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Yong Tian, Patrick Perré

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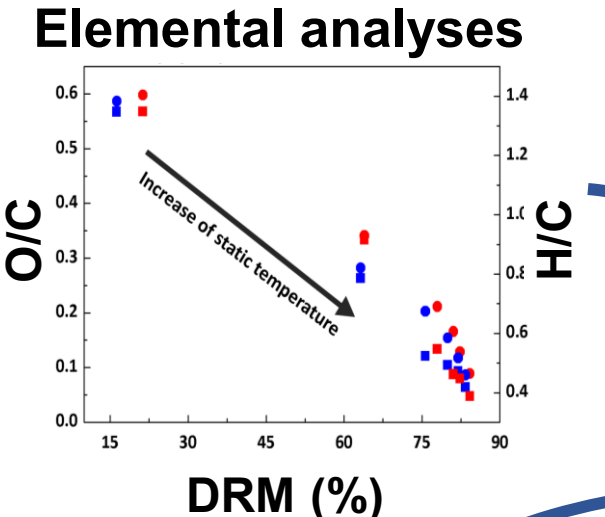
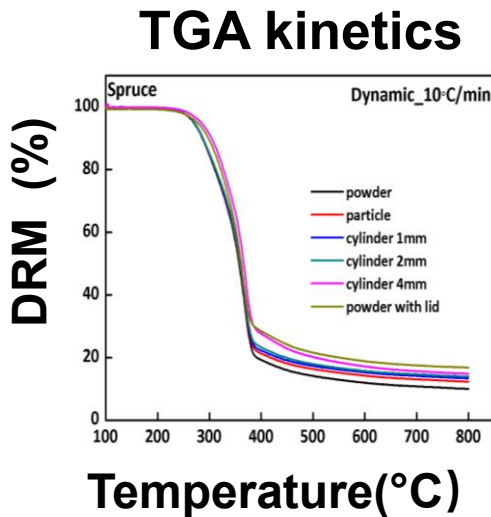
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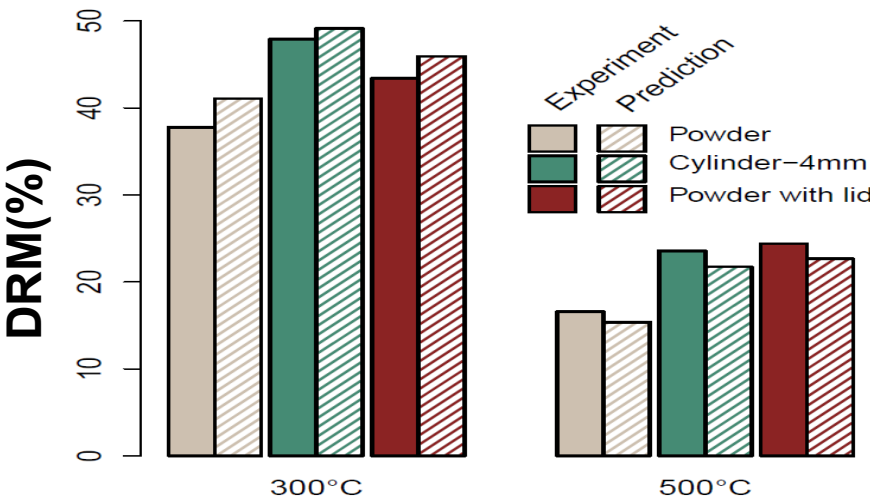
Experiments with different particle sizes

Learning database with **dynamic tests**

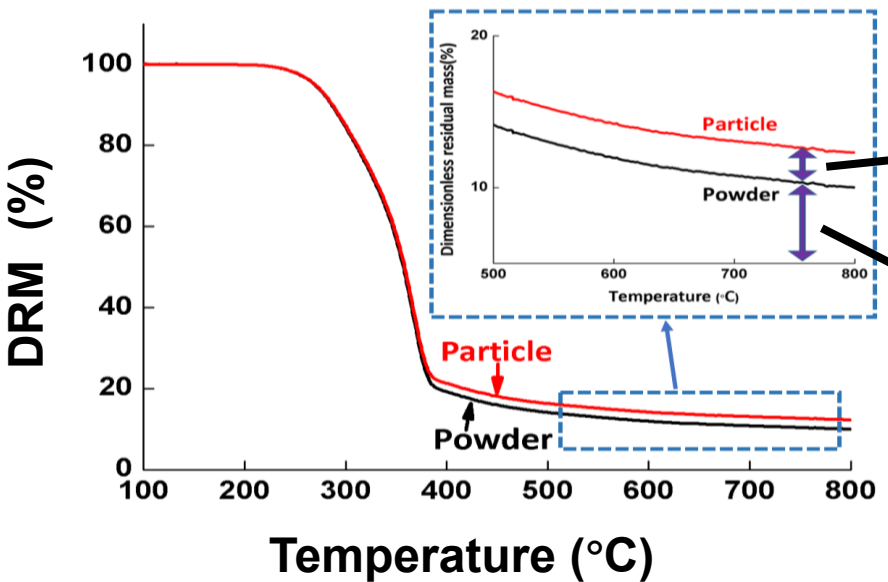
Validation database with **static tests**



DAEM modelling
2 Gaussian + 1 exponential distributions



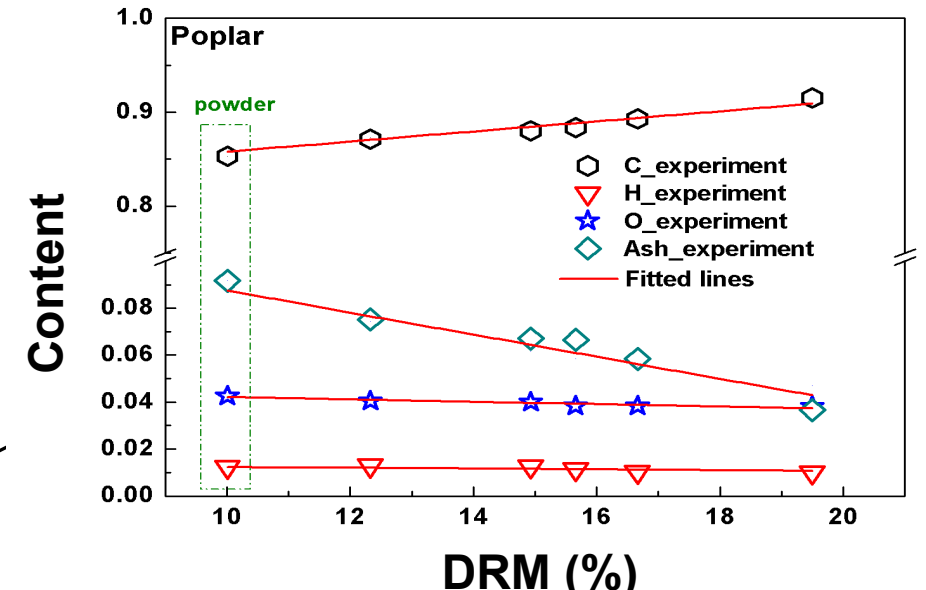
Prediction of kinetics differences



Prediction of elemental composition

Secondary charring
(mainly carbon)

Powder
C, H and O = functions of DRM



Highlights:

- (1) Multiple sample geometries revealed effects of particle size on char formations
- (2) A negative carbonization / mass loss correlation occurred while increasing particle size
- (3) Synthetic indexes built from model parameters depicted kinetic differences
- (4) Model's prediction ability regarding particle sizes was validated
- (5) Strategy proposed to predict char compositions for a given size at any temperature-time pathway

1 **Effects of particle size on the pyrolysis of spruce and poplar:** 2 **thermogravimetric analyses, DAEM modelling, validation, and** 3 **prediction of secondary charring**

4 Yong TIAN^{a,b*}, Patrick PERRÉ^{a,b}

5 ^a LGPM, CentraleSupélec, Université Paris-Saclay, 3 Rue Joliot Curie, 91190 Gif-sur-Yvette, France

6 ^b LGPM, Centre Européen de Biotechnologie et de Bioéconomie (CEBB), 3 Rue des Rouges Terres, 51110,
7 Pomacle, France

8
9 *Corresponding author.

10 E-mail address: tianyong_2021@126.com (Yong TIAN), patrick.perre@centralesupelec.fr (Patrick Perré)

12 **Abstract:**

13 Particle size plays a crucial role in biomass pyrolysis mechanisms and their subsequent
14 industrial uses. However, an applicable kinetic method that combines thermogravimetric data
15 with distributed activation energy model (DAEM) adapted to the sample size is still missing.

16 This work investigated pyrolysis kinetics of two wood species (spruce and poplar) with five
17 particle shapes (powder, particle, 5-mm diameter cylinders with heights of 1 mm, 2 mm, and
18 4 mm) and one additional reaction condition (powder with lid). The experimental data were
19 numerically simulated by two Gaussian + one exponential DAEM distributions.

20 Thermogravimetric results evidenced a significant effect of particle geometry on char yields,
21 which increased by 81% and 66%, from powder to 4-mm high cylinders, for spruce and
22 poplar respectively. The increase in particle size and use of a crucible lid led to an increase of
23 exothermic heat. Elemental analysis demonstrated a contradictory relation between

24 carbonization and mass loss, which was explained by secondary charring. Synthetic indexes
25 built from the kinetics parameters of the DAEM model clearly depicts the effect of particle
26 sizes. The prediction ability of the model was checked by further experiments performed at
27 different time-temperature patterns with several particle sizes. Finally, correlations between
28 dimensionless residual mass (DRM) and element compositions allowed us to determine the
29 composition of secondary charring, which consists mainly of carbon. The elemental
30 composition of char can therefore be predicted using the difference of DAEM kinetics
31 between fine powder and a given particle size.

32
33 Keywords: Biomass; Elemental analysis; Particle size; Pseudo-component; Wood.

35 **1. Introduction**

36 Lignocellulosic biomass is an important renewable energy source for the worldwide
37 energy supply. Its large deposits and carbon neutrality offer an enormous potential to meet
38 future energy demands and reduce environmental pollutions [1]. Pyrolysis is part of the
39 thermochemical route to convert biomass into high value-added chemical products: bio-oil,
40 charcoal, and gaseous fuels. It is the initial step before further thermochemical technologies
41 such as combustion and liquification, making pyrolysis a key link in the BtL (biomass to
42 liquid) industrial chain and subsequent exploitation. Process factors including temperature,
43 heating rate, particle size, and residence time could effectively alter product categories and
44 yields [2-4]. Among them, the particle size specifically affects the pyrolysis mechanism in
45 relation to volatile interaction, mass, and heat transport, which imposes strict requirements on
46 industrial reactors [5]. Therefore, both experimental and theoretical kinetic works are
47 necessary to determine and predict the effect of particle size.

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48 A considerable number of studies have been conducted to test the effect of particle
49 size on biomass pyrolysis. As well acknowledged, mass and heat transfer were severely
50 affected in large particles (>1.5mm) during both pyrolysis experiments and modeling [6]. Di
51 Blasi [7] calculated that, in terms of thermal transfer, particle size affects the internal heating
52 rate in fast pyrolysis, which decreased from 760 °C /s to 23 °C /s when the particle diameter
53 was increased from 0.1 mm to 1 mm. Okekunle [8] found the intra-particle temperature
54 gradient increased with particle size and aspect ratio, which promoted intra-particle char
55 formation. Perré and co-workers [9, 10] developed comprehensive computational models that
56 emphasized the effect of particle size or particle beds on the evolutions of the temperature
57 profiles, with opposite effects in the heating period and during the reaction period due to
58 exothermic reactions. A model developed by Anshu [11] claimed more devolatilization delay
59 occurred in larger biomass samples because of intra-particle transfer retardation. Suriapparao
60 [12] and Acma [13] claimed higher apparent activation energy with increasing particle size
61 due to mass transfer limitation and the intra-particle thermal gradient.

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62 It was well-accepted that the increasing non-isothermal processes in large particles led
63 to low oil and high char yields [14, 15]. Shen [16] postulated that a decreased heating rate in
64 large particles was primarily responsible for lower bio-oil yield, and the fiber destruction in
65 small particles favored high oil yield. Ayhan [17] observed the reduction in char yield when
66 imposing high heating rate in small particles. Zhou [18] proved that physical trapping of
67 thermally ejected oligomers occurred as a function of particle size, from milled particles (0.3–
68 0.55 mm) to cylinders (3–14 mm). Westerhof [19] argued that physical retainment of vapors
69 or aerosols caused excessive volatile condensation in large particles and cylinders.

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70 With an increase in particle size, the added cellular- and tissue-scale barriers have an
71 increasing impact on pyrolysis [20]. More specifically, their effects originated from two parts:
72 (1) different degrees of destruction of fiber structures in milled particles; and (2) different

73 dimensions in an integral cylinder or chip. In the first scenario, milled samples lose most
74 typical wood channel structures. Small particles usually impose less resistance on both heat
75 and mass transfer profiles due to their microstructures; tissue expansion and lumina cell wall
76 stretch are therefore less restricted [20], leading to easier volatile release. For the second
77 scenario, geometry differences in cylinders cause hermetic spaces and anisotropic channels
78 that can obstruct internal volatilization to varying degrees, and the vapor outflow pattern is
79 largely affected by internal heat transfer limitations [19]. The increase of particle size, in this
80 case, delays volatile's escape inside the material matrix and offers additional possibilities for
81 secondary charring. Moreover, axial conductivity values have been found to be three times
82 larger for thermal transfer and fifteen times larger for mass transfer than their corresponding
83 radial conductivity values [21], larger anisotropic degree in the cylinder leads to significant
84 temperature gradients and flow gradients, generally causing volatile blockage and char
85 generation [22].

86 Particle size clearly linked with the extent of secondary reactions, which usually occur
87 in two competitive pathways: charring and cracking, causing carbon deposition and gas
88 production, respectively. As long residence time of volatiles in high-temperature zone favors
89 polymerization and carbonization, the reduction of heating rate inhibits the complete
90 vaporization [23], and high pressure stimulates carbonization by concentrating the vapor
91 phase [24]. All these process parameters help secondary charring prevail over cracking.
92 Meanwhile, other factors such as chemical compositions, density, and the presence of
93 inorganics (alkali metals) also influence charring reactions by different mechanisms [25, 26].
94 In contrast, secondary cracking converts volatiles into small molecular gases, which normally
95 accompanies with short residence times, high heating rates, or dilute vapor phases [27].
96 Regarding the main constituents of biomass, hemicellulose undergoes charring through
97 rearrangement reactions of polysaccharides and further demethylation [28]; cellulose

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98 undergoes secondary charring by the oligomerization of primary pyrolysis product:
99 levoglucosan [29]; lignin is a fine charring precursor due to its original high aromatic ring
100 content, whose short substitutes cleaves increase the aromaticity and reticulation in the
101 residue over the temperature range of 500–800 °C [28].

102 It is worthwhile to investigate the effect of particle size from the angle of kinetic
103 models, which can be potentially applied in complicated multi-scale simulations and
104 operational controls in industrial processes [30]. The DAEM is an efficient and robust
105 approach to represent the kinetics of complex decomposition reactions [31], and at present, is
106 widely used to model the biomass pyrolysis [32, 33]. The model assumes that biomass
107 pyrolysis occurs as a series of independent and parallel reactions with continuous activation
108 energy distributions, representing the variability of interactions due to complex
109 macromolecular structures and their interactions in the cell wall [34]. Three-parallel-
110 distribution DAEM presents an even more accurate approach to the description of the
111 pyrolysis kinetics of various lignocellulosic biomasses [35-37], and the interpretation of
112 pseudo-components as chemical constituents (hemicellulose, cellulose, and lignin) is justified
113 as a useful method in kinetic research [38-40]. The kinetic additivity of the three main
114 constituents provides universal applicability for various biomass species [41], being crucial
115 for single-particle reaction kinetics as well as large-scale process implementations. However,
116 the nature of devolatilization theory in the DAEM formulation makes it difficult to account
117 for recondensation and secondary charring reactions among different particle sizes or shapes.
118 To our best knowledge, DAEM has rarely been applied to distinguish the effects of particle
119 size; furthermore, the three-distribution DAEM has never been employed to distinguish the
120 kinetics of different particle sizes. The two Gaussian + one exponential DAEM was recently
121 proved to be very efficient in handling multiple temperature profiles and complex heat fluxes,

122 including at the validation stage [42]. Hence, this model was applied in the present work to
123 analyze the pyrolysis kinetics of different particle sizes.

124 This study aims to investigate the effects of particle size by coupling thermogravimetric
125 kinetics and numerical methods. Thermogravimetry (TG) and differential scanning
126 calorimetry (DSC) will be performed at two heating rates for a wide range of particle sizes.
127 Elemental analyses will demonstrate that the relation between carbonization and mass loss is
128 directly linked to the particle size. Further, Synthetic indexes will be built from the kinetics
129 parameters of the three-distribution-DAEM model to clearly depict the effect of particle sizes.
130 Importantly, the prediction ability of the model will be validated using an additional set of
131 experiments performed with different temperature pathways: a linear increase of temperature
132 followed by a plateau at constant temperature (different temperature levels will be
133 performed). Finally, correlations between mass loss (ML) and element compositions will
134 allow us to determine the composition of secondary charring. This composition will be used
135 to predict the elemental composition of char for a given particle size.

137 **2. Material and methods**

138 **2.1 Material**

139 One gymnosperm and one angiosperm species were used in this study: European spruce
140 (*Picea abies*, softwood, 450 kg/m³, cut from a 73-year-old tree grown in the forest in the
141 Auvergne region, France) and poplar (*Populus euroamericana* ‘Koster’, hardwood, 364
142 kg/m³, cut from a 25-year-old tree grown in the forest in La Suipe Valley in la Marne,
143 France). The complete sample preparation protocol is depicted in Figure 1. Second-bottom
144 tree logs (2 m long, cut at 2 m high above the ground) of 40–50 cm diameter were used. They
145 were cut evenly into 2.5 cm-thick boards, and the one 10 cm from the pith was taken for the

146 present study. Rectangular sticks of 2.5 cm × 2.5 cm × 20 cm (length × width × height) were
147 cut from a healthy sapwood part of the board to ensure uniform properties. The stick was
148 further processed into cylinders with a diameter of 5 mm and a length of 3 cm by a lathe
149 (PROMAC 961V), then cut into regularly shaped cylinders by a precision cut-off machine
150 (Struers, Secotom-15) with two successive sequences of 1 mm, 2 mm, and 4 mm. The rest of
151 the stick was ground with an M20-IKA universal mill, then put into sieve stacks of 0.063 mm,
152 0.08 mm, 0.63 mm, and 0.8 mm opening sizes on a vibratory sieve shaker (RETSCH AS 200)
153 at 90% amplitude for 30 minutes. The sieving cut between 0.063–0.08 mm was taken as wood
154 powder, and the cut between 0.63–0.8 mm was taken as wood particles. The strict protocol
155 defined here intended to limit any difference in composition between all types of samples and
156 to constrain the size of the small particles. Therefore, it was reasonable to assume that
157 differences in pyrolysis behavior were derived exclusively from the particle geometry. After
158 the preparations, all samples were dried at 105 °C in an oven for 24 h and stored in a
159 desiccator.

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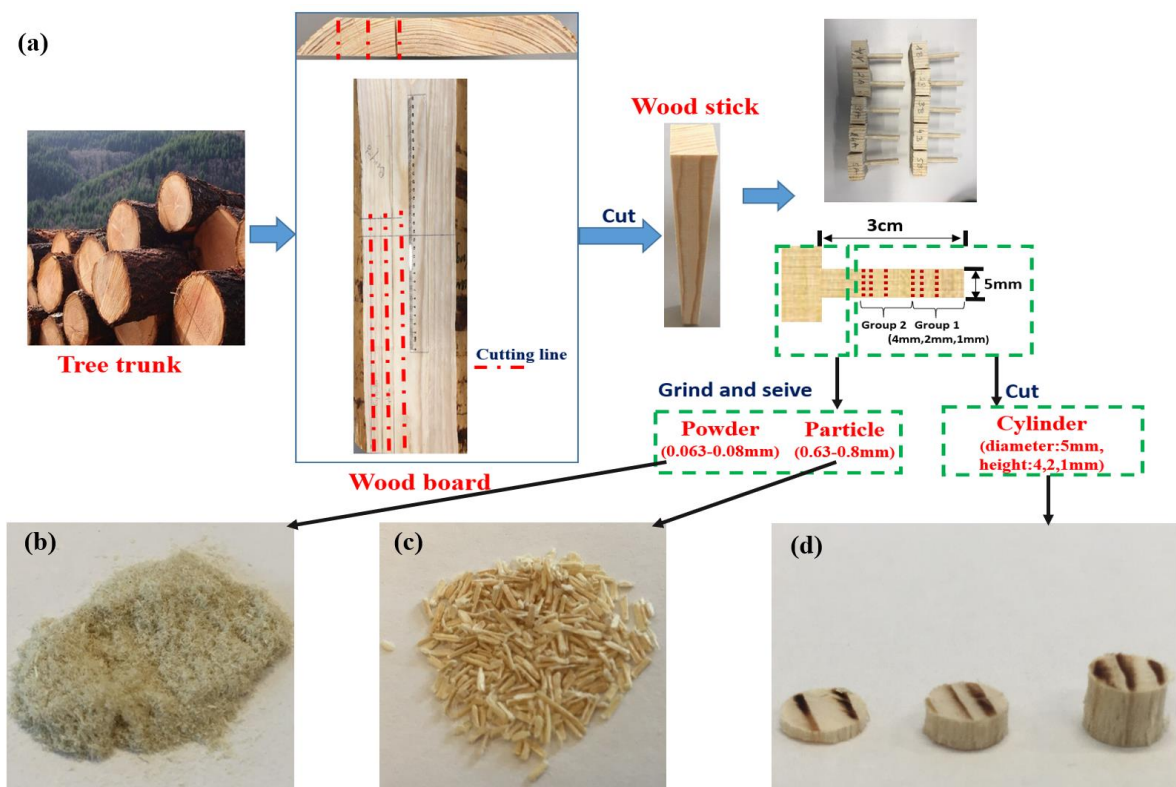


Figure 1. (a) Flow chart of the preparation protocol of the wood samples; and pictures of three scales of samples (using spruce as an example): (b) powder, (c) particles, and (d) cylinders.

Ultimate and proximate analyses were conducted in a Thermo Fisher Scientific FLASH 2000 organic elementary analyzer and a Nabertherm LV/9/11 furnace, respectively, by the standards ASTM E1755 and E872. The basic chemical properties of two types of wood on a dry basis are shown in Table 1.

Table 1. Proximate and ultimate analysis of spruce and poplar

Biomass type	Proximate analysis (wt.%)			Ultimate analysis (wt.%)		
	Volatile	Ash	FC	C	H	O
Spruce	84.93	0.29	14.78	47.07	5.97	43.65
Poplar	86.29	0.37	13.34	48.06	5.95	43.76

171 All samples' microstructures had been visualized (photos could be found in supporting
172 material). Powder and particles were analyzed by environmental scanning electron
173 microscopy (ESEM, FEI Quanta electron microscope), and cylinders were examined using
174 3D X-ray tomography (RX Solutions EasyTom XL Ultra 150-160) with a spatial resolution of
175 3 μ m. For both spruce and poplar, the differences in microstructure between the different
176 particle sizes were obvious. As shown in the Supplementary Figure 1, the powder presented
177 broken, fragmented pieces, with damaged lumens and inner cell wall structures were largely
178 exposed. Particle samples preserved the cellular structure of wood: cells retained partial intact
179 structures and exposed lumens at the edges. As expected, wood cylinders maintained the
180 original anatomical structure of wood. Spruce, despite obvious annual rings, had a uniform
181 anatomical pattern that consisted mainly of tracheids. As a diffuse ring-porous hardwood,
182 poplar presented two contrasting sizes of pore: vessels and fibers.

183

184 **2.2 Experimental method**

185 Wood pyrolysis was carried out in a thermogravimetric analyzer (STA 449 F3 Jupiter,
186 NETZSCH). Thermal gravimetric (TG) and differential scanning calorimetry (DSC) signals
187 were simultaneously acquired at a time interval of 0.1 min. Measurements were conducted
188 under a nitrogen purge (99.999%) of 50 ml/min and a protective gas flow of 20 ml/min.
189 Dynamic tests at two heating rates (1 °C/min and 10 °C/min) were applied for all wood
190 samples. The program began by heating the sample from 30 °C to 100 °C at 10 °C/min and
191 was held for 30 minutes to eliminate the residual water in sample. Then the temperature was
192 increased from 100 °C to 800 °C at the aforementioned heating rates. Finally, the temperature
193 dropped to 30 °C with unchanged nitrogen sweeping. Additional tests with a pierced lid
194 (central hole of 0.5 mm) were also performed with biomass powder. Therefore, three particle

195 geometries: powder, particles, and cylinders (heights: 1 mm, 2 mm, and 4 mm) together with
 196 another type of reactor (crucible with lid) resulted in six sample configurations performed for
 197 spruce and poplar at two heating rates. In addition, static tests were performed for validation
 198 purposes. Their temperature programs began with the same sequence, heating powder
 199 samples from 30 °C to 100 °C at 10 °C/min and holding for 30 minutes. Then the temperature
 200 was raised at a rate of 10 °C/min to the plateau temperature (from 250 °C to 500 °C by an
 201 increment of 50 °C plus one test at 800 °C). The plateau temperature was maintained for 2 h,
 202 followed by cooling to 30 °C with unchanged nitrogen sweeping.

203 Temperature and sensitivity calibrations were performed specific to crucible type,
 204 temperature rate, and gas type. The certified standards (NETZSCH calibration set) include
 205 indium, tin, bismuth, zinc, aluminum, and silver. The accuracy of the DSC signal was also
 206 checked with sapphire, according to the NETZSCH handbook. Blank tests were conducted
 207 before every sample test with the same crucible to keep the same buoyancy effects and ensure
 208 the same heat capacity. Dimensionless residual mass (DRM) and conversion rate (X_{exp}) were
 209 used to process TG signals:

$$210 \quad DRM(t) = m_t/m_0 \times 100\%, \quad X_{exp}(t) = 1 - DRM(t) \quad (1)$$

211 where m_t is the remaining mass at time t , and m_0 is the anhydrous mass after the 30-
 212 minute plateau at 100 °C.

213 2.3 DAEM formulation

214 DAEM calculates the volatile contributions from parallel and irreversible first-order
 reactions. The integral form of conversion degree, $X(t)$, could be expressed as:

$$215 \quad X(t) = V(t)/V^\infty = 1 - \int_0^\infty \exp\left(-\int_{t_0}^t A_0 e^{-E/RT(t)} dt\right) f(E) dE \quad (2)$$

215 where V^∞ is the theoretical total volatile amount, $V(t)$ is the volatile production at time
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 2 216 t , and E is the activation energy. The important assumption of keeping pre-exponential
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 4 217 factors of all reactions as a constant, A_0 , has been justified by the accurate identification and
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 6 218 model concision [42, 43], and similar concept had been accepted and applied in relevant
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 9 219 researches [44-46]. R is the universal gas constant and $T(t)$ is the temperature at time t .
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 12 220 $f(E)$ is the statistical function for describing the activation energy distribution.
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215 221 Wood is treated as an aggregate of three pseudo-components based on the assumptions
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 17 222 that no interactions exist during pyrolysis, and they correspond to three distributions ($f_j(E)$)
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 19 223 with different weighting factors $V_{max}(j)$, ($j = 1,2,3$). The final formulation of biomass
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 21 224 conversion degree is therefore expressed as:
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$$X(t) = 1 - \sum_{j=1}^3 V_{max}(j) \int_0^\infty \exp\left(-A_0 \int_0^t e^{-E/RT(t)} dt\right) f_j(E) dE \quad (3)$$

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 30 31 225 In this work, two Gaussian and one exponential distributions are chosen for its excellent
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 33 226 trade-off between accuracy and model conciseness [43]. Two Gaussian distributions are used
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 35 227 to represent the first and second pseudo-components. They are formulated using the mean
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 37 228 activation energy E_0 and standard deviation σ as:
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$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(E - E_0)^2}{2\sigma^2}\right) \quad (4)$$

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 42 229 The third pseudo-component is represented by an exponential distribution, one
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 44 230 degeneracy form of the gamma distribution:
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$$f(E) = \beta \exp\left(-\beta \frac{E - E_{min}}{E_{min}}\right) \quad (5)$$

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 51 231 where β is the rate parameter and E_{min} the minimum activation energy. The integral
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 53 232 term of equation (3) demands further numerical discretization for each type of distribution,
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 55 233 which has been presented in detail in our recent works [42, 43]. High temperature level and
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234 wide range of activation energy might cause small characteristic time. For better accuracy in
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 3 235 numerical integration, the effective approximation value of chemical reaction dV_i over the
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 5 236 time step is therefore expressed in its original exponential form [47, 48]:

$$dV = \sum_{j=1}^3 \sum_{i=1}^{N_p} [1 - \exp(-k_i^j dt)] (V_i^{j,\infty} - V_i^j(t)) \quad (6)$$

$$k_i^j = A_0 \exp\left(-\frac{E_i^j}{RT(t)}\right); \quad V_i^{j,\infty} = V_{max}(j) \cdot m_0 \cdot f_j(E_i^j); \quad V_i^j(t=0) = 0 \quad (7)$$

237 Where N_p is the number of increment points in each distribution, k_i^j is the reaction rate
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 19 238 constant for i th reaction in distribution j , E_i^j and $f_j(E_i^j)$ are corresponding activation energy
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 22 239 and distribution value. The final form of the conversion rate $X_{cal}(t)$ at experimental points
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 24 240 $a(t_a)$ can be expressed as:

$$X_{cal}(t) = 1 - \frac{1}{m_0} \sum_{t=0}^{t=t_a} \sum_{j=1}^3 \sum_{i=1}^{N_p} [1 - \exp(-k_i^j dt)] (V_i^{j,\infty} - V_i^j(t)) \quad (8)$$

241 Finally, kinetic parameters in the three distributions are identified by optimizing the
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 34 242 objective function F , which is the residual sum of squares (RSS) between the experimental
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 37 243 conversion rate $X_{exp}(t)$ and the calculated conversion rate $X_{cal}(t)$. Here, N_{exp} is the total
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 40 244 number of experimental values:

$$F(parameters) = \sum_{a=1}^{N_{exp}} \sum_{t=0}^{t_a} (X_{exp}(t) - X_{cal}(t))^2 \quad (9)$$

245 The numerical discretization was combined with in-house MATLAB code, and the
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 50 246 derivative-free Nelder–Mead simplex algorithm [49] was used to minimize the objective
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 52 247 function. Herein, an entire set of data from two dynamic tests was used to compute the
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 54 248 objective function. In order to avoid local minima, the initial set of parameters was derived
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 57 249 from the solution values obtained in our previous study [42]. In addition, intentional
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 59 250 perturbations were applied after identification to restart the procedure and check the stability

251 of the solution. To evaluate the discrepancy between experiments and model, two criteria,
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2 252 root mean square error (RMSE) and maximum deviation (D_m), were used:
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$$RMSE = \frac{\sqrt{\sum_{a=1}^{N_{exp}} \sum_{t=0}^{t_a} (X_{exp}(t) - X_{cal}(t))^2}}{N_{exp}} \quad (10)$$

$$D_m = \text{Max}|X_{exp}(t) - X_{cal}(t)|, \quad \forall t \in [0, t_a] \quad (11)$$

253 3. Results and discussions

254 3.1 Thermogravimetric results

255 Figure 2 depicts the DRM curves of spruce and poplar at two different heating rates.

256 Three distinct regions could be identified for both species. In the first temperature region, the

257 DRM was stable from 100 °C to 200 °C. At this temperature, hemicelluloses melt into the

258 liquid form [50], but the production of volatiles remained very limited. The second region,

259 from 250 °C to 400 °C, exhibited the most important release of volatiles due to the

260 decomposition of hemicelluloses and cellulose. Within this region, random fragmentation of

261 glycosidic bonds in cellulose and hemicellulose generated volatiles with high oxygen contents

262 and left carbonaceous residues [51]. Lignin pyrolysis and secondary charring of volatiles

263 mainly corresponded to the last region, from 400°C to 800 °C, where the main charring

264 process occurred in the form of re-organization of benzene rings into polycyclic structures

265 [28].

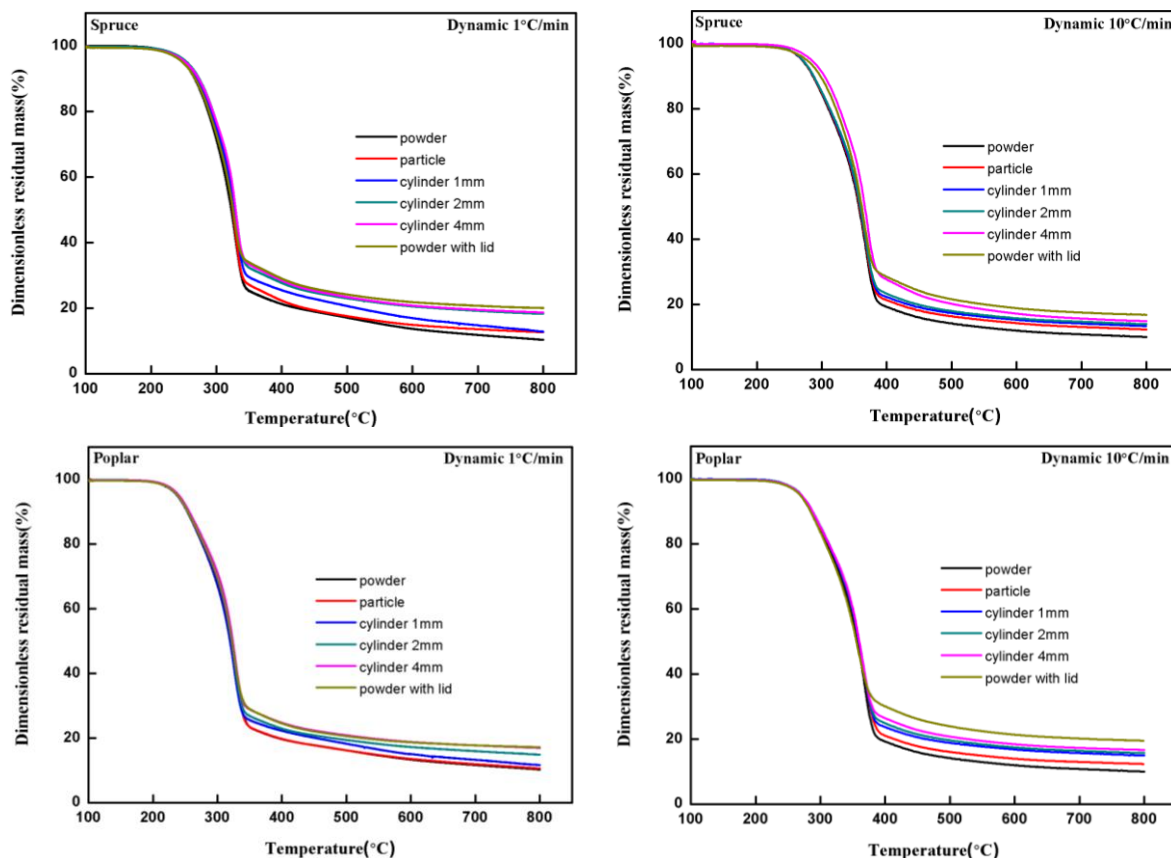
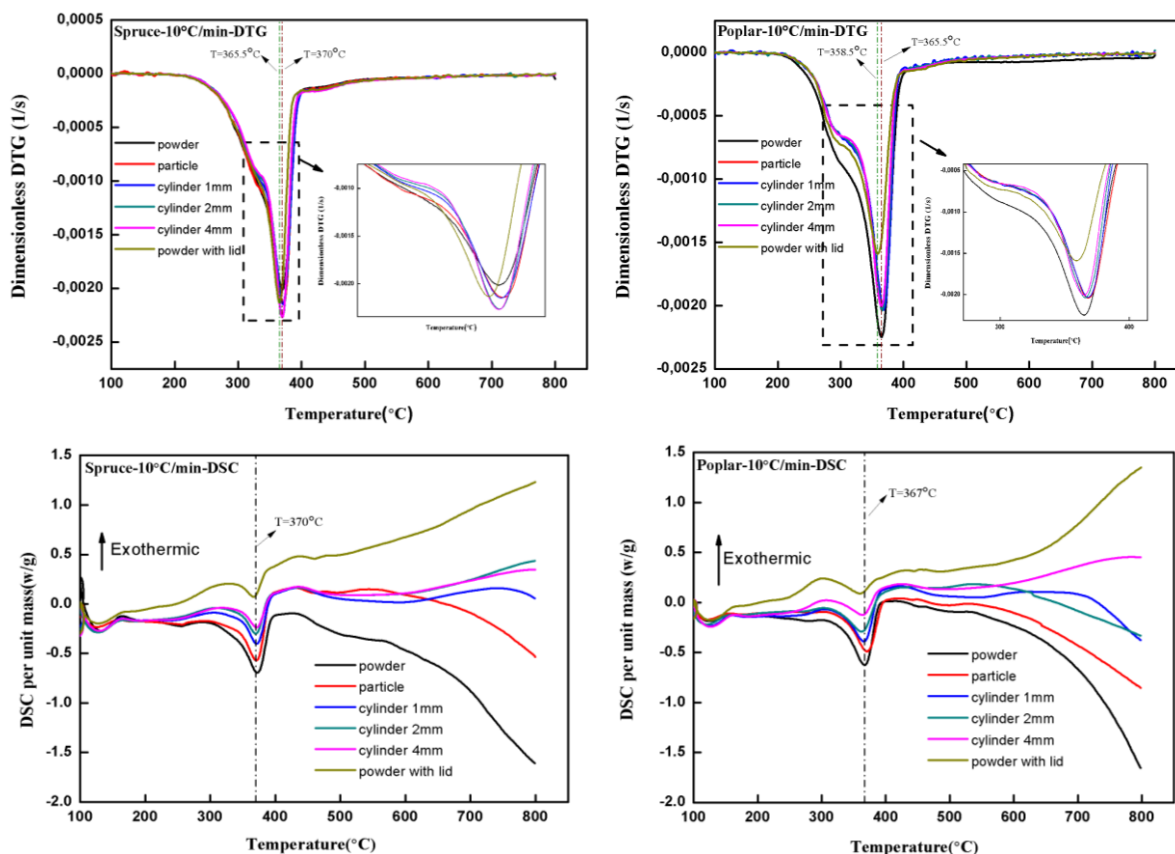


Figure 2. Pyrolysis DRM curves of spruce and poplar samples at two heating rates.

Mass transfer limitations occurring in large particles or in the crucible with lid promoted final char yields, and major differences emerged in the last temperature regions, which clearly indicated different pyrolysis mechanisms. These deviations began at around 330 °C at 1 °C/min and 370 °C at 10 °C/min for both spruce and poplar. The effect of particle sizes enlarged differences at high temperatures, where the mass loss was mainly associated with the rearrangement of residue in the charring process [52], including the important conversion of aromatic structures through demethoxylation [53], dehydration, cross-linking, and re-polymerization [27]. Specifically for the final DRM values (final char yields) of all particle types, the powder presented the lowest values due to the open microstructure and fast release of volatiles. Yet, accompanied by enlargement from powder to the 4 mm-cylinder, kinetic differences turned into noticeable char yield increases. Spruce had an increase in DRM from 10.3 wt.% to 18.7 wt.% at 1 °C/min and from 10.0 wt.% to 14.8 wt.% at 10 °C/min, and

280 poplar rose from 10.3 wt.% to 16.9 wt.% at 1 °C/min and from 10.0 wt.% to 16.7 wt.% at 10 °C/min. Therefore, setting the wood powder as a reference, the increase of particle size
 281 °C/min. Therefore, setting the wood powder as a reference, the increase of particle size
 282 promoted char yields by 81% (1 °C/min) and 48% (10 °C/min) for spruce, and 65% (1 °C/min)
 283 and 66% (10 °C/min) for poplar. In contrast, the powder with a lid exhibited the maximum
 284 increase for all cases, confirming the occurrence of further charring reactions among the
 285 gaseous phase [54]. Obstruction of the mass transfer efficiency decisively promotes charring
 286 in the sample matrix [25], either by increasing the residence time or promoting secondary
 287 reactions within the solid matrix. Therefore, increased char formation by both intra- and extra-
 288 particle mass transfer limitations caused different thermogravimetric behaviors.



289 Figure 3. DTG (first row) and DSC (second row) signals normalized to the mass of spruce
 290 and poplar at 10°C/min.

291 In light of the shift of DSC baseline over long times and the fluctuation of derivative
 292 thermogravimetry (DTG) baseline for 1 °C/min tests, DSC and DTG curves at 10 °C/min

293 were selected here to further analyze the kinetic differences (Figure 3). The DTG and DSC
294 signals were divided by the initial anhydrous mass of the samples. DTG curves exhibited
295 similar trends between samples, but with noticeable differences between 300 °C and 400 °C
296 in spruce, while more differences appeared between 270 °C and 415 °C in poplar. Major
297 peaks appeared around the same temperatures: 370 °C for spruce and 365.5 °C for poplar,
298 attributed to the rapid decomposition of cellulose. Curve shoulders at lower temperatures,
299 320–350 °C, belonged to hemicellulose decomposition, which flattened and shifted towards
300 higher temperatures at increasing particle sizes, indicating the delayed decomposition of
301 hemicellulose. Meanwhile, the peak temperatures for the powder sample with lid shifted from
302 370 °C to 365.5 °C for spruce and from 365.5 °C to 358.5 °C for poplar, which is attributed to
303 the condensation of highly reactive tarry volatiles inside the lidded crucibles [55].

304 The analysis of DSC data will be focused on the temperature range of 250–600 °C. Since
305 the signal was very small below this range and, as seen on the curves in Figure 3, the heat flux
306 signal was seriously affected by radiation at higher temperatures [56]. From powder to
307 cylinders, endothermic DSC peaks (around 370 °C for spruce and 367 °C for poplar) were in
308 good accordance with the DTG peaks of cellulose decomposition. This major endothermicity
309 corresponded to the depolymerization of the 1,4-glycosidic bond and ring breakage of light
310 oxygenates [57]. The transition from endothermic to exothermic in large particles was
311 possibly caused by cellulosic char formation due to the presence of alkyl furans, benzenoid
312 aromatics, and condensed aromatics [58, 59]. An obvious tendency of heat release was
313 observed as the particle size increased for both wood species. This important exothermicity
314 was assigned to carbonization including re-polymerization and cross-linking in aromatic
315 residues [60], in which exothermic heat had been proven to be proportional to char yield [61].
316 The alteration of thermal profile therefore indicated the enhancement of exothermic charring
317 in large particles. In contrast, for the powder sample with lid, its largest exothermicity was

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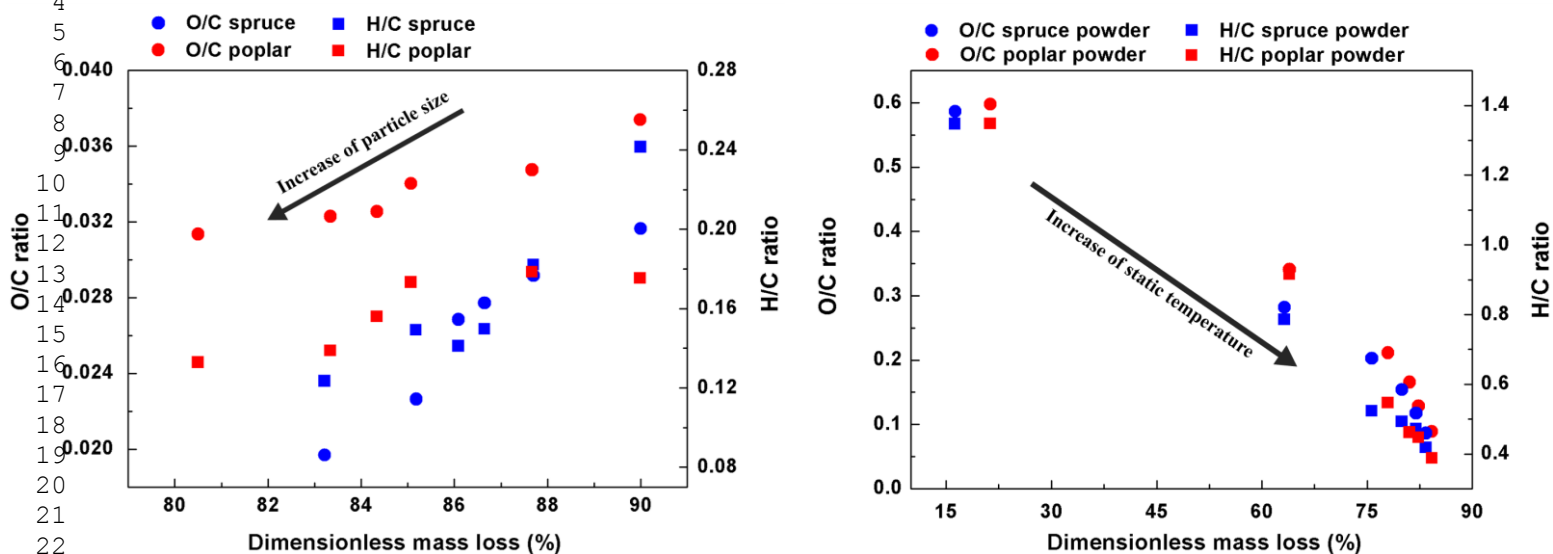
318 attributed to the hindered volatile escape that enhanced condensation and charring [62].

319 Detained volatiles went through severe secondary carbonizations both homogeneously and
320 heterogeneously, evidenced by the experimental observations of carbon depositions on the
321 inner walls of the crucible, and the lid.

322 The O/C and H/C ratios of residual char were indicators for carbonization degree [63],
323 they were therefore coupled with the dimensionless mass loss (DML) of different particle
324 sizes for analysis purposes (full set of data can be found in the supporting material,
325 Supplementary Table 1). For both wood species at both heating rates, DML decreased
326 consistently due to secondary charring. Meanwhile, the decreasing trends of H/C and O/C
327 ratios indicated that char became more carbonaceous [64] because of dehydration and
328 demethylation. Dehydration drove the oxidation of saturated hydrocarbons to form aromatic
329 structures, serving as the precursor for biochar [65]. And the methyl removal in demethylation
330 decreased the H/C ratio for C enrichment in the char product [66].

331 Static tests of two wood types at six temperature levels were conducted in advance,
332 (detailed data of atomic ratios vs. DML can be found in the supporting material,
333 Supplementary Table 2). Then, dynamic tests at 10 °C/min, were chosen as reference and
334 further compared in Figure 4. Two opposite relations were identified: dynamic tests had
335 increasing DML values that matched with decreasing carbonization degree (increases in O/C
336 and H/C), while static tests showed the opposite relation between DML and carbonization.
337 Small size and low temperature (<500 °C) dominantly triggered the decompositions of non-
338 aromatic carbon bonds in lignin [67], causing the changes in the DML. However, different
339 thermochemical pathways in the dynamic tests indicated interceptions of primary volatiles
340 that interacted with recondensation products, contributing directly to decreased DML in large
341 particles. And the simultaneous polymerization and secondary charring reactions caused
342 higher degrees of carbonization. Therefore, abovementioned two converse matching

343 relationship between DML and carbonization clearly indicated the traces of enhanced charring
 344 while increasing particle sizes.



345 Figure 4. Atomic O/C, H/C ratios vs. DML in dynamic tests with different particle sizes of
 346 spruce and poplar (left); in static tests of spruce and poplar powder (right)

347 3.2 DAEM modeling

348 3.2.1 Model identification

349 Kinetic parameters fitted to the two Gaussian distributions and one exponential
 350 distribution in DAEM are listed in Table 2 for all samples. The corresponding full sets of
 351 experimental and simulated DRM curves could be found in the supporting material
 352 (Supplementary Figure 2). The root mean square error (RMSE) and maximum deviation (D_m)
 353 for each particle condition assessed the quality of identification. The reasonably low ranges of
 354 RMSE values: 0.98×10^{-4} – 1.64×10^{-4} for spruce and 0.47×10^{-4} – 0.84×10^{-4} for poplar indicated
 355 very small deviations in general, which confirmed the relevancies of number and shapes of
 356 the distributions [68]. Furthermore, the maximum deviation D_m presented in acceptable
 357 ranges: 2.77% – 4.08% for spruce and 1.87% – 3.34% for poplar. Usually, this error was not
 358 visually obvious in the curves because it tended to appear in fast decomposition regions
 359 (250 °C to 350 °C), where the curve slopes were very large. Therefore, these two indexes

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360 exhibited reasonably small deviations and ensured simulation accuracies. While the identified
361 model parameters had ensured correct overlaps between the simulated and experimental
362 curves, they can also capture the detailed kinetic differences thanks to the “point-by-point”
363 fitting nature during identification process.

364 General characteristics of three distributions’ parameters were consistent with previous
365 work [35, 69], namely the lowest content of the first Gaussian, the largest content and
366 narrowest range of the second Gaussian, and the exponential exhibited partial overlap with the
367 other two distributions. Herein, V_{max1} , the weighting factor of the first distribution, generally
368 decreased when particle size increased from powder to 4-mm cylinder for both wood species,
369 indicating that secondary charring undermined the volatile contributions of the first pseudo-
370 component (hemicellulose) in large particles. V_{max1} was less affected for powder with lid,
371 which was possibly due to the heterogeneous gaseous reactions outside particles that led to
372 devolatilization [70]. The other two weighting factors followed complicated variation trends
373 that will be further investigated in the subsequent section. Nonetheless, the comprehensive
374 parameters of various particle sizes served as good resources for other kinetic researches.

375 An advantage of the robust DAEM model was that devolatilization in the three pseudo-
376 components can be analyzed independently. The inverse reconstructions of devolatilization
377 profiles of pseudo-components allows the effect of particle size to be further analyzed. This
378 merit was exemplified by the devolatilization profiles of three extreme sample sizes (powder,
379 4-mm cylinder, and powder with lid), and detailed comparisons were also presented in
380 supporting material.

Table 2. Identified two Gaussian + one exponential DAEM parameters for different particle sizes of spruce and poplar

Biomass	Spruce				Poplar							
	Powder	Particle	Cylinder 1 mm	Cylinder 2 mm	Cylinder 4 mm	Powder with lid	Powder	Particle	Cylinder 1 mm	Cylinder 2 mm	Cylinder 4 mm	Powder with lid
V_{max1}	0.1670	0.1130	0.1115	0.1140	0.1070	0.1520	0.1704	0.1402	0.1316	0.1183	0.0951	0.1620
V_{max2}	0.4704	0.4683	0.4801	0.4248	0.4149	0.3643	0.4902	0.5258	0.5136	0.4960	0.4622	0.4179
V_{max3}	0.2913	0.3168	0.3129	0.2540	0.2862	0.2866	0.2556	0.2461	0.2713	0.2452	0.2777	0.2496
A_0 (s ⁻¹)	8.19×10^{15}	3.60×10^{16}	1.55×10^{14}	1.90×10^{15}	1.07×10^{15}	4.66×10^{14}	1.94×10^{13}	3.75×10^{12}	1.03×10^{12}	8.03×10^{12}	7.30×10^{13}	8.24×10^{13}
E_{0_1} (kJ/mol)	201.30	209.56	182.40	191.18	187.12	184.69	169.05	160.52	154.10	163.75	174.11	171.86
E_{0_2} (kJ/mol)	216.58	224.08	197.38	209.95	206.80	201.21	186.39	178.31	171.15	181.73	192.72	193.10
E_{min} (kJ/mol)	176.10	185.94	160.88	188.35	184.00	180.32	150.29	143.99	137.76	148.15	158.54	169.37
σ_1 (kJ/mol)	3.86	2.12	1.20	10.23	12.53	12.55	4.43	2.75	1.47	1.84	1.34	7.51
σ_2 (kJ/mol)	9.82×10^{-7}	7.21×10^{-3}	5.93×10^{-8}	7.37×10^{-7}	1.27×10^{-6}	4.98×10^{-6}	2.84×10^{-7}	2.83×10^{-6}	4.79×10^{-7}	1.61×10^{-7}	2.45×10^{-7}	5.76×10^{-9}
β	0.49	0.31	0.56	0.27	0.26	0.24	0.51	0.51	0.63	0.40	0.32	0.26
RMSE ($\times 10^{-4}$)	1.11	0.98	1.07	1.64	1.58	1.34	0.84	0.47	0.60	0.48	0.58	0.81
D_m (%)	3.46	4.08	2.92	3.78	3.74	2.77	3.34	1.87	2.26	2.12	2.22	2.79

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383 Since kinetic parameters in each group interacted with dependences, their direct analysis
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 2 384 might suffer from complicated interactions that led to non-specific effects of particle size.
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 5 385 Instead, synthetic indexes were therefore built: $T_p(j)$ and $V_p(j)$, $j \in [1:3]$ were the temperature
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 7 386 and dimensionless volatile quantities corresponding to the maximum devolatilization rate for
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 10 387 the three pseudo-components (Table 3).

$$V_p(j) = \text{Max} \left| [1 - \exp(-k_i^j dt)] \left(V_i^{j, \infty} - V_i^j(t) \right) \right|, \forall i \in [1, N_p] \quad (12)$$

16 388 $T_p(1)$ generally decreased in spruce when particle size increased but was stable in
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 19 389 poplar, possibly due to their different hemicellulose structures. Namely, monosaccharide units
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 21 390 in spruce which are more easily decomposed [71, 72] than the glucomannan units in poplar.
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 23 391 The decreasing trend of $V_p(1)$ for both species indicated that the first pseudo-component
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 26 392 reduced its devolatilization contributions in large particles. $T_p(2)$ underwent limited changes
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 29 393 while particle size increased in both species. This can be explained by the cellulose crystalline
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 31 394 structure that decomposed rapidly once reaching the melting point [73]. This stable
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 34 395 temperature-dependence indicated that the $T_p(2)$ value was more related to chemical
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 36 396 alteration than to particle size [74]. Furthermore, the devolatilization amount of spruce second
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 39 397 pseudo-component was more affected by the particle size, as revealed by more decrease trend
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 41 398 of $V_p(2)$ in spruce compared to that in poplar. A general increase of $T_p(3)$ in spruce indicated
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 44 399 that the decomposition of the third pseudo-component was shifted towards higher
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 46 400 temperatures in large particles, which was possibly caused by the increase of activation
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 49 401 energy during charring reactions [75].

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405 Table 3. Synthetic values of three pseudo-components in spruce and poplar in dynamic tests
 406 at 10°C/min.

Pseudo-component	Peak values	Spruce						Poplar					
		Powder	Particle	Cylinder, 1mm	Cylinder, 2mm	Cylinder, 4mm	Powder With lid	Powder	Particle	Cylinder, 1mm	Cylinder, 2mm	Cylinder, 4mm	Powder with lid
First	Tp(1)	283.75	288.94	282.94	270.74	265.84	269.34	267.45	264.74	263.33	265.33	268.05	254.84
	Vp(1)	3.85	3.14	2.68	1.79	1.22	1.54	3.26	3.08	3.12	2.87	2.51	2.37
Second	Tp(2)	327.65	328.34	328.06	329.04	328.14	323.55	325.24	324.93	321.84	324.14	325.05	324.35
	Vp(2)	12.77	12.81	12.42	11.38	10.98	9.54	11.86	12.21	11.59	11.76	11.56	10.49
Third	Tp(3)	234.46	242.55	238.36	284.54	279.54	279.63	231.24	232.34	229.95	234.84	237.74	269.55
	Vp(3)	1.13	1.85	1.06	1.56	1.84	1.99	0.96	0.91	0.83	1.12	1.57	1.59

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408 * $T_p(j)$: Peak temperature, °C.

409 $V_p(j)$: Dimensionless volatile, 10^{-4} .

410 j : Pseudo-component, $j \in [1: 3]$.

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413 3.2.2 Model validation

414 *Prediction of mass loss*

415 The model parameters commented previously were identified from the learning database,
 416 which consisted of dynamic tests performed at 1 and 10 °C/min. To further assess model's
 417 prediction potential, these identified parameters were subsequently used to simulate static
 418 tests (Figure 5). The final DRM (Dimensionless Residual Mass) values ($DRM = 1 - DML$)
 419 were calculated for all samples. Three temperature levels (300, 500, and 800 °C) were chosen
 420 to represent three typical pyrolytic stages: initial decomposition, major pyrolysis, and
 421 secondary reaction [1, 76].

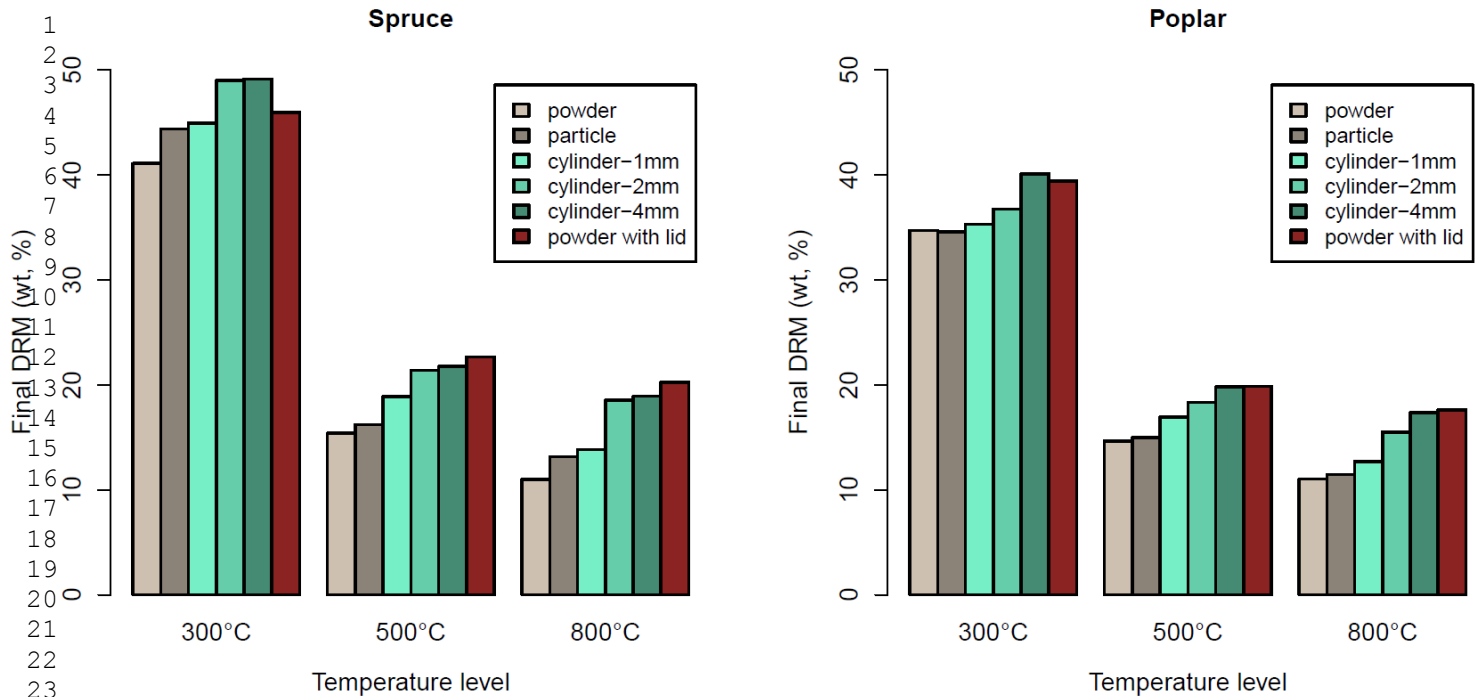
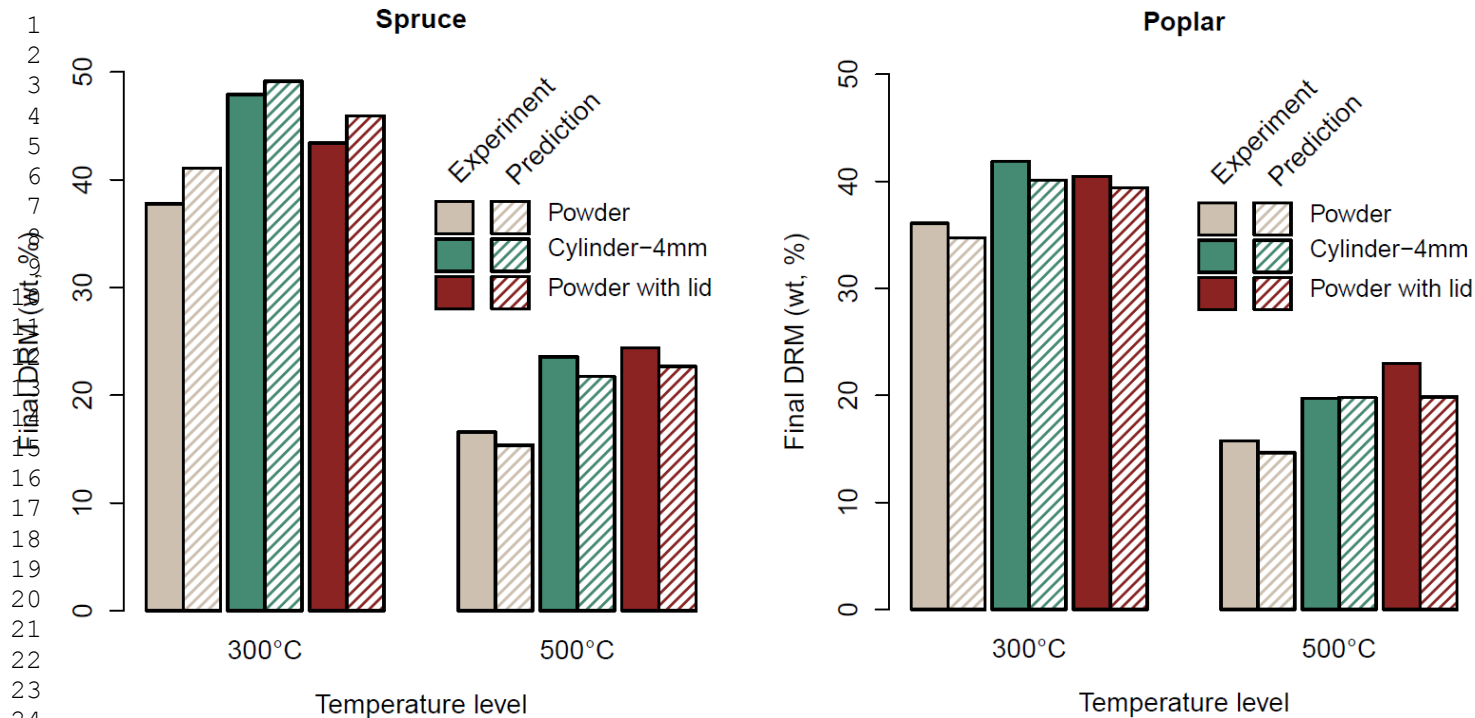


Figure 5. Predictions of final DRM values of spruce and poplar samples in three static tests performed at different temperature levels (300, 500, and 800 °C)

For both spruce and poplar, the predicted DRM values at all chosen temperature levels simultaneously increased when increasing the particle size from powder to the 4-mm cylinder. As direct effect of particle size, the promotion of char formation by intra-particle mass transfer limitations is well-admitted [25] and included in the learning database, proving the logical and reasonable features of numerical predictions. Regarding the effect of temperature level, it was understandable that further devolatilization caused generally lower DRM values at 500 °C compared to those at 300 °C, and the final high-temperature decomposition of lignin and partial secondary cracking reactions caused the lowest DRM values at 800 °C. Meanwhile, the powder with lid exhibited the largest char yield at 500 and 800 °C levels for both species, corresponding to the experimental findings of the most severe char depositions inside the lidded crucibles. Note however that the DRM of powder with lid found at 300°C is smaller than the two longer cylinders.



436 Figure 6. Experiment validations of residual mass for powder, 4mm cylinder and powder with
 437 lid for static tests at 300°C, 500 °C for spruce and poplar

438 Static tests at 300 °C and 500 °C were performed for the purpose of validation (Figure
 439 6). Herein, the static test at 300 °C was a particularly demanding validation case because the
 440 kinetics was very slow at this temperature, resulting in very partial volatilization at the end of
 441 the experiment, likely to introduce prediction errors. In this research, due to the strict
 442 sampling protocol that largely limited the sample amount, only representative sample types
 443 (powder, 4-mm cylinder, powder with lid) were tested. The comparison between experiment
 444 and prediction depicted excellent trends with limited errors for all conditions. The error
 445 ranges, 1.20–3.31% for spruce and 1.09–3.12% for poplar, were more acceptable compared to
 446 previously published works proposing predictions [77]. And it was remarkable to observe that
 447 the smaller DRM value of powder with lid predicted at 300 °C was confirmed by the
 448 experiment.

449 To conclude, kinetic differences originated from intra-particle limitations were nicely
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2 450 predicted by the model, despite the very different time–temperature pathways between
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4 451 validation database and learning database. And this section demonstrated model’s prediction
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7 452 ability on the volatilizations for contrasted pyrolysis conditions.
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10 453 *Prediction of char composition*

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13 454 As commented in the experimental section, the relation between char composition and
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16 455 DML revealed the presence of secondary charring when changing particle size. Assuming that
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18 456 the extra char produced from secondary charring has the identical elemental compositions,
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21 457 i.e., not affected by the particle size. Accordingly, the elemental composition can be deduced
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23 458 as a weighted average value of primary reactions and secondary charring (eq.13). Herein,
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26 459 wood powder is used as the reference for primary reactions.
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29 460 This weighted average allows the element contents of char (c_1 to c_4) to be predicted from
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31 461 the elemental contents of powder and secondary charring, the DRM of powder and the change
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34 462 of DRM with the considered particle:
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$$36 \quad c_i = \frac{(DRM_{powder}) \cdot \alpha_i + \Delta DRM \cdot \beta_i}{DRM_{powder} + \Delta DRM}, \quad i \in [1:4] \quad (13)$$

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41 463 Where DRM_{powder} is the dimensionless residual mass of wood powder, ΔDRM the
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43 464 additional residual mass of the particle compared to powder, α_i the contents in the char of
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46 465 wood powder, and β_i , the element contents in char produced by secondary charring. Indices i
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49 466 stands for carbon, hydrogen, oxygen, and ash. It is assumed that char from secondary charring
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51 467 contains no ash:
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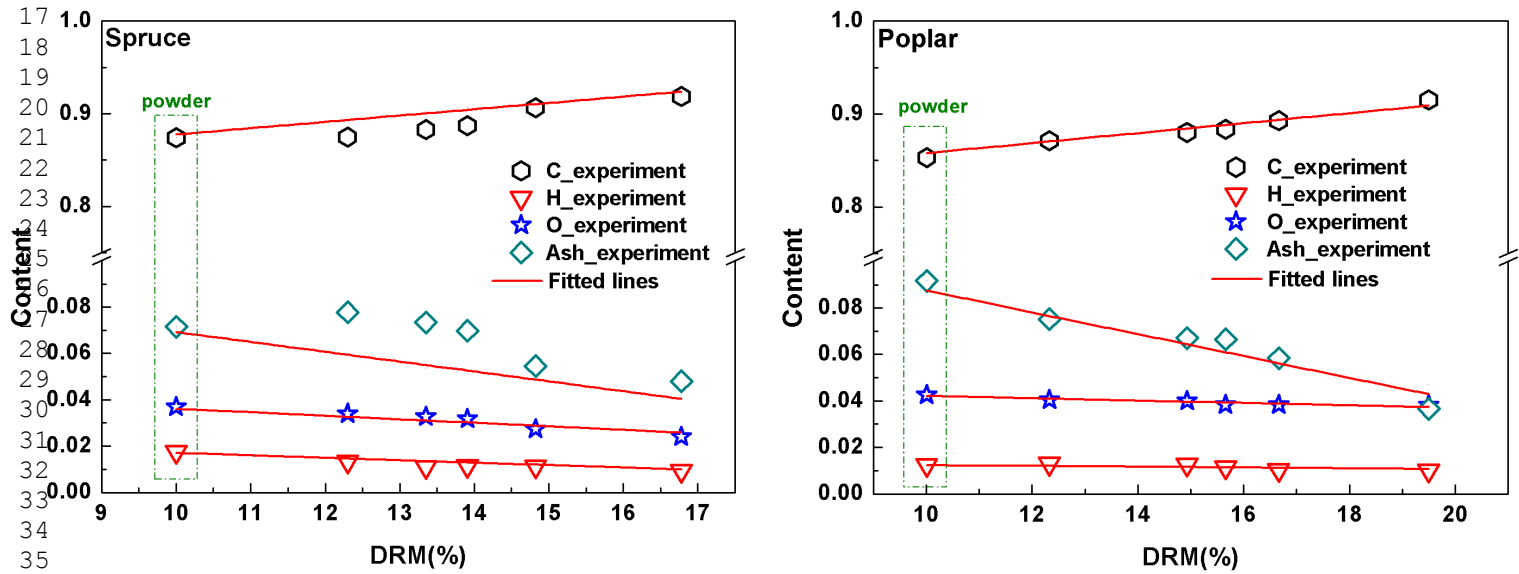
$$53 \quad \beta_C + \beta_H + \beta_O = 1; \quad \beta_{ash} = 0 \quad (14)$$

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56 468 An identification process was conducted for minimizing the RMSE between c_i and
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59 469 actual experimental values at 10 °C/min, to obtain β_i for both wood species (Table 4). To be
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470 noted, the highly dominant content of carbon (β_C) confirms that carbonization is the major
 471 effect of secondary reactions.

472 Table 4. Identified element content parameters in two wood species at 10 °C/min

Wood Species	β_C	β_H	β_O
Spruce	0.9885	4.4712×10^{-10}	0.01149
Poplar	0.9582	9.1484×10^{-3}	0.03265



474 Figure 7. Elementary contents vs. dimensionless residual mass (DRM) of samples with
 475 different particle sizes in the 10 °C/min dynamic tests, and corresponding fitted curves

477 The predictions using equation (13) together with the composition of secondary charring
 478 (Table 4) were plotted for both species (Figure 7), which depicts an excellent correlation
 479 between the change of composition and the change of DRM. The good correlation obtained
 480 for ash is consistent with the assumption on the absence of ash in secondary reactions. In
 481 practice, this observation allows a clear conclusion to be drawn. As the kinetic prediction of
 482 the DAEM model is already validated, the change of DRM between a certain particle size and
 483 powder can be predicted for any time-temperature profile. Hence, equation (8) supplied with

484 the data of table 4, can be used to predict the elemental analysis of char whatever the
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2 485 conditions underwent by the particle. To that purpose, the elemental analysis of char from
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4 486 powder could be predicted as a function of the Dimensionless Residual Mass (DRM) thanks
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7 487 to the correlation proposed in [42]:
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$$\frac{O}{C} = 1.134 - 0.219 \times \exp(1.815 - 1.815DRM)$$
$$\frac{H}{C} = 0.1534 - 0.0268 \times \exp(1.783 - 1.783DRM)$$
(15)

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17 488 This opens new possibilities in process design and control, as this method can be applied
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20 489 to any industrial process, as long as the conditions imposed to the particles were provided.
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22 490 This could be applied, for example, to the prediction of elemental composition along the
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25 491 reactor height for the pyrolysis of a packed bed [34].
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492 4. Conclusions

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32 493 This study is devoted to the effect of particle size on the pyrolysis of two wood species:
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34 494 spruce and poplar. Various sample geometries treated in TG/DSC allowed comprehensive
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36 495 analyses of the mass and heat limitations from intra-particle (powder to cylinder) and reactor
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39 496 type (crucible with and without lid). A negative mass loss/carbonization pathway confirmed
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42 497 additional charring at increasing particle size. Exothermicity from char formation was
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44 498 promoted by particle size (or extra-particle limitations).
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47 499 From this learning database, a robust DAEM model, with two Gaussian and one
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50 500 exponential DAEM distributions, was derived. The DAEM model was used to simulate and
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52 501 predict mass loss for different time-temperature profiles. These predictions were successfully
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54 502 validated by additional experiments. The composition of char produced by secondary
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57 503 charring was determined from the linear relation found between elemental analyses and
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59 504 residual mass. This allows the elemental composition of char to be predicted for a given
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505 particle size for any time-temperature pathway. This prediction involves the kinetic
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2 506 differences between powder and a given particle, as predicted by the DAEM model.
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5 507 In conclusion, this paper addresses the important question of the effect of particle size on
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7 508 biomass pyrolysis and proposes simulation tools to predict the kinetics and the elemental
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9 509 composition of char. These tools are intended for use in the design and control of industrial
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24 514 (CSC) is also gratefully acknowledged.
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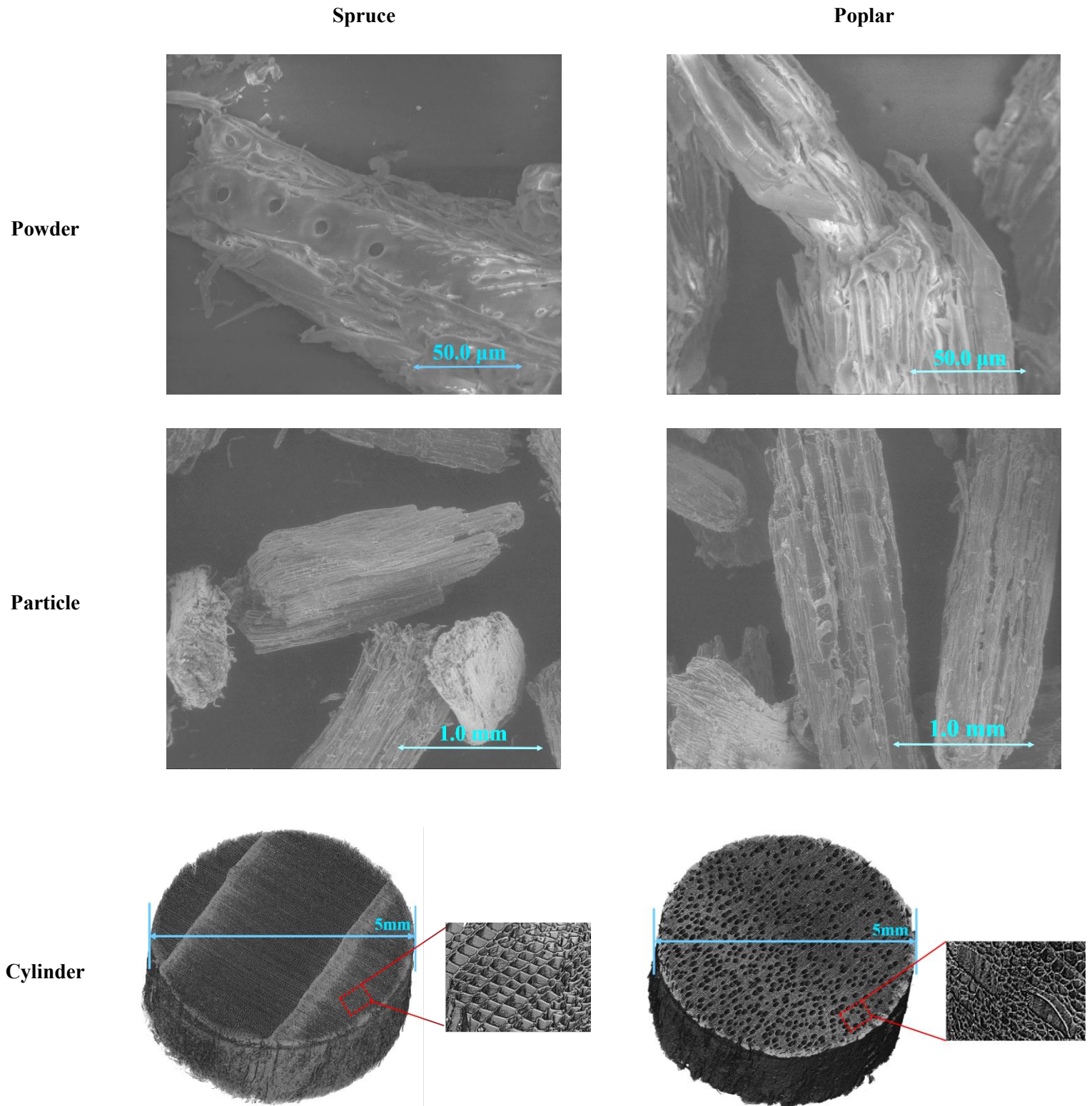
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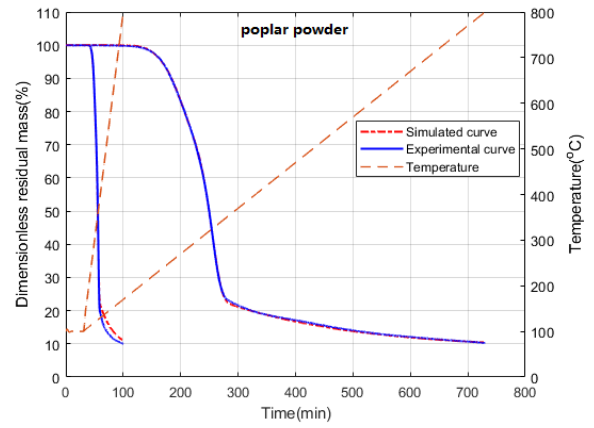
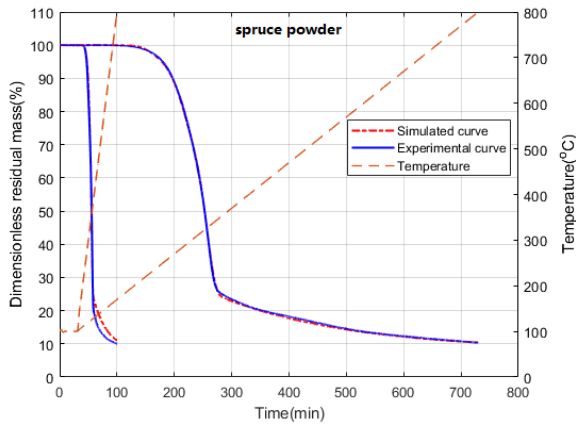
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1 Appendix

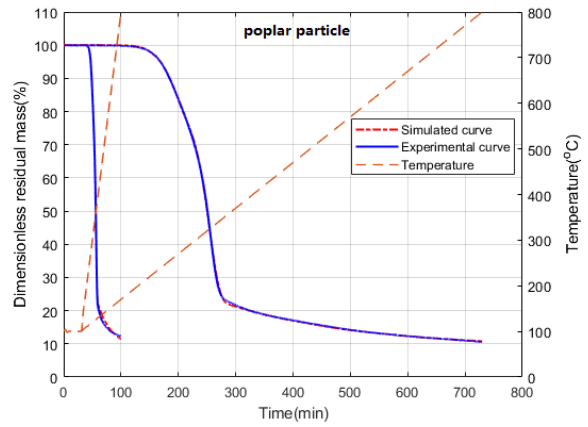
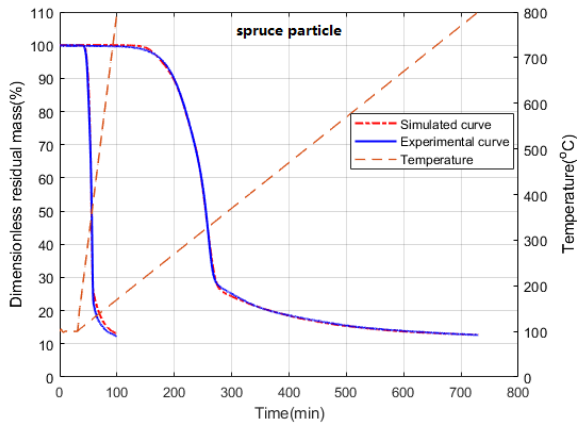


2 Supplementary Figure 1. SEM images of biomass powder and particles, tomographic images of
3 cylinders (spatial resolution: 3 μ m) of spruce (first column) and poplar (second column)

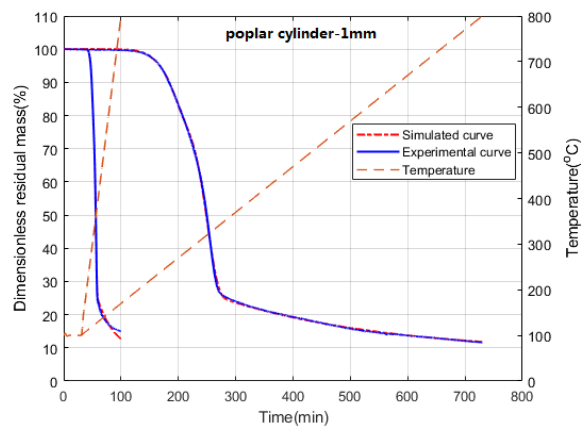
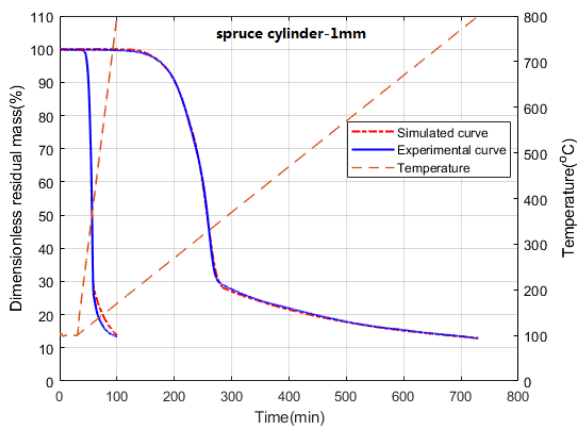
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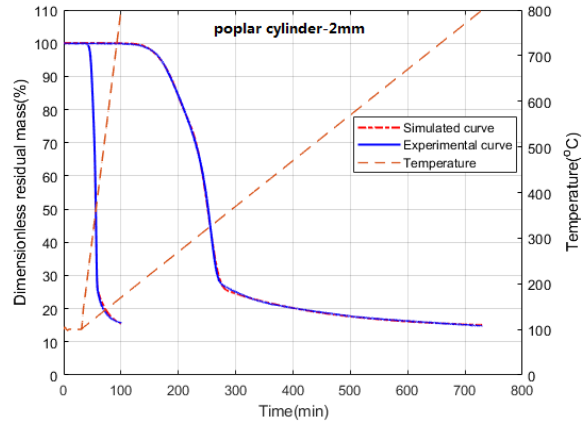
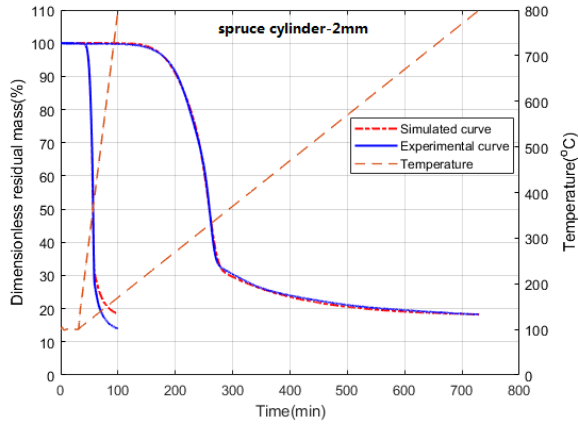
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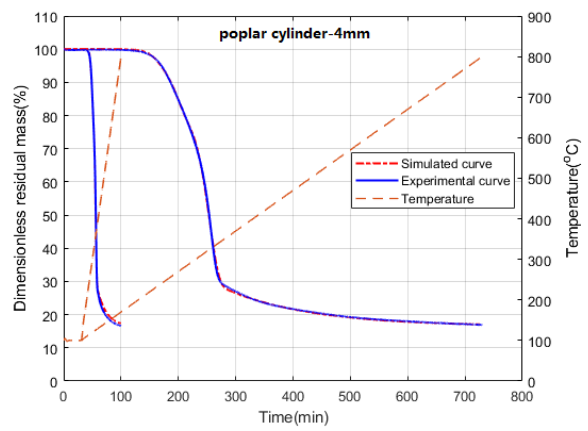
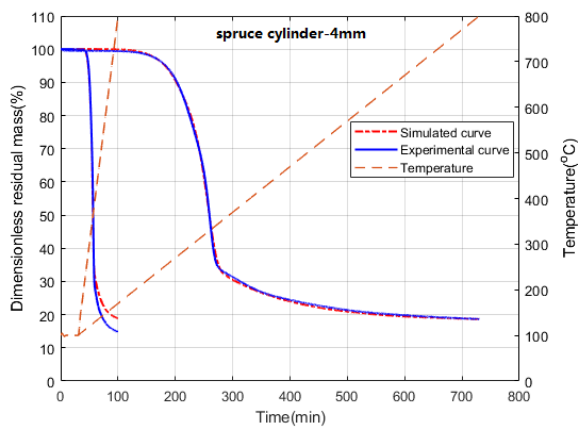
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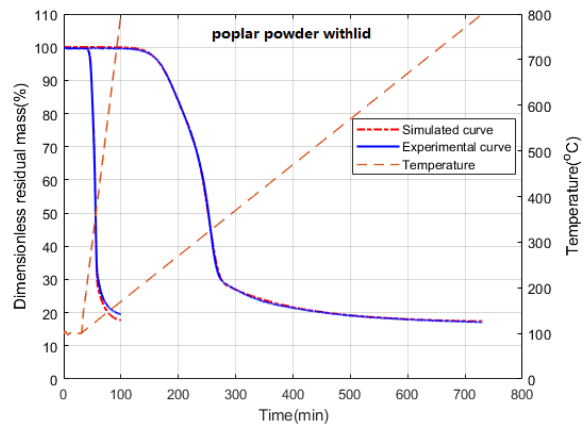
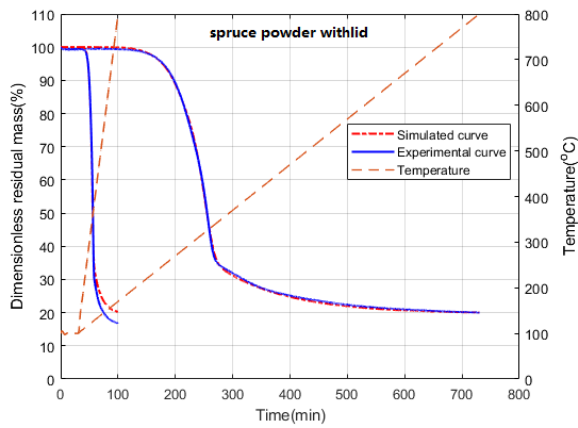
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11 Supplementary Figure 2. Thermogravimetric DRM curves of experiments and model simulations at
12 different sample conditions of spruce (left column) and poplar (right column)

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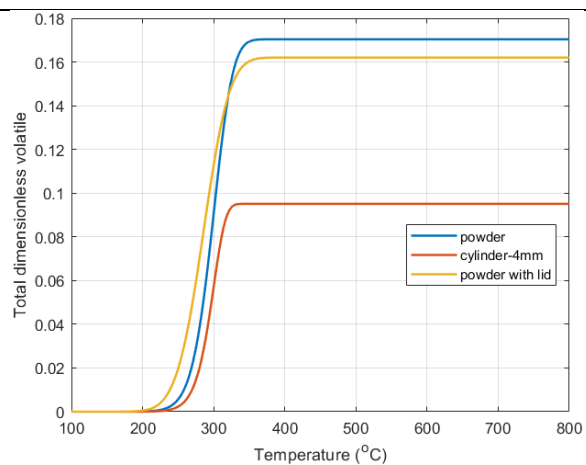
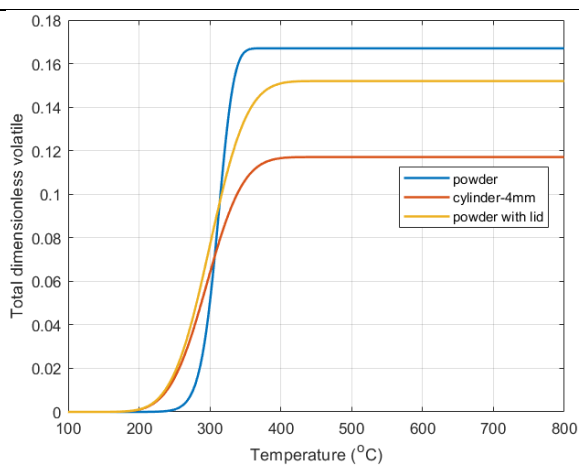
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**Pseudo-
component**

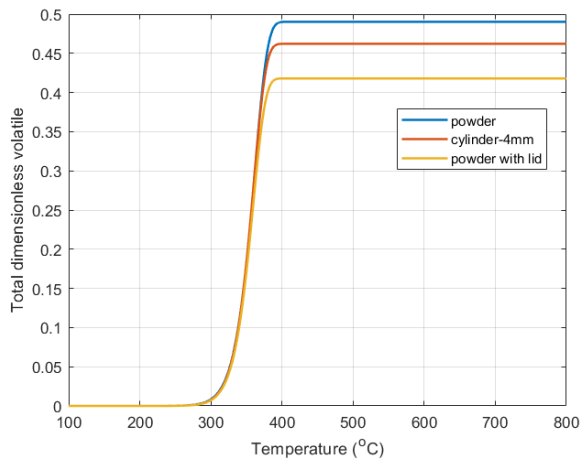
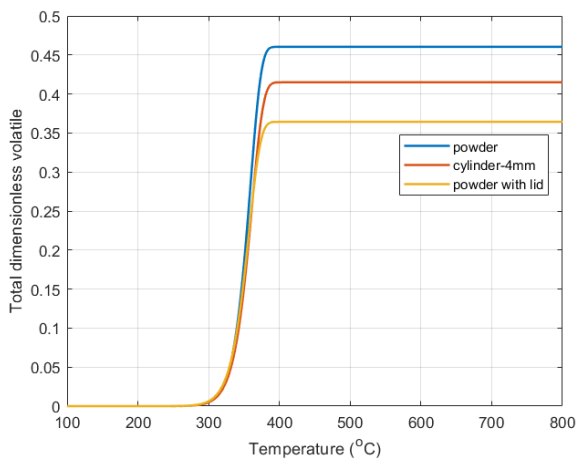
Spruce

Poplar

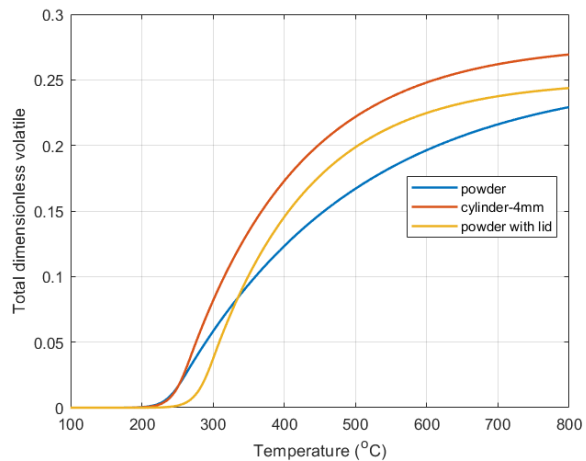
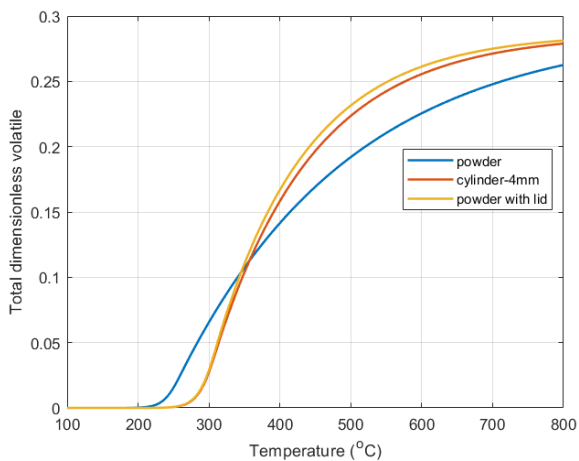
First



Second



Third



17 Supplementary Figure 2. Devolatilization profiles of three pseudo-components in 10 °C /min tests of
18 powder, 4-mm cylinder, and powder with lid, computed from the identified model parameters for
19 spruce and poplar

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21 Devolatilization of the first pseudo-component generally occurred between 163–355 °C;
22 it corresponded to the hemicelluloses that were more reactive at lower temperatures [1], in
23 agreement with similar temperatures reported in the literatures [2, 3]. The narrow pyrolytic
24 range and high volatile yield of the second pseudo-component closely matched cellulose,
25 which made up the largest portion of the wood and decomposed at a specific narrow
26 temperature range around 320 °C [4-6]. The temperature of the third pseudo-component had
27 the largest range, from 180 to 800 °C, which was consistent with lignin decomposition
28 characteristics, in which irregular phenolic polymers endowed extended decomposition ranges
29 [7].

30 Among the three sample types, major differences caused by secondary charring were
31 clearly distinguished by the devolatilization profiles of the pseudo-components. Accompanied
32 by the enlargement of particle size and the use of lid, the first and second pseudo-components
33 reduced their volatile formation rates and final yields, possibly due to the volatile
34 interceptions in hemicellulose and cellulose fractions. On the other hand, the higher volatile
35 content in the third pseudo-component of cylinder-4mm and powder with lid, could be caused
36 by the predominance of lignin devolatilization at high temperatures that raised gas formation
37 rate [8]

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44 Supplementary Table 1. Atomic O/C, H/C ratios and corresponding DML values in dynamic tests with
 45 different particle sizes of spruce and poplar

Wood type	Particle condition	1 °C /min			10 °C /min		
		O/C	H/C	DML(%)	O/C	H/C	DML(%)
Spruce	powder	0.032	0.20	89.69	0.032	0.24	90.00
	particle	0.027	0.15	87.36	0.029	0.18	87.70
	cylinder, 1mm	0.026	0.16	87.18	0.028	0.15	86.65
	cylinder, 2mm	0.026	0.12	81.76	0.027	0.14	86.09
	cylinder, 4mm	0.025	0.12	81.33	0.023	0.15	85.18
	powder with lid	0.023	0.11	79.97	0.019	0.12	83.22
Poplar	powder	0.037	0.16	89.73	0.037	0.17	89.99
	particle	0.034	0.15	89.41	0.035	0.18	87.67
	cylinder, 1mm	0.033	0.15	88.39	0.034	0.17	85.07
	cylinder, 2mm	0.033	0.15	85.20	0.032	0.15	84.34
	cylinder, 4mm	0.029	0.13	83.08	0.032	0.14	83.34
	powder with lid	0.027	0.13	82.90	0.031	0.13	80.50

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48 Supplementary Table 2. Elemental analyses of char in static tests of wood powder

Temperature (°C)	spruce powder						poplar powder					
	250	300	350	400	450	500	250	300	350	400	450	500
C (wt.%)	50.77	65.26	71.01	74.28	79.22	82.67	50.30	62.28	70.90	74.44	77.11	81.50
H (wt.%)	5.70	4.27	3.09	3.05	3.11	2.88	5.65	4.75	3.23	2.86	2.87	2.63
O (wt.%)	39.69	24.53	19.19	15.24	12.42	9.49	40.10	28.32	19.99	16.44	13.21	9.62

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