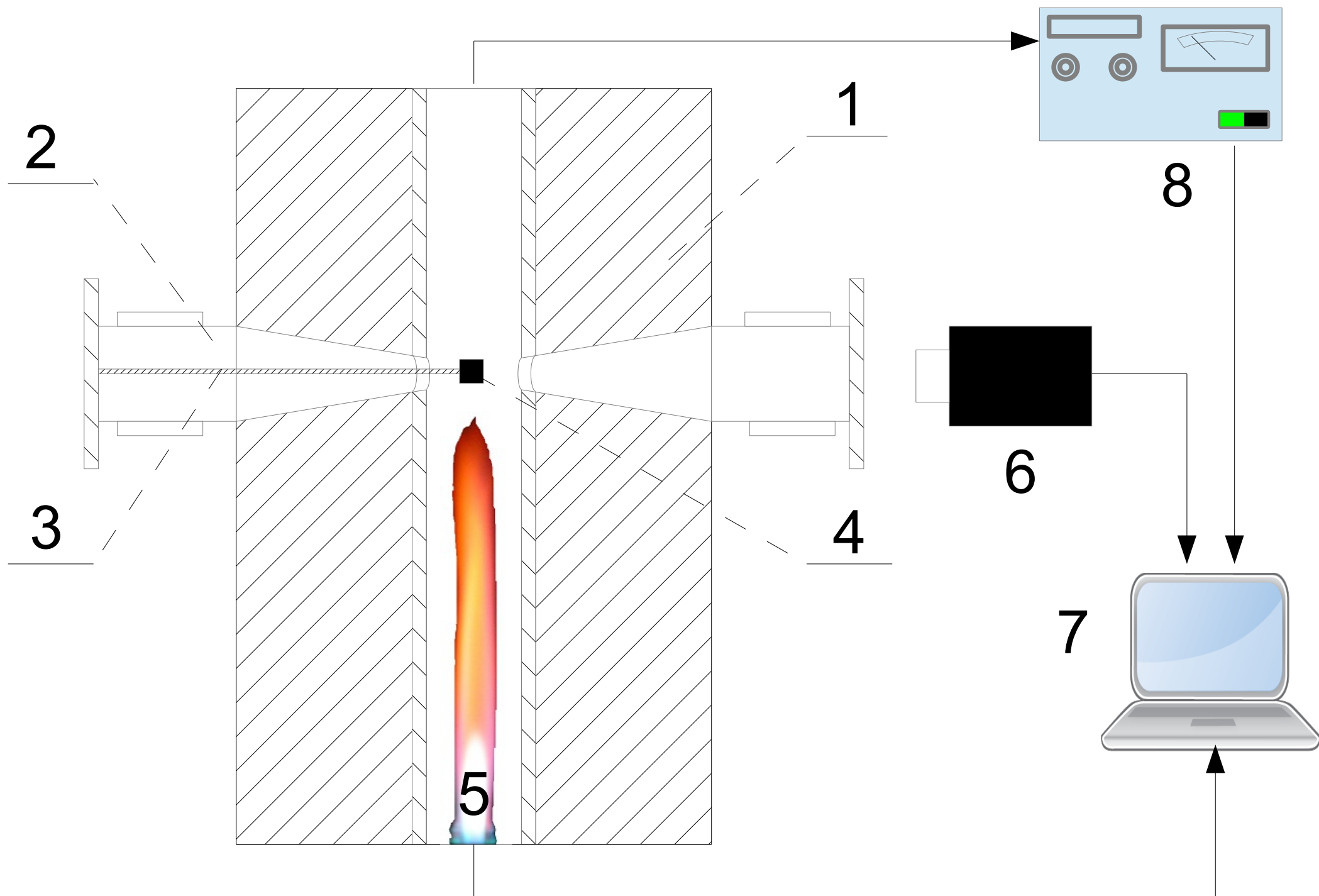
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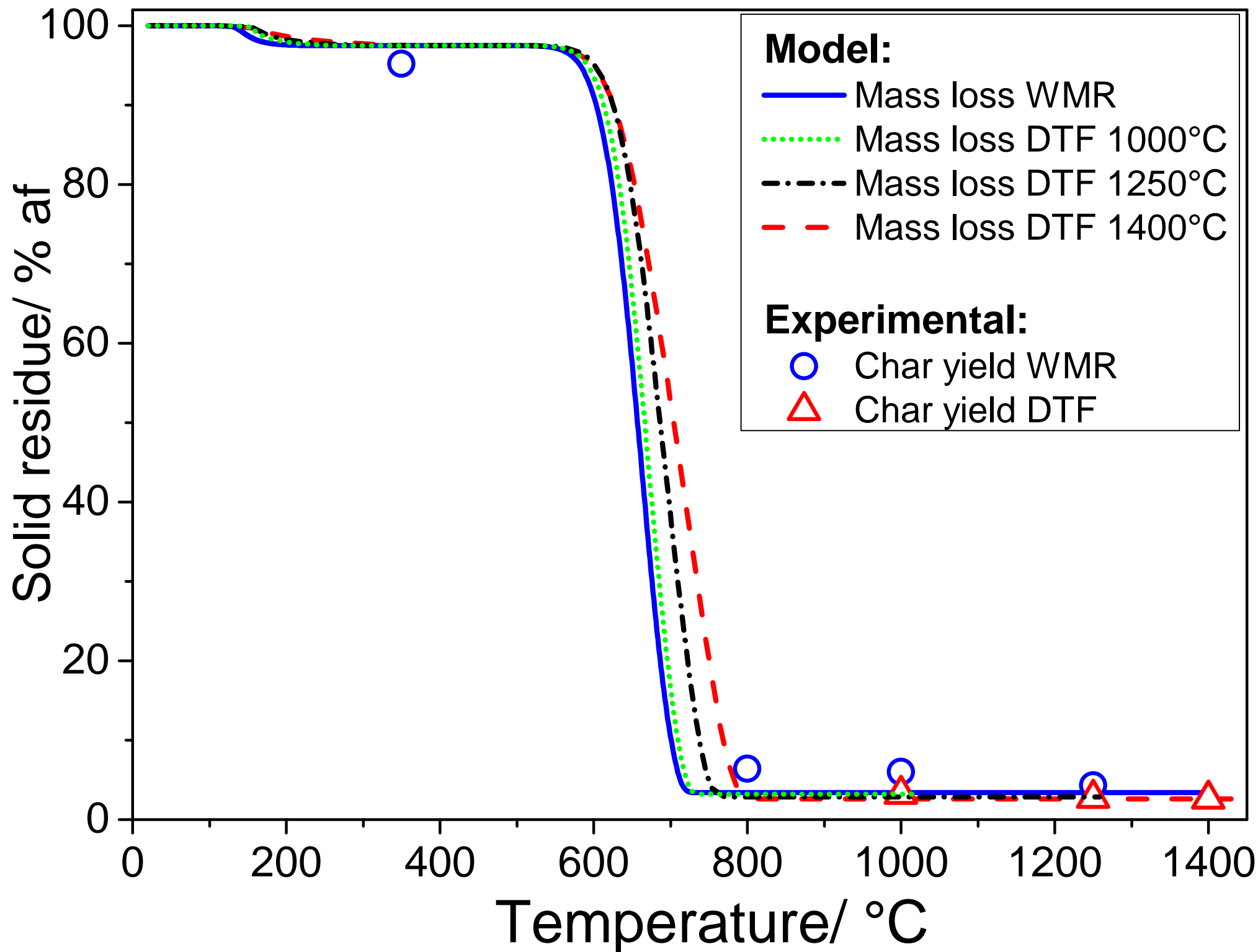
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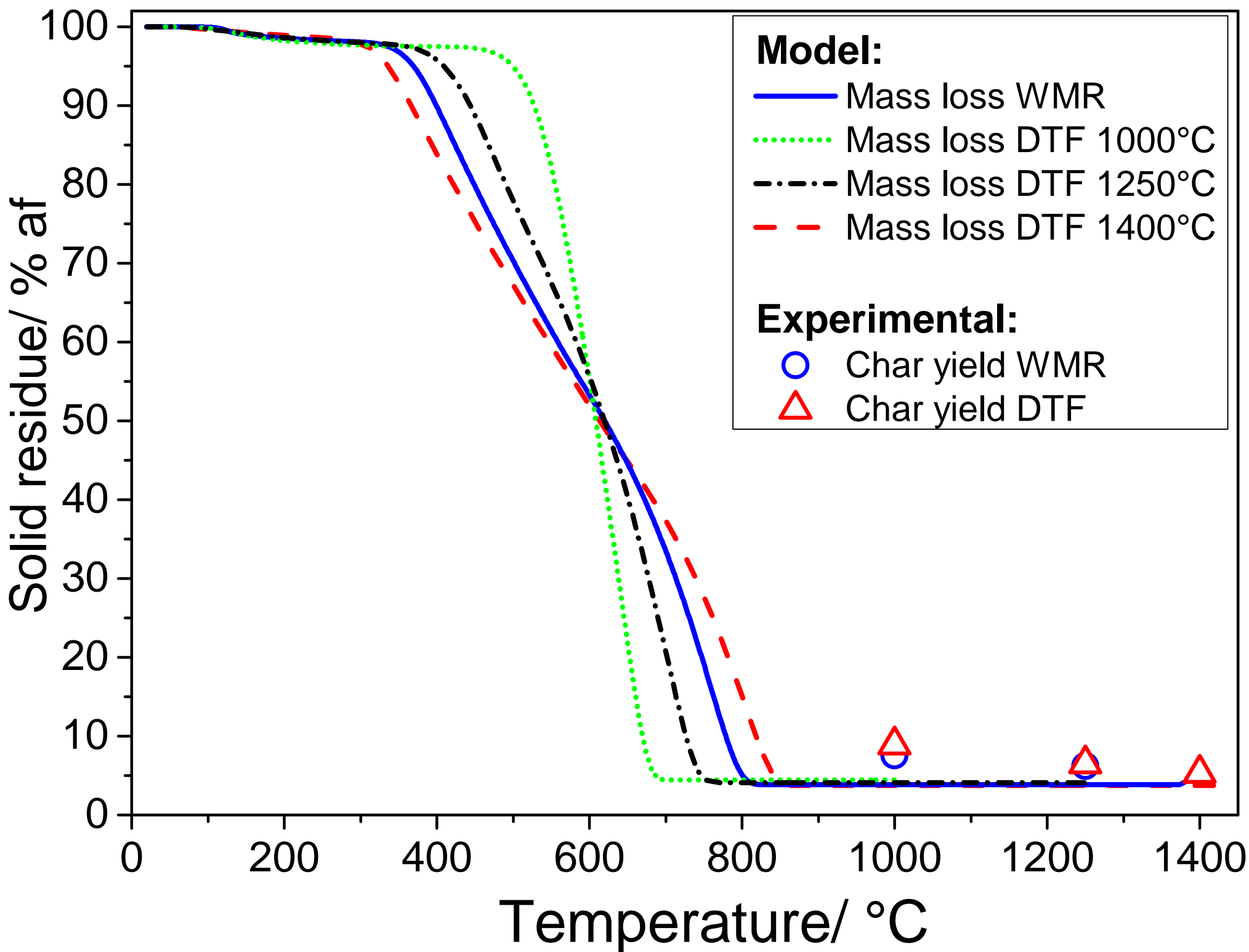
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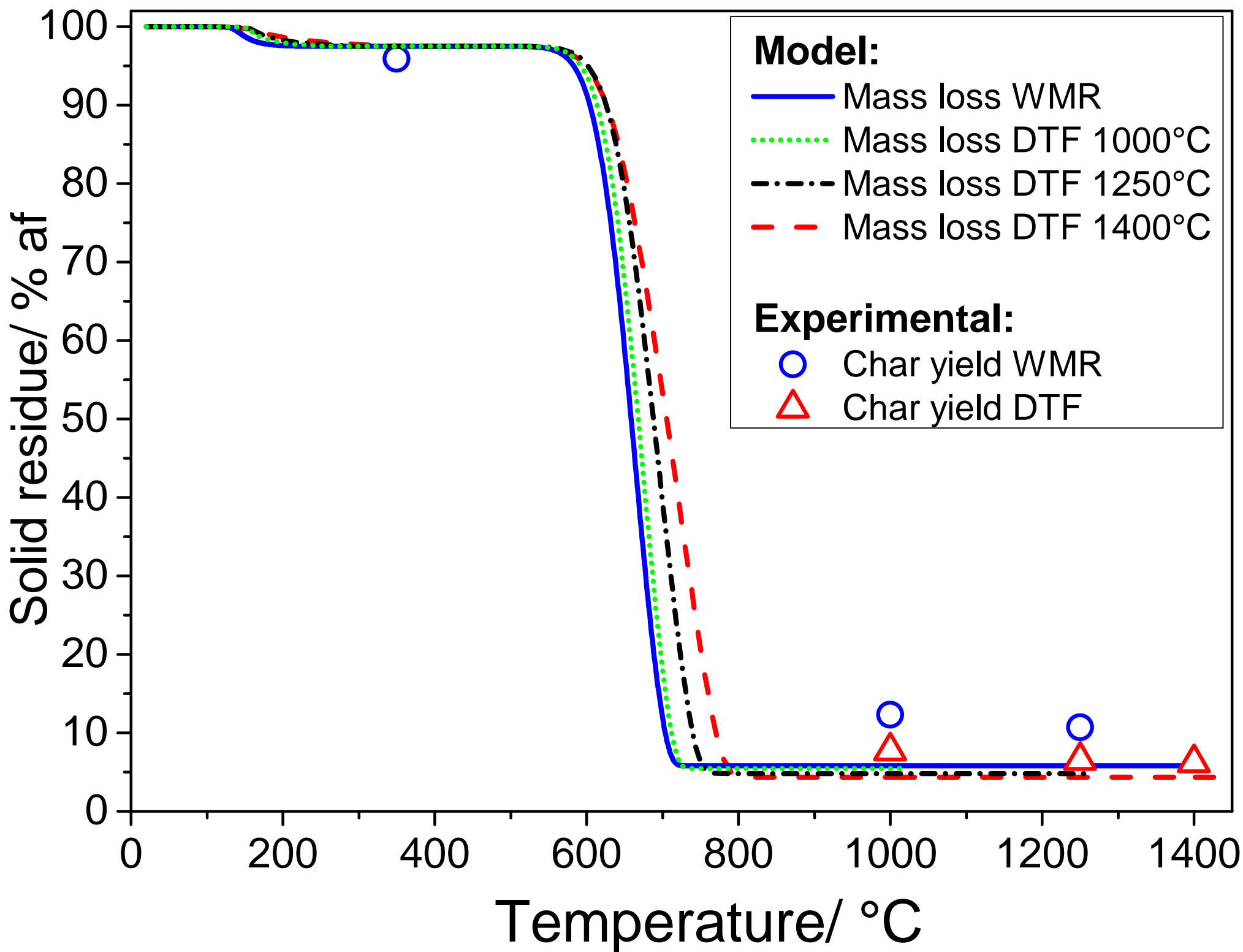


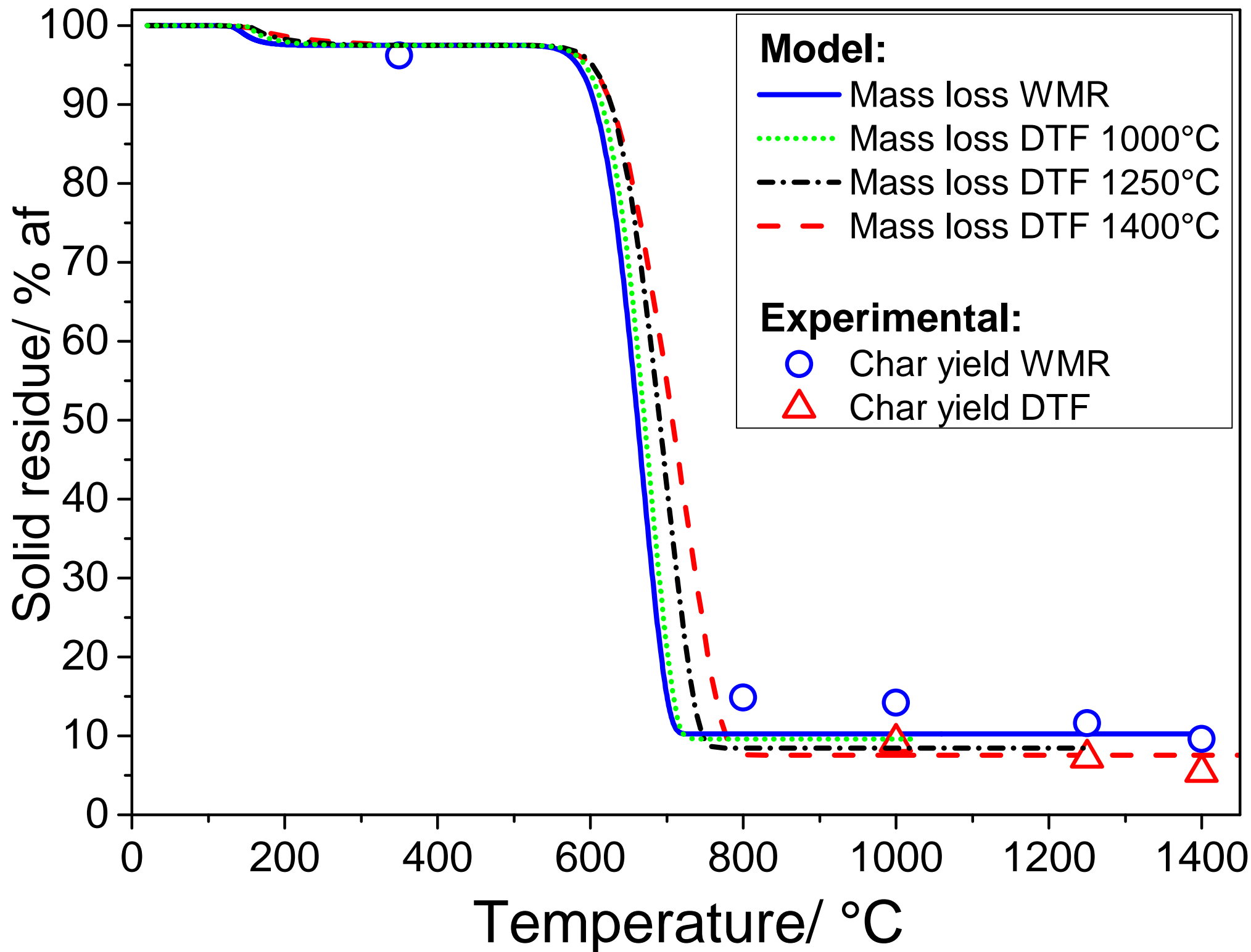


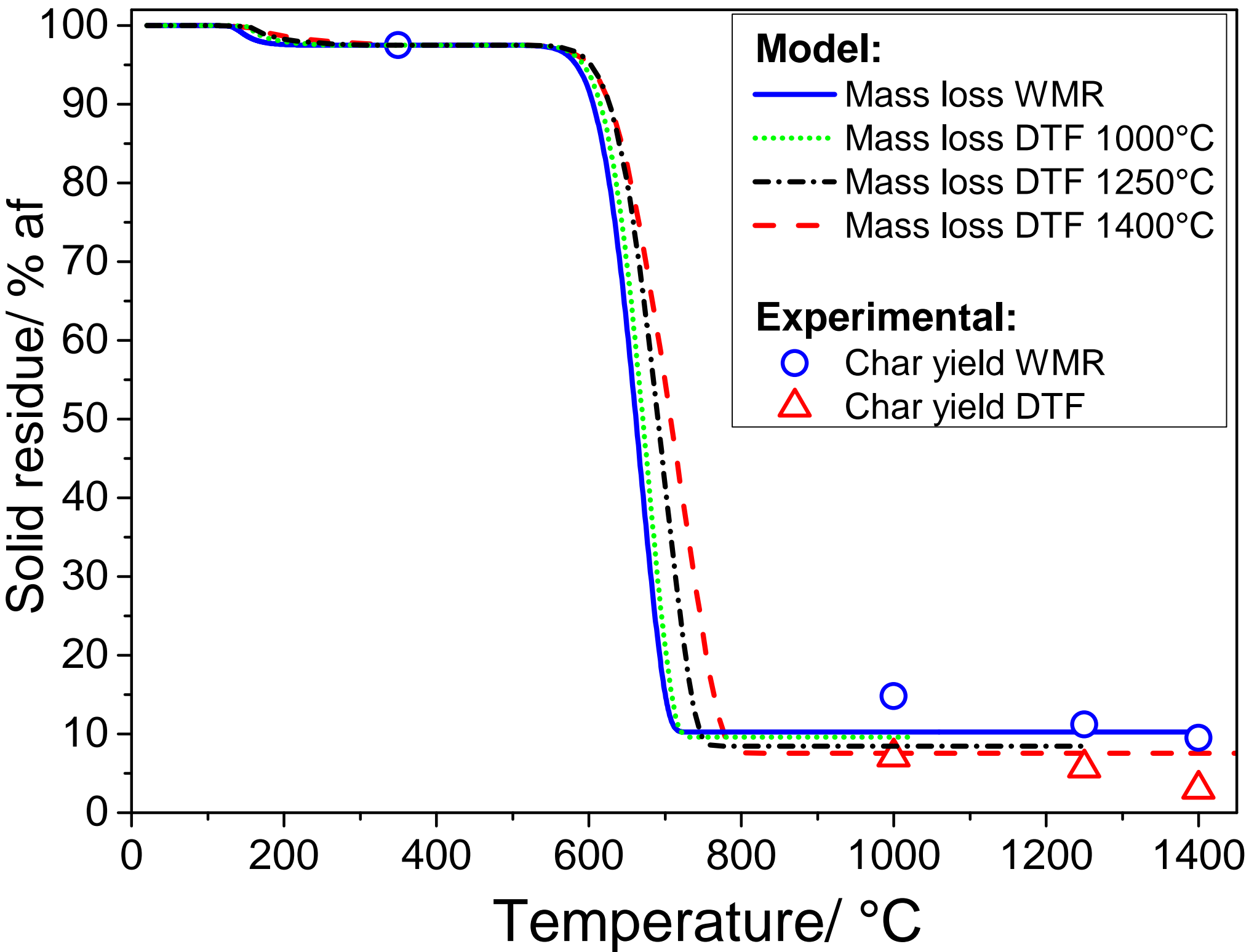


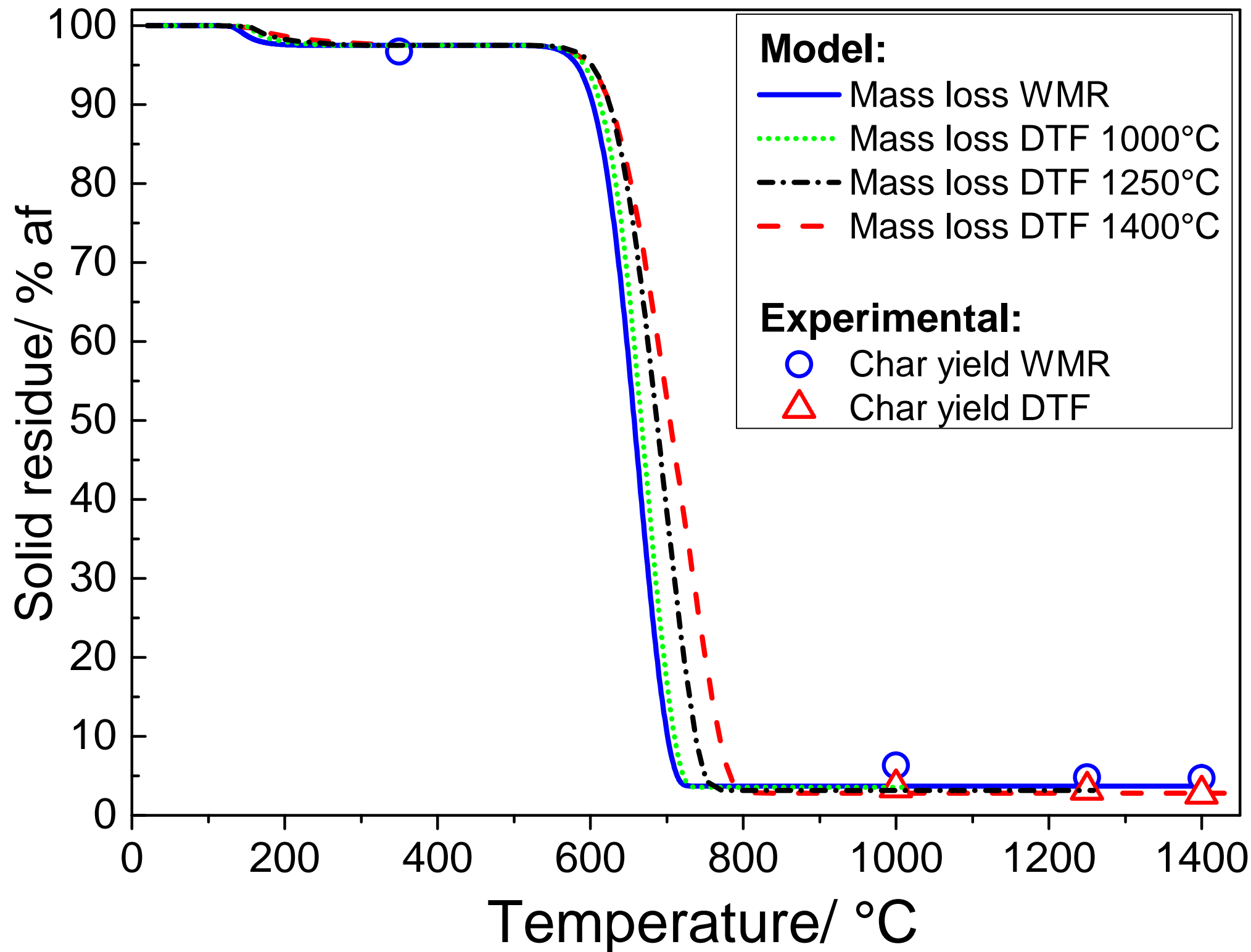


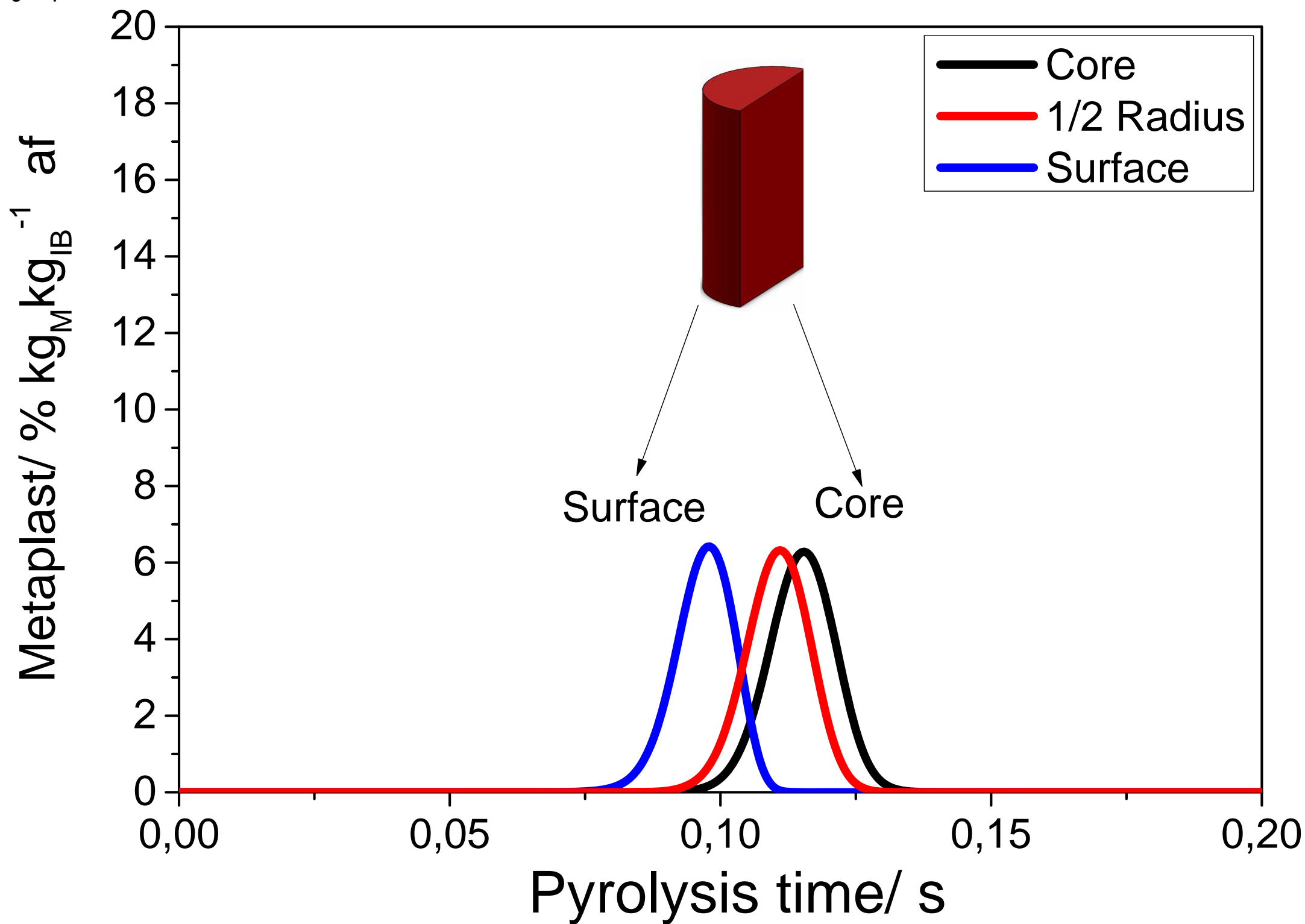


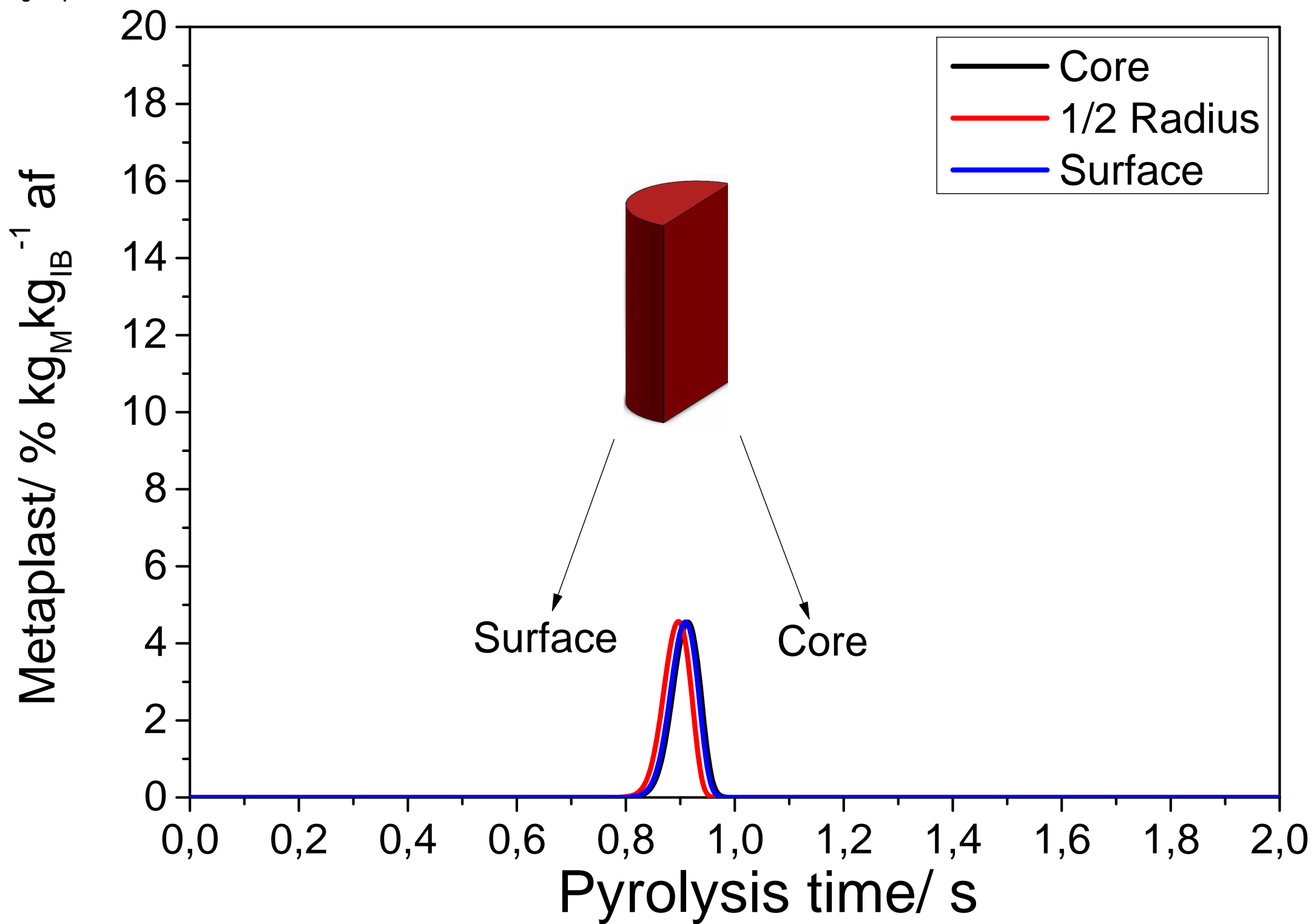


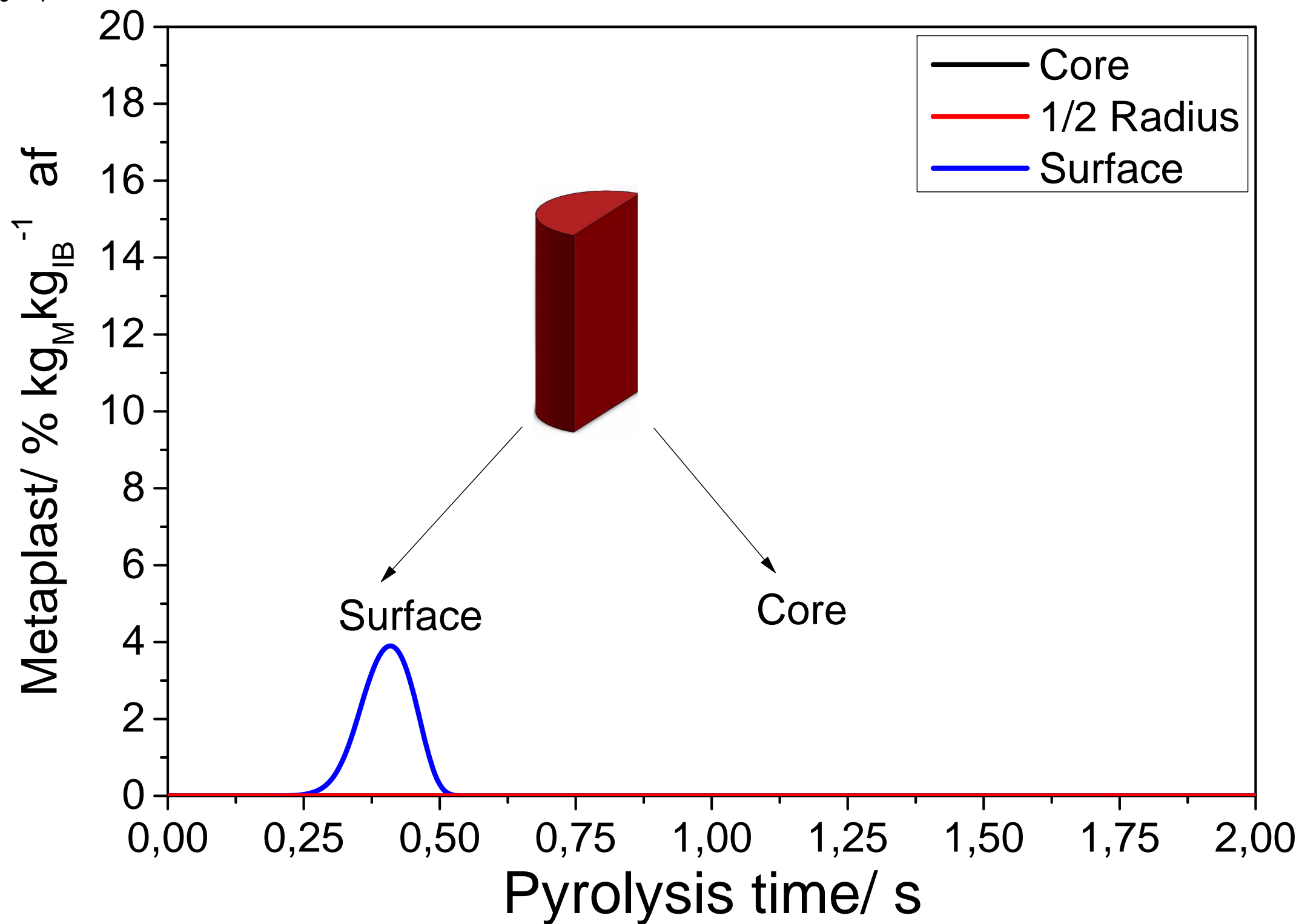


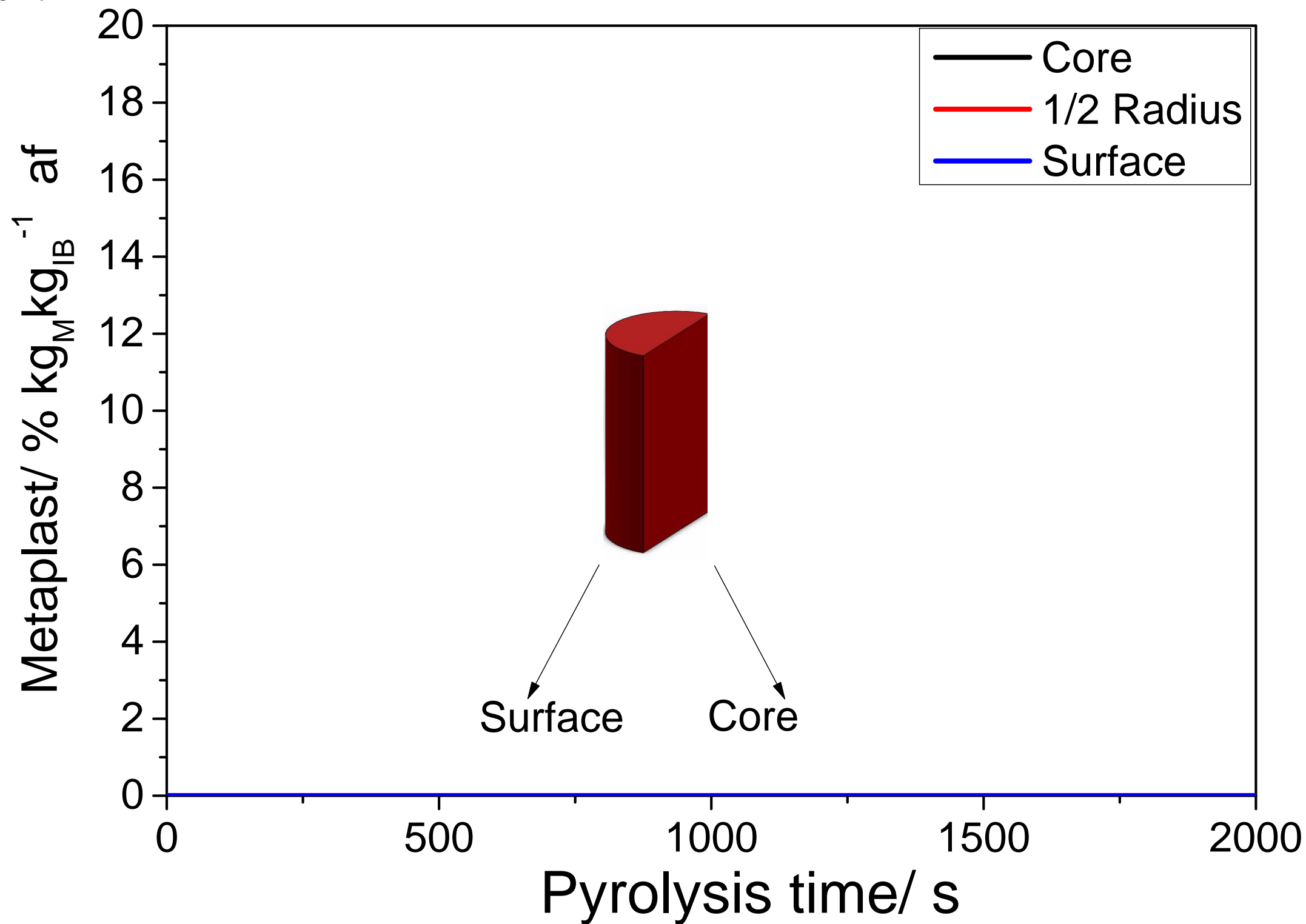


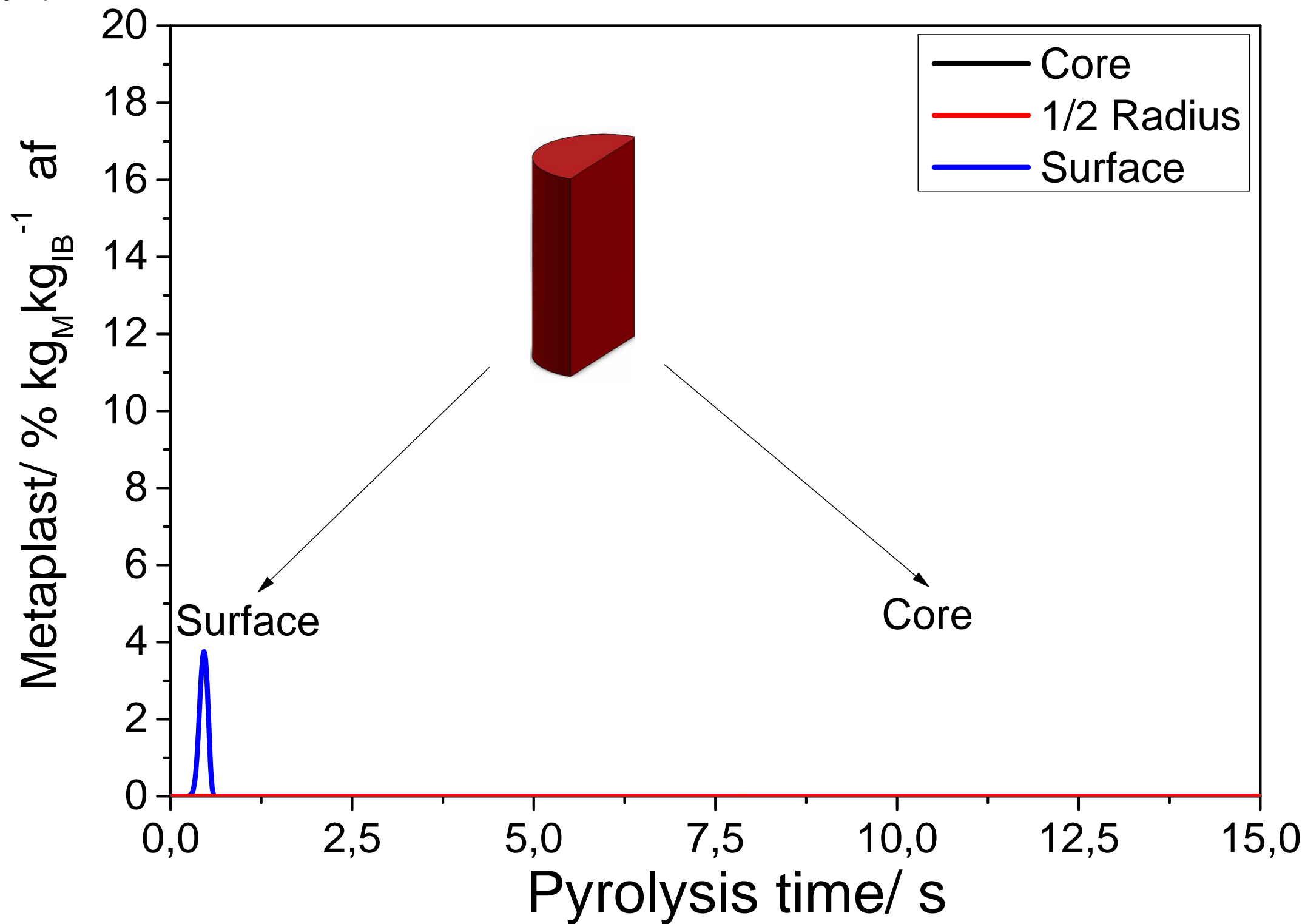


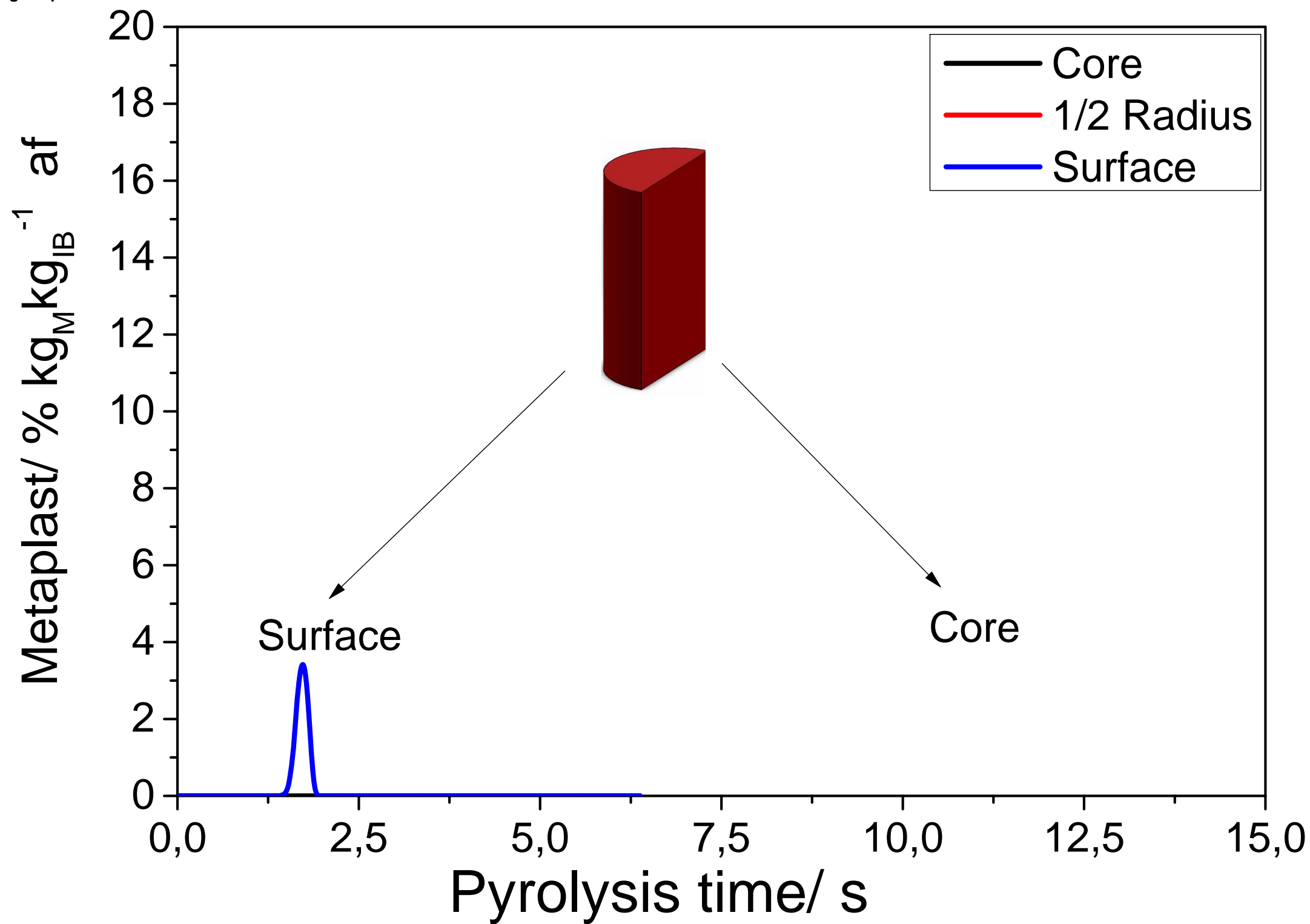


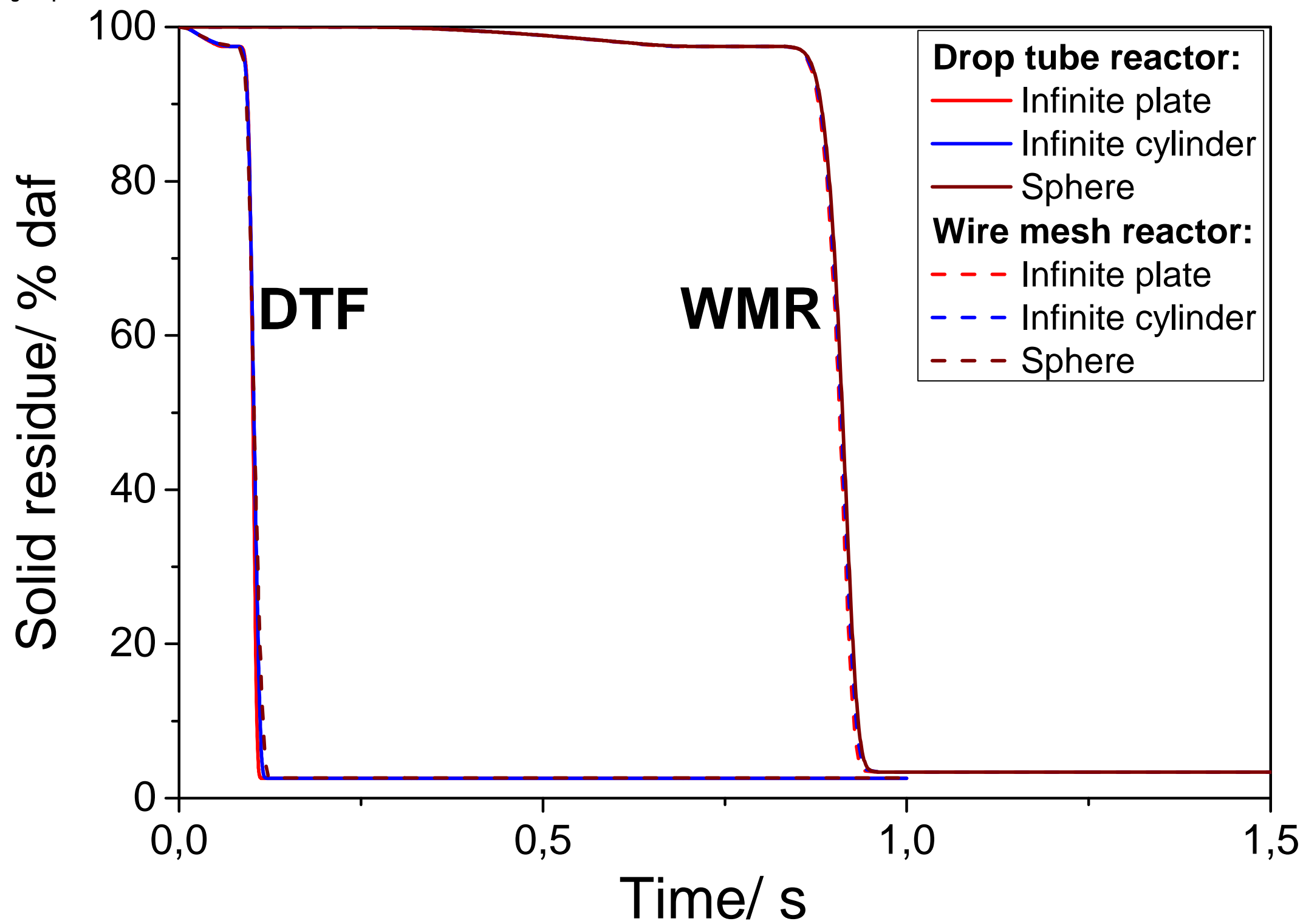


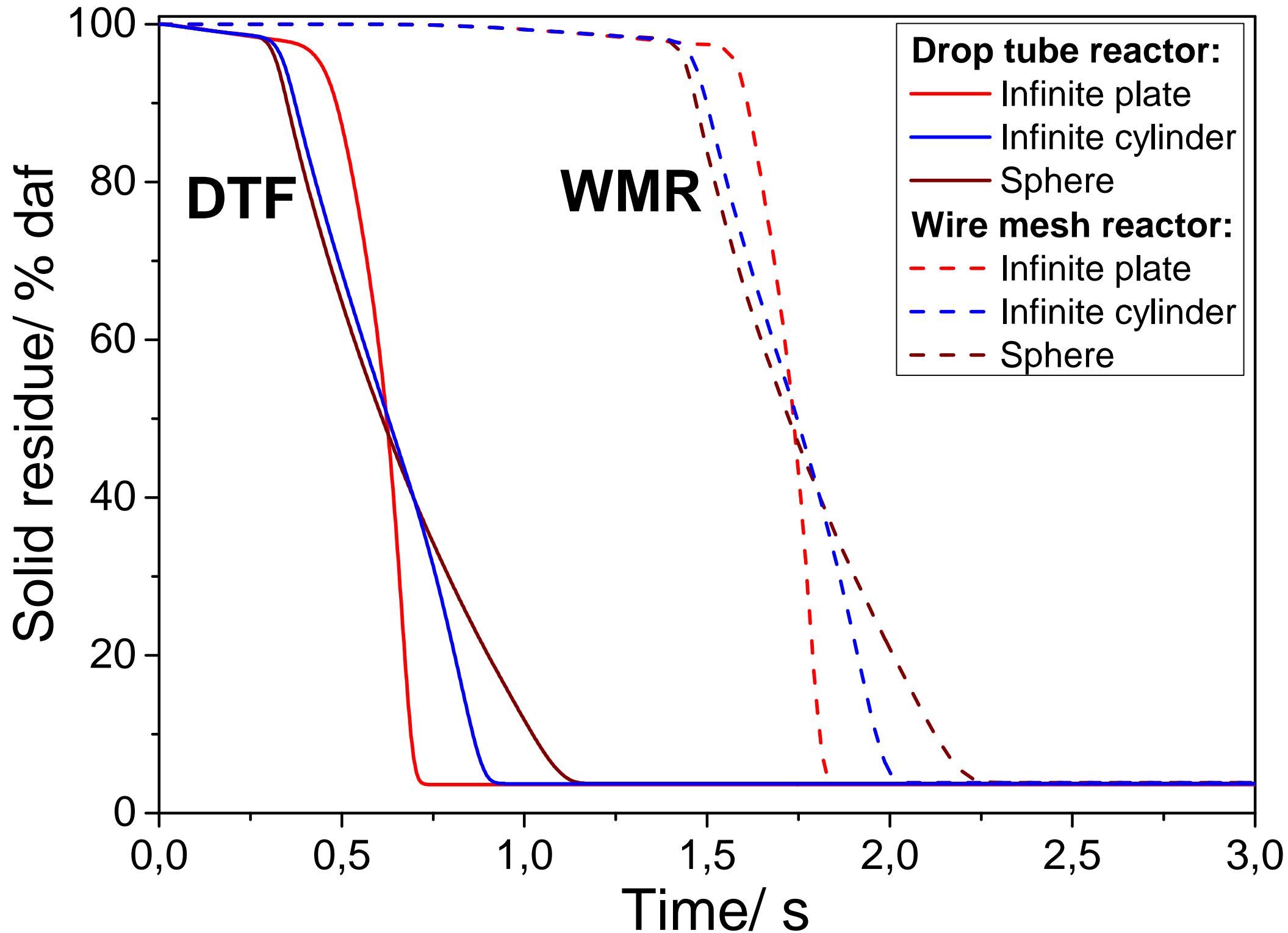


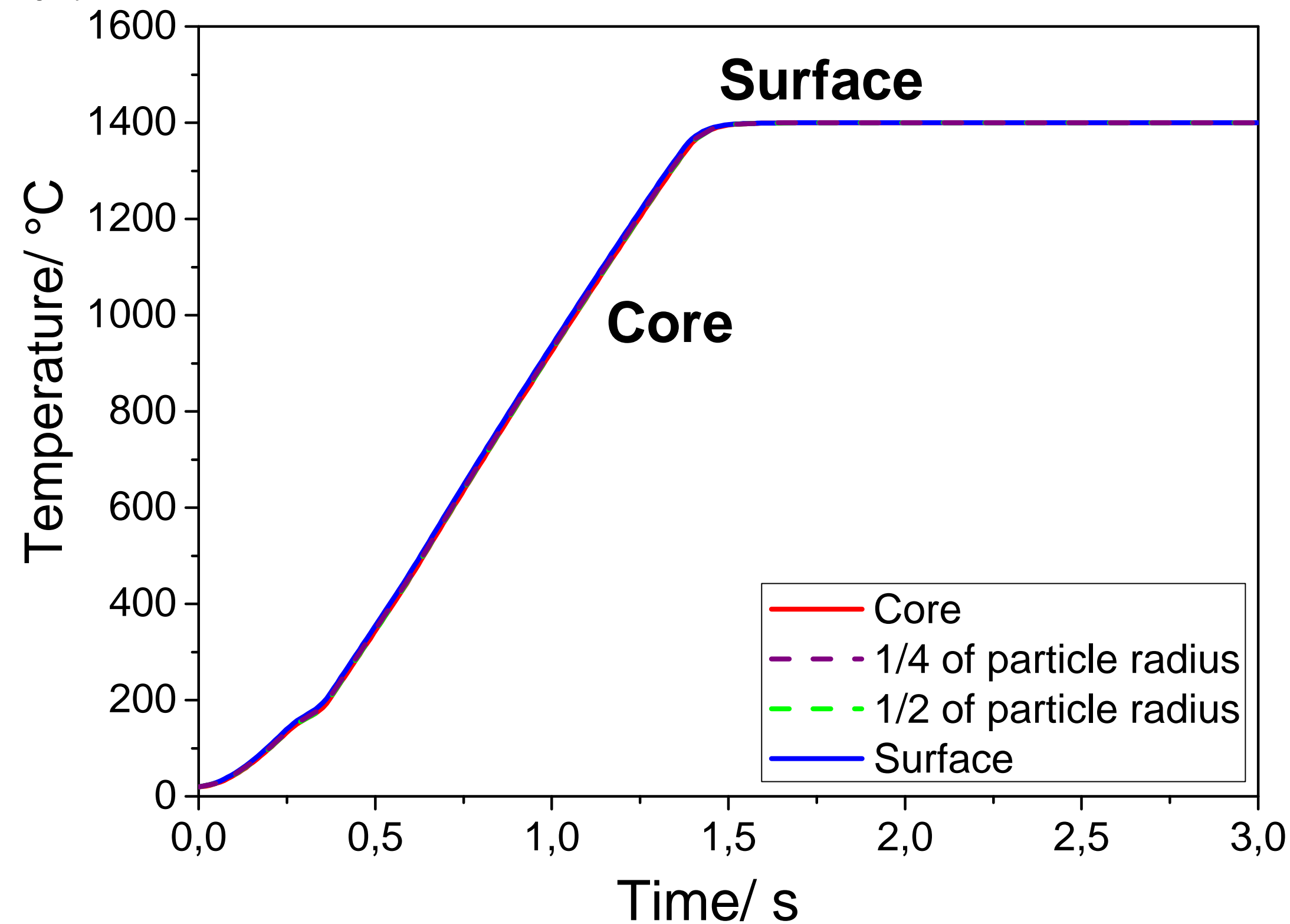


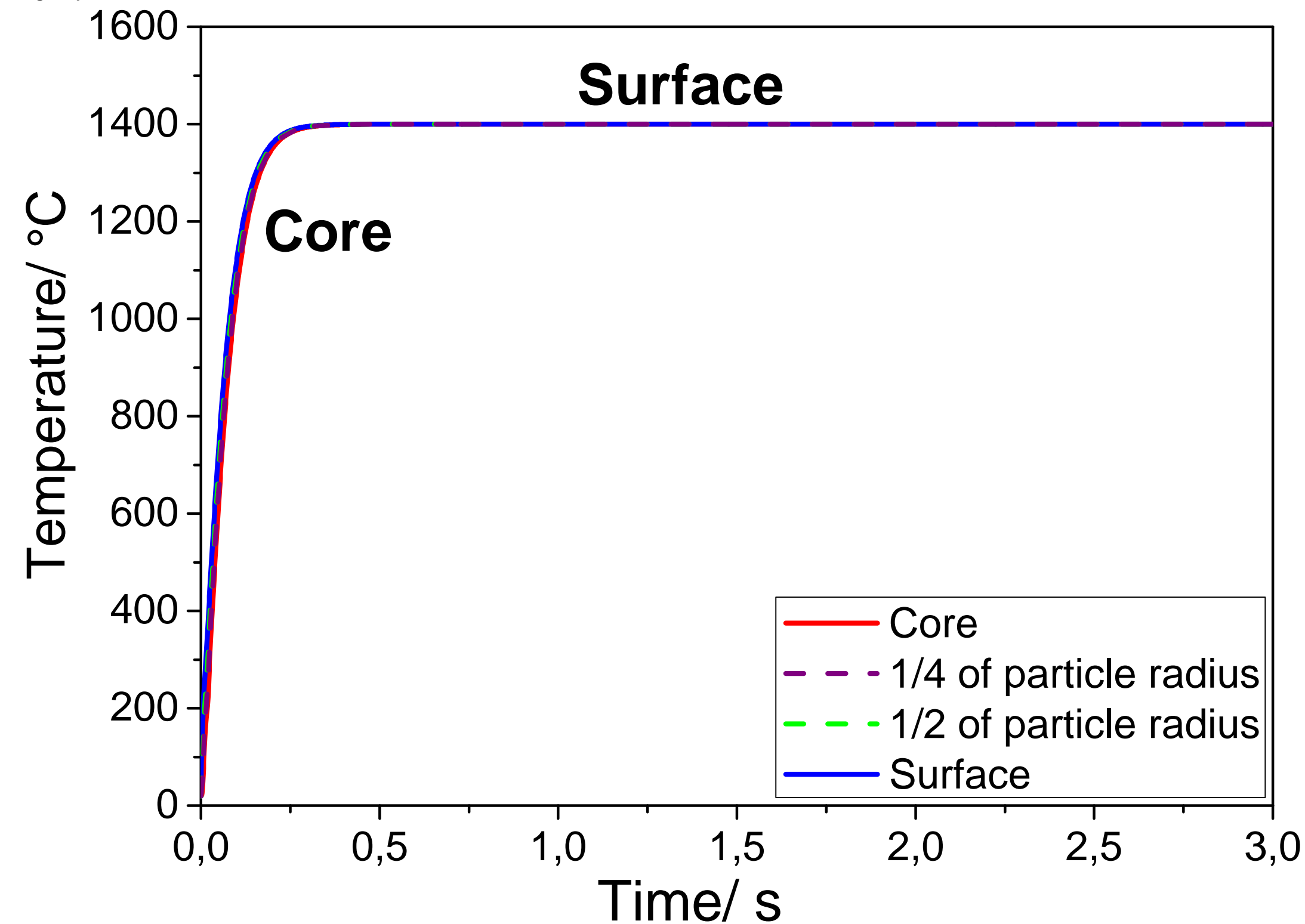


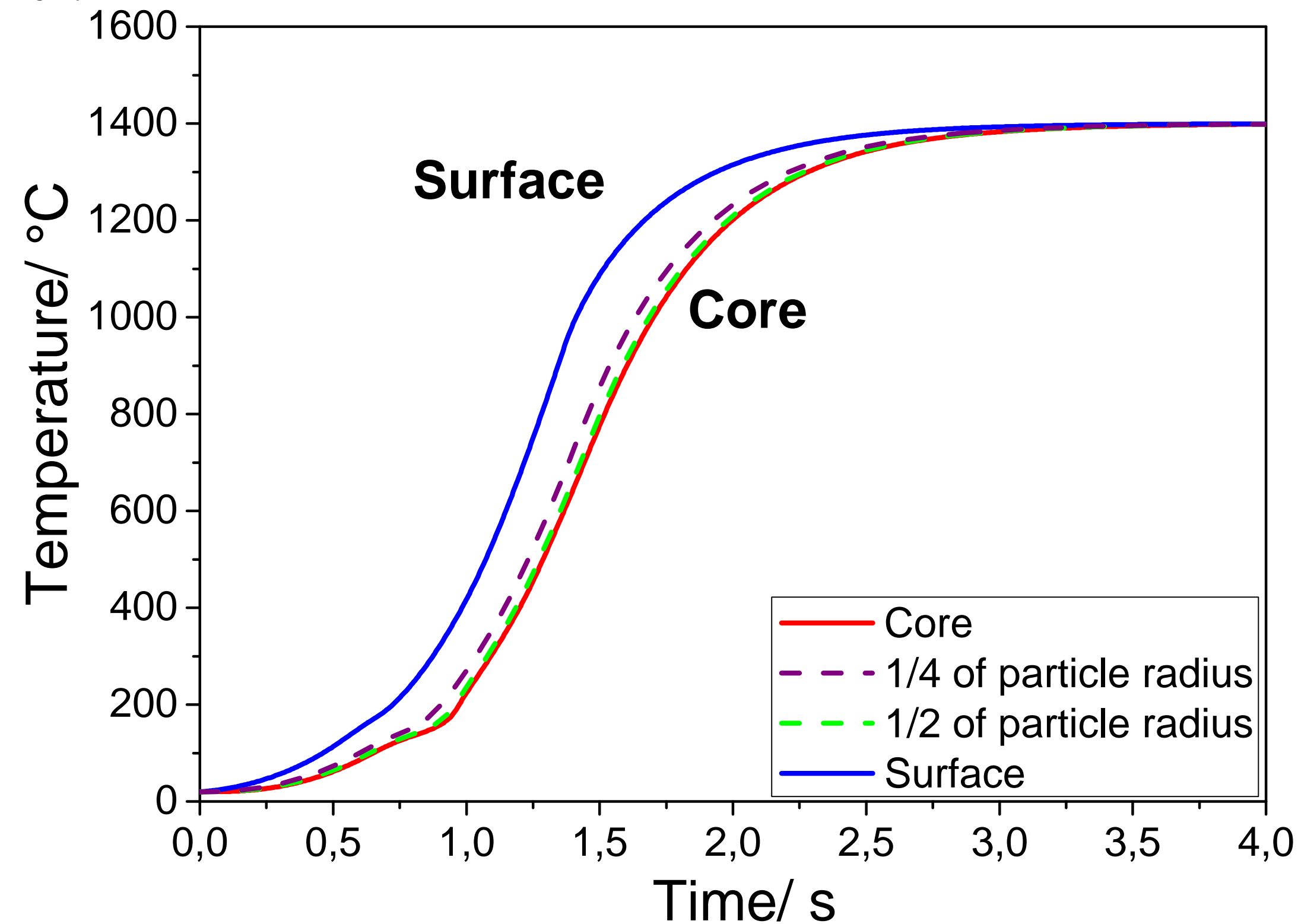


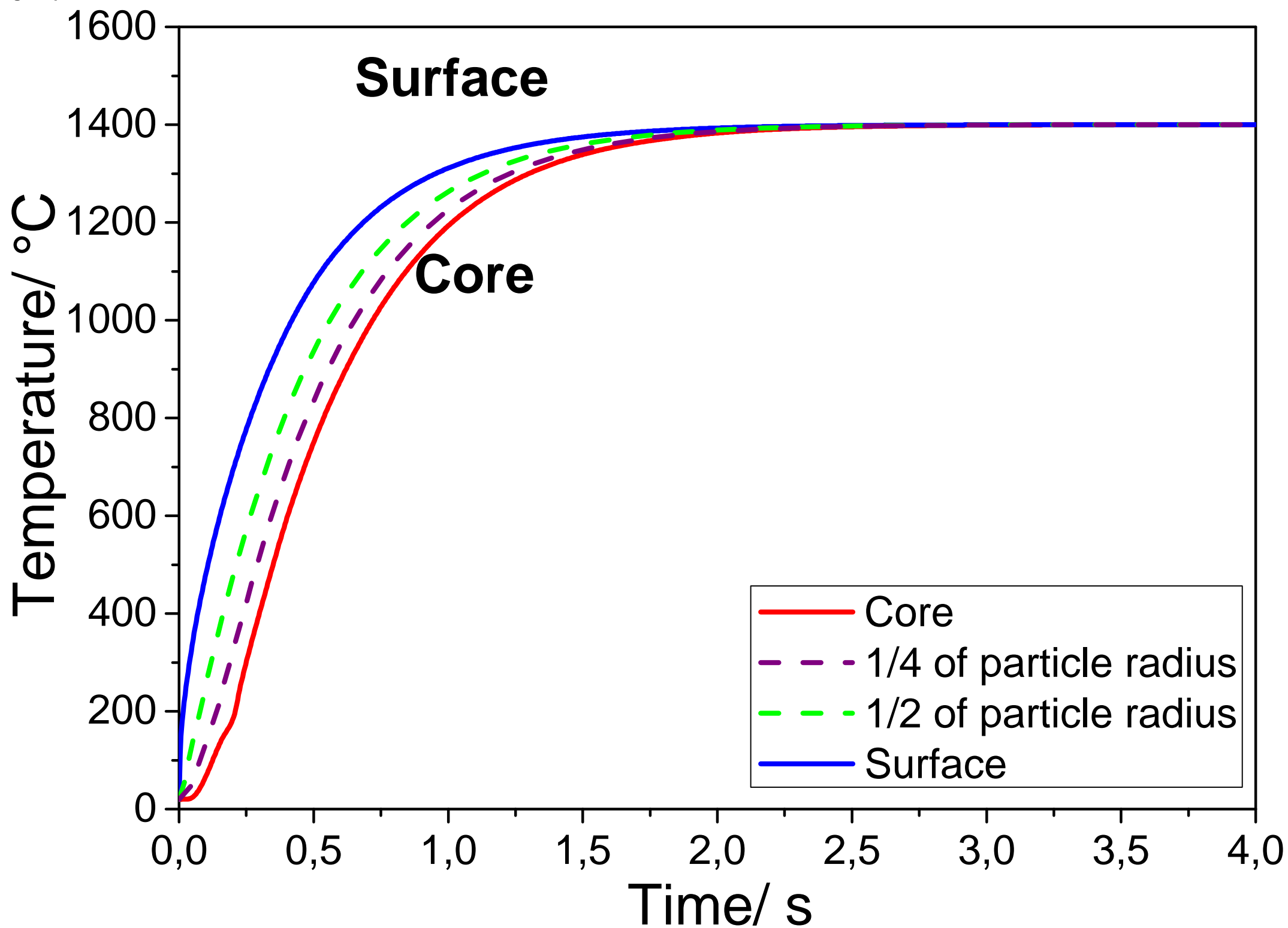


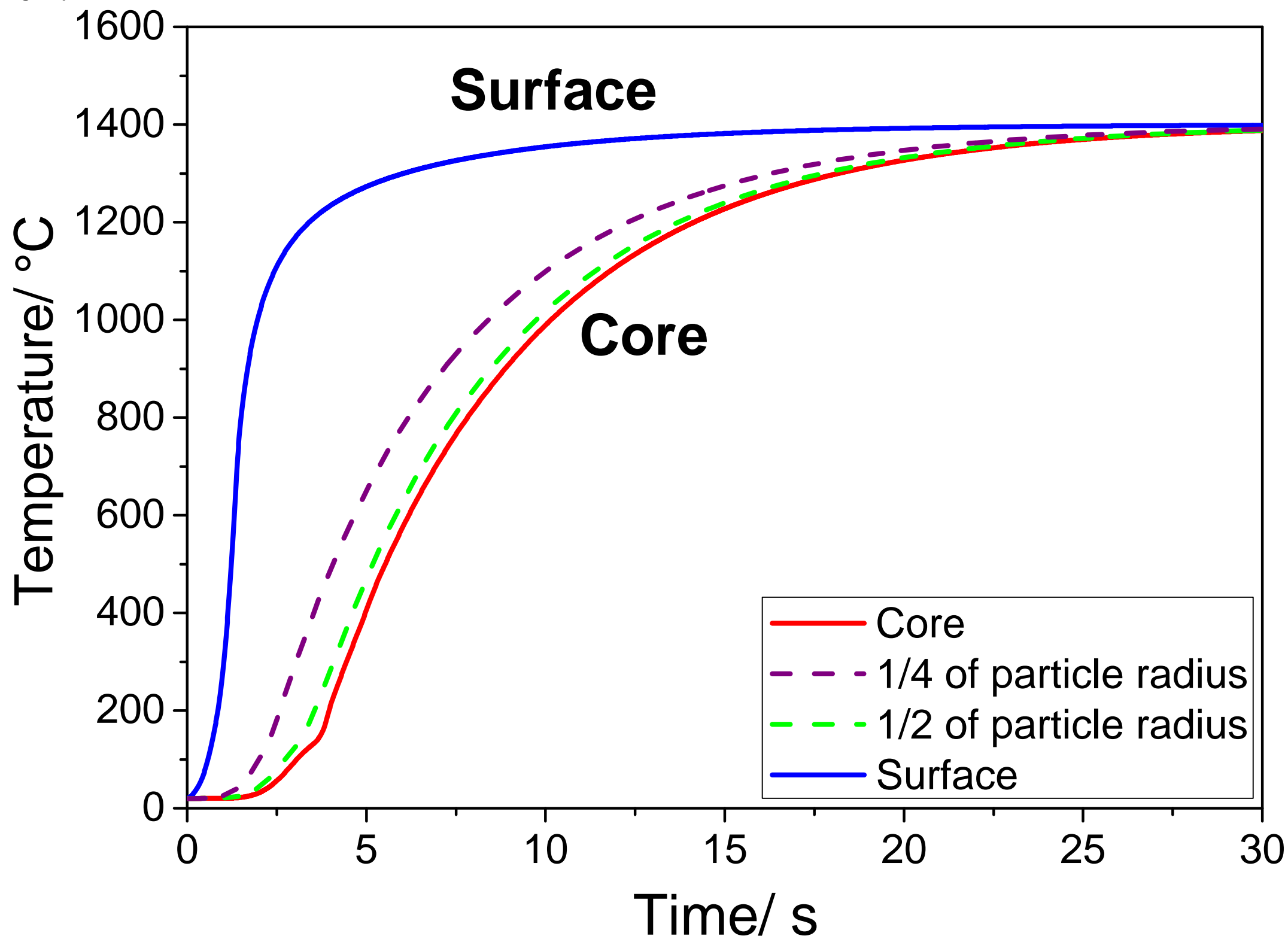


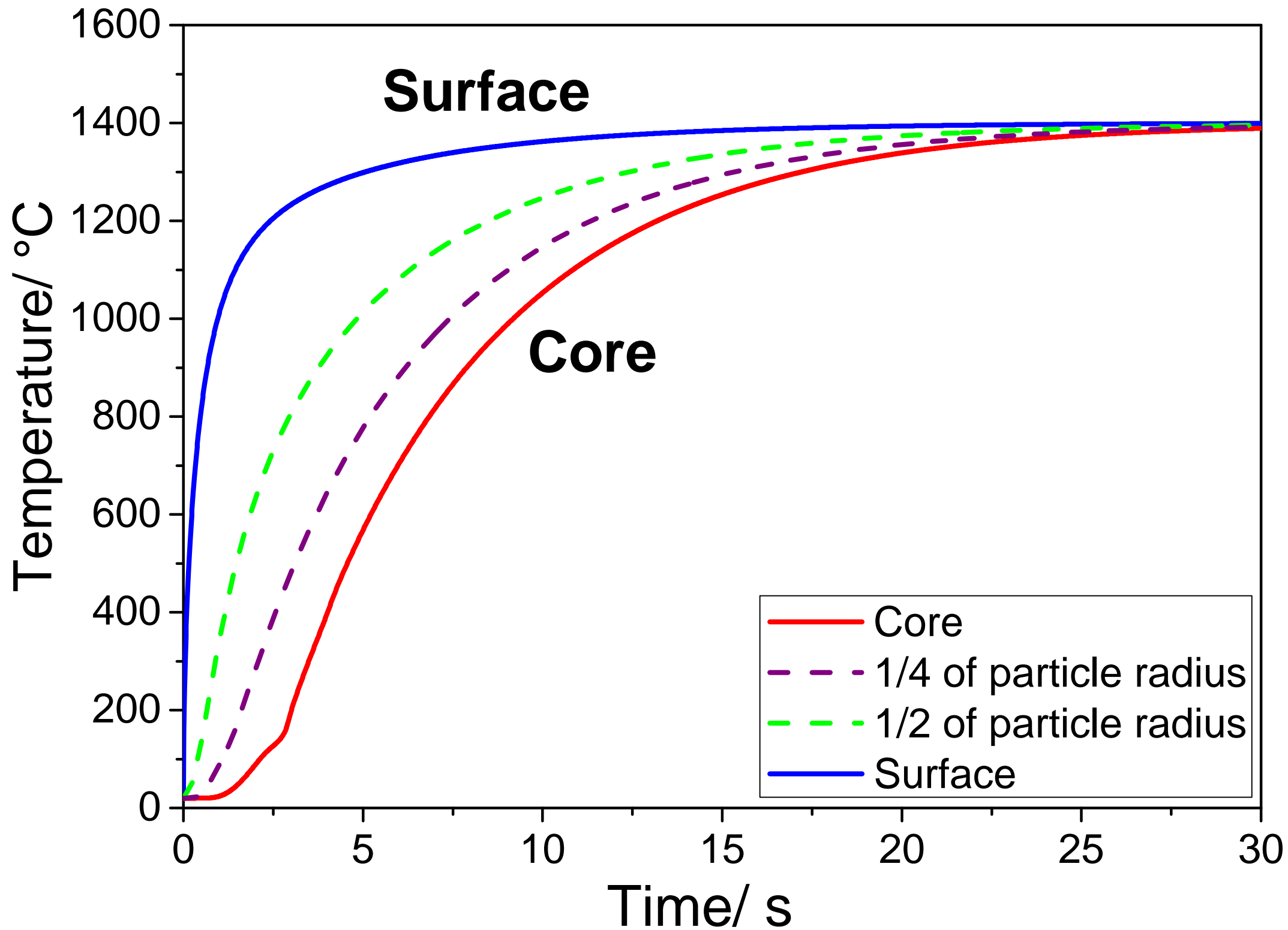


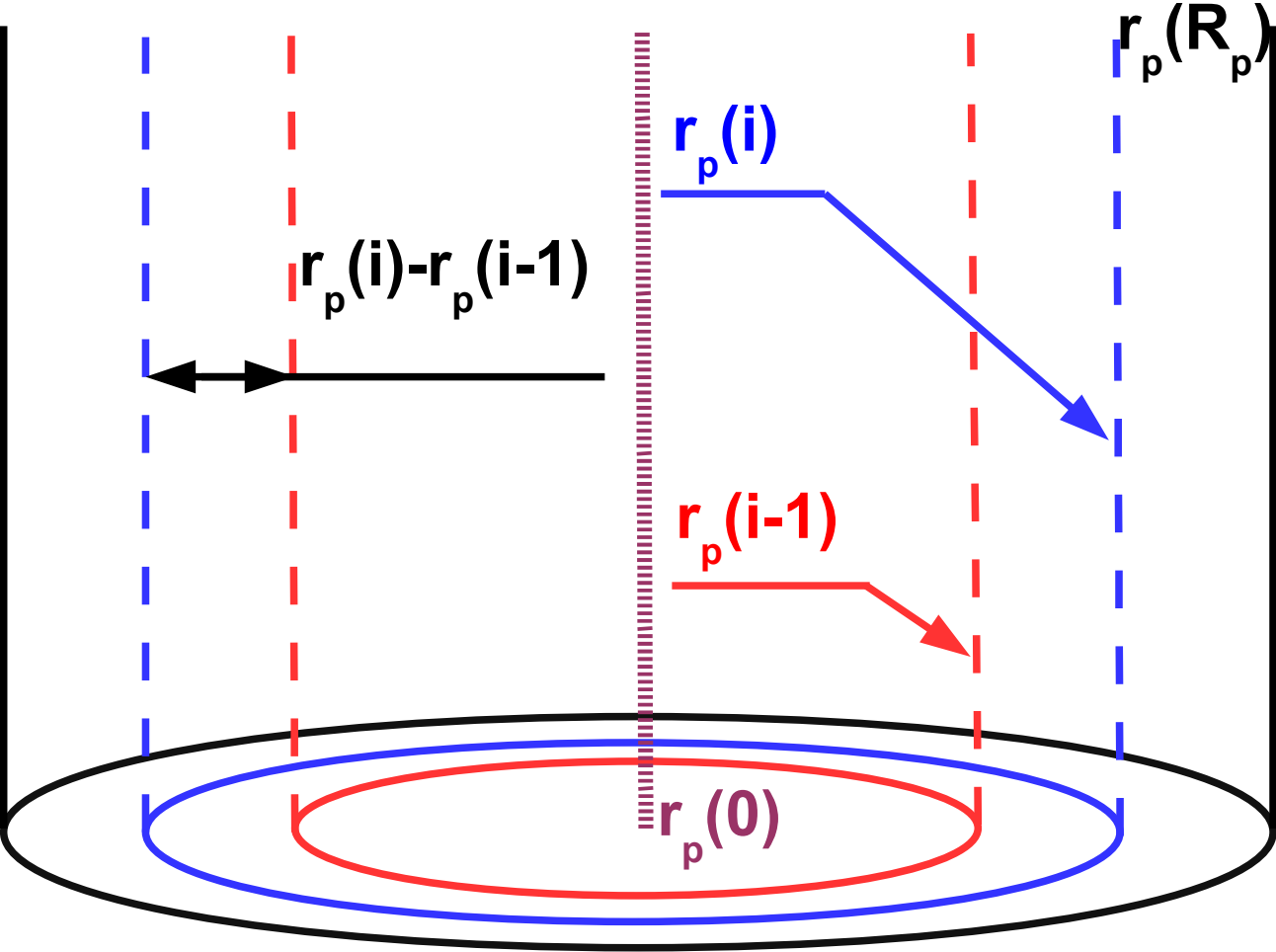


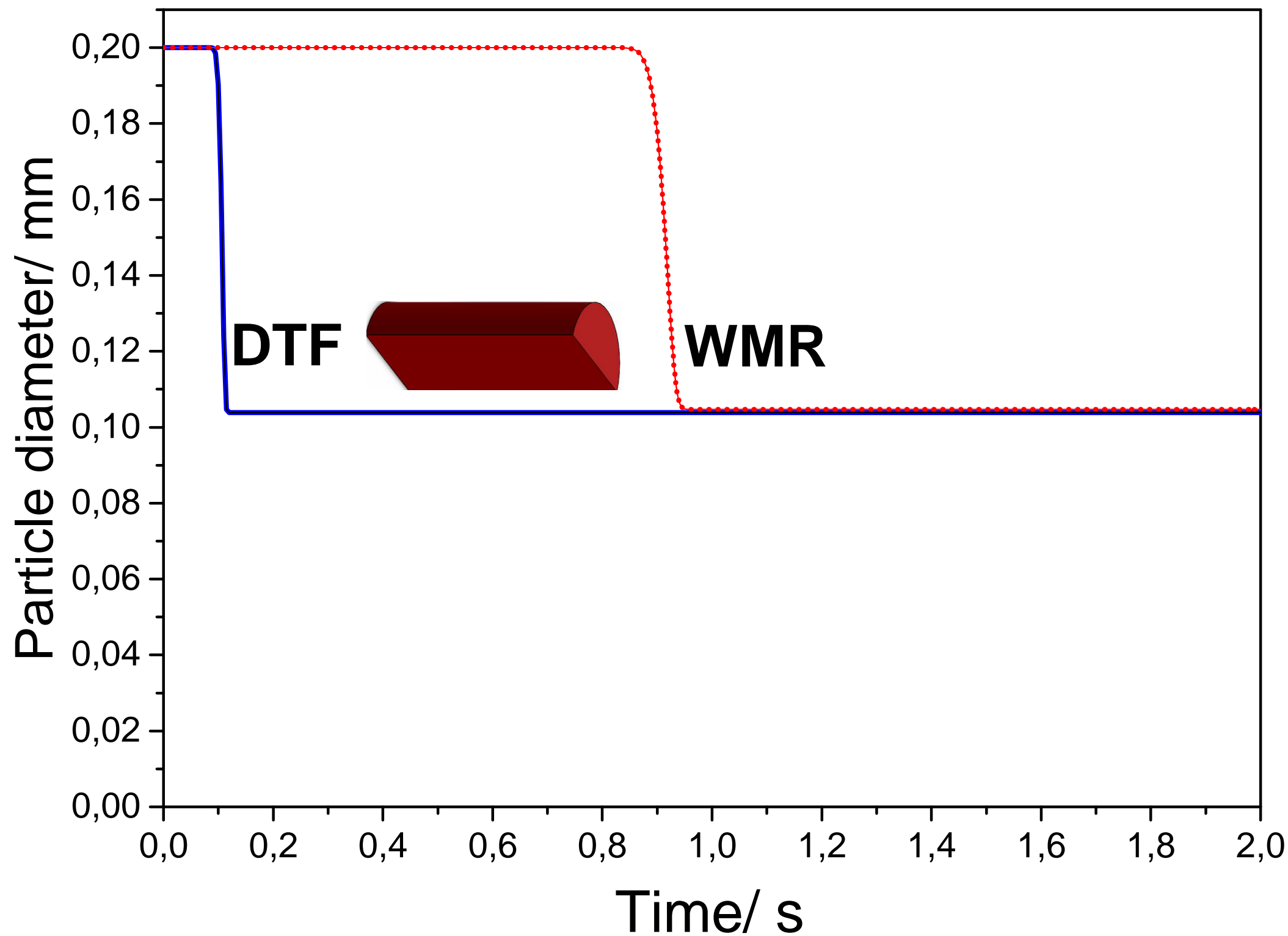


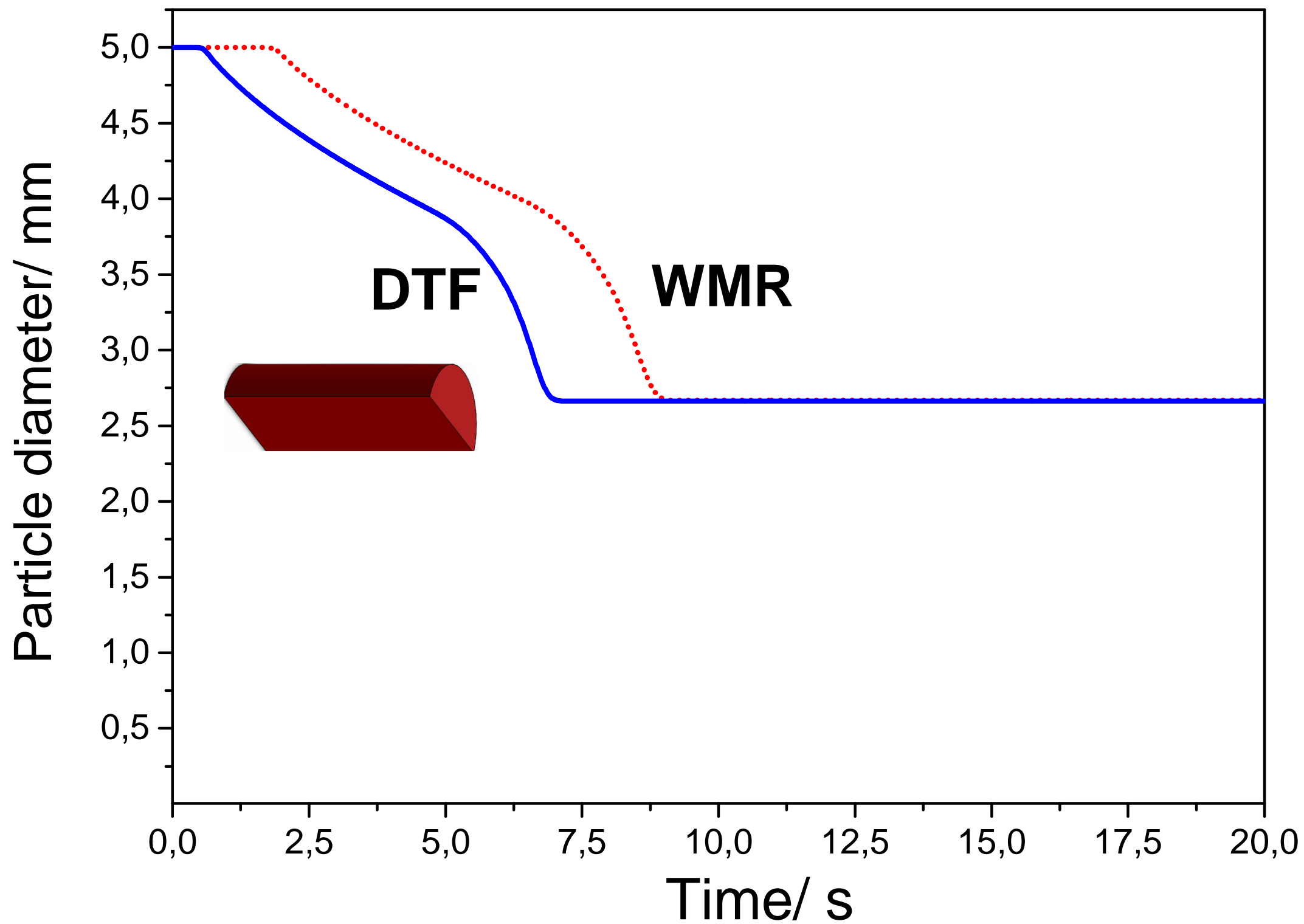




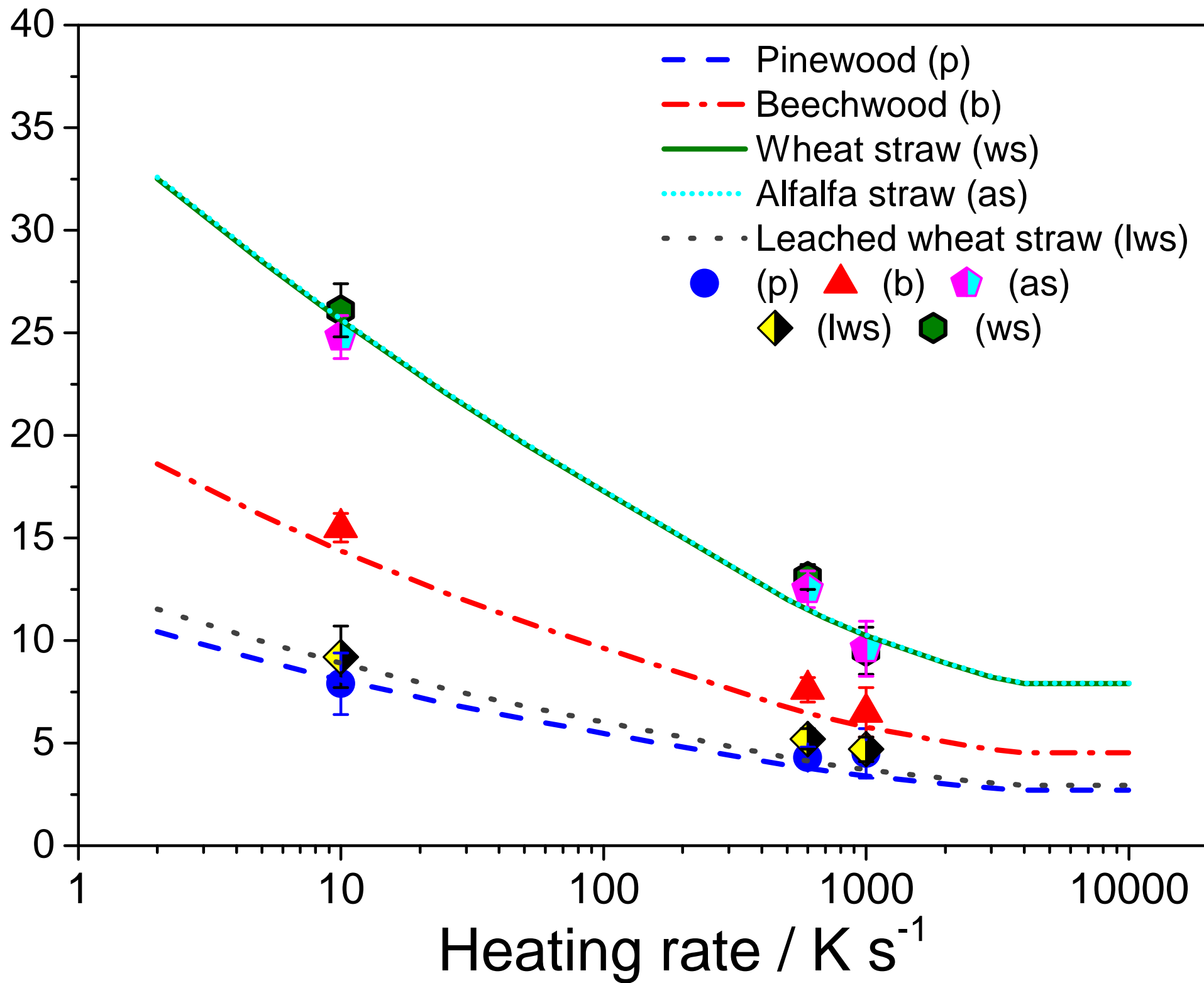








Solid residue/ % daf



Solid residue/ % daf

