

# 1 Characterization of high-temperature rapid char oxidation of raw and 2 torrefied biomass fuels

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## 10 Abstract

11 The promising properties of torrefied biomass provide a valid co-firing option for large  
12 percentage biomass utilization in existing coal-fired boilers. Torrefied biomass is expected  
13 to have a better combustion stability than raw biomass and similar to that of coal. The  
14 present work will characterizes the oxidation properties of torrefied biomass char and  
15 compare with that of raw biomass char. The studied two chars are produced from both raw  
16 and torrefied biomass in an Isothermal Plug Flow Reactor (IPFR) at high temperature and  
17 heating rate, a sufficient residence time is applied for the completion of the high  
18 temperature devolatilization. Char oxidation tests are carried out in the IPFR by varying  
19 temperature, oxygen concentration and residence time. The reactivity of two studied chars  
20 are analyzed and compared with referenced biomass char and coal char, and the impact of  
21 torrefaction on char is discussed in this paper. Finally, the char oxidation kinetic parameters  
22 are determined using a parameter optimization method, and the obtained kinetics are  
23 examined by comparing the experimental and predicted mass conversions.

## 25 Keywords

26 Torrefaction, Char oxidation, Kinetics, High temperature

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27 **1. Introduction**

28 The handling and combustion characteristics of biomass can be substantially improved  
29 through torrefaction[1]. The promising properties of torrefied biomass provide a co-  
30 utilization option incorporating large percentage biomass co-firing ratio in existing coal-  
31 fired boilers without major modifications. Accordingly, a torrefaction based co-firing  
32 system in pulverized coal boilers has been proposed toward the goal of a 100% fuel  
33 switch[2].

34 When the biomass particles enter a pulverized fuel flame, they are rapidly heated to a final  
35 temperature in the range of 1400 to 1600°C at a rate of about  $10^4$  °C /s[3]. The study of  
36 the char oxidation kinetics of biomass obtained at the high temperatures and heating rates  
37 is very limited. Lin et al. [4] proposed an aerosol-based method to characterize particles  
38 fragmented from biomass chars during oxidation at high temperatures, and the oxidation  
39 of char particles in the reactor was investigated by determining on-line the particle size  
40 distributions before and after the passage through the reactor. Campbell et al. [5]  
41 characterized coal and biomass char at high temperatures using a heterogeneous reaction  
42 mechanism that not only describes the variations in char reactivity with conversion at low  
43 temperatures but also predicts high enough reaction rates at high temperatures to yield the  
44 mass loss rates observed in a laminar flow reactor, their results indicate that the char  
45 intrinsic reactivity decreases progressively during oxidation at high temperatures. Jiménez et  
46 al. [6] performed devolatilization and combustion experiments of pulverized biomass in an  
47 entrained flow reactor under realistic combustion conditions, to derive the kinetic  
48 parameters that can be used in particle combustion model with good fitting the observed  
49 behaviors. However, in general, there is still lack of a work that investigates and compares  
50 the char reactivity before and after torrefaction under real combustion conditions.

51 Tapasvi et al.[7] characterized the combustion behavior of four torrefied wood samples and  
52 parent feedstock (birch and spruce) at slow heating programs by thermogravimetric  
53 analysis (TGA), and the experimental data was used for the kinetic evaluation. Fisher et al.  
54 [8] performed TGA to study the char reactivity of raw and torrefied biomass in O<sub>2</sub> and  
55 steam atmospheres; the studied chars were prepared from torrefied and raw willow under  
56 both high- and low-heating-rate conditions and it was concluded that torrefaction  
57 consistently reduces char reactivity. Arisa et al.[9] carried out TGA on raw and torrefied  
58 biomass to study their reactivity, and the torrefaction process was found to influence the  
59 parameters at the first stage, whereas those corresponding to the second remained  
60 unaffected. An analysis based on TGA could be employed to generally understand the char  
61 reactivity, but mass and heat transfer limitations make it impossible to determine the  
62 accurate kinetics by using TGA methods [4, 10], due to the relatively low temperatures  
63 (<1000°C) and low heating rate (<1°C/s).

64 Torrefied biomass is supposed to be a coal-like fuel used in industrial furnaces, and thus its  
65 combustion performance is expected similar to that of coal. In our previous paper [11],  
66 high-temperature rapid devolatilization of biomasses with varying degrees of torrefaction  
67 have been investigated, concluding that biomass decreases its reactivity after torrefaction,  
68 and the deeper the torrefaction degree, the lower is biomass reactivity. During the  
69 combustion process of biomass, the rate of char oxidation is slower than biomass thermal  
70 decomposition and volatiles combustion[12]. Accordingly, the rate of char oxidation  
71 determines the overall combustion efficiency, and a good understanding of the reactivity of  
72 biomass char becomes more important for a biomass combustion process. Compared to  
73 the char produced at low heating rate, a more reactive char is produced after  
74 devolatilization at high heating rates, associating with larger pores and larger total surface  
75 area [12]. Also Biagini et al. [13]found that biomass chars produced during the rapid

76 pyrolysis (in a drop tube reactor) were more reactive versus oxidation than chars produced  
77 in milder conditions (in thermogravimetric balance). In this study, two char samples were  
78 previously produced from both raw palm kernel shells (PKS) and torrefied PKS in an  
79 Isothermal Plug Flow Reactor (IPFR) under an almost oxygen-free atmosphere and a  
80 sufficient residence time, to guarantee the completion of the high temperature  
81 devolatilization. Finally, the char samples were tested in the IPFR by varying reactor  
82 temperature, oxygen concentration and residence time to study the biomass char oxidation  
83 behavior before and after torrefaction, and determine the char oxidation kinetics of  
84 torrefied biomass in combustion conditions that similar to those of full size power plants.

85

## 86 **2. Fuel and Methods**

### 87 2.1 Fuel preparation

88 Two fuels are used in this work, PKS and torrefied biomass. PKS is the studied raw  
89 biomass material, abbreviated as RB. The torrefied biomass, abbreviated as TB, is the raw  
90 PKS torrefied at 300°C for a residence time of 30 minutes in a horizontal rotary furnace.  
91 The proximate and ultimate analyses of those two biomass materials are summarized in  
92 Table 1. More detailed introduction of torrefaction furnace and the studies on the biomass  
93 torrefaction tests can be found in previous work [11, 14, 15], where the yields of torrefied  
94 fuels and released gaseous species during torrefaction and the impacts of torrefaction on  
95 the biomass devolatilization performances and the biomass flame properties were well  
96 addressed. Continue to the previous studies, the char oxidation properties of the torrefied  
97 biomass will be characterized in this work and compared to that of raw biomass.

98 <Table 1>

99 A sufficient amount of char is required to perform char combustion tests in the IPFR. In  
100 this work, char is produced in the IPFR at 900°C under an almost oxygen-free atmosphere

101 and a residence time of 300ms. The proximate and ultimate data of the studied two chars  
102 are also listed in Table 1, the chars of RB-char and TB-char are collected after the designed  
103 devolatilization of RB and TB, respectively. It can be noted that the chars still contain a  
104 considerable amount of volatiles (between 16% and 21%), but this is significantly lower  
105 than their parent biomass fuels (between 50% and 70%). Similarly, the carbon content of  
106 biomass char increases and the oxygen content of biomass char decreases with the  
107 torrefaction degree. Due to this study is to characterize the char oxidations, the heating  
108 values of RB-char and TB-char were not measured via standard calorific value tests,  
109 however, their high heating values of the chars can be easily estimated according to the  
110 proximate and ultimate data[16].

111

## 112 2.2 Isothermal Plug Flow Reactor

113 Char characterization tests were performed in the Isothermal Plug Flow Reactor (IPFR), a  
114 4 m long drop tube furnace, which allows to characterize solid fuels under conditions  
115 similar to those of large power combustion plants, such as heating rates on the order of  $10^4$   
116 °C/s, and a maximum temperature of 1400°C. The scheme of the IPFR is shown in Figure  
117 1. The temperature of the tube is adjusted through eight electrically heated modules, and  
118 each of them can be controlled independently. A K-tron solid fuel feeder provides a  
119 continuous mass flow of about 100 g/h of pulverized fuel, which is fed to the reactor  
120 through one of the 19 available ports at different heights. The same ports can be used also  
121 to measure either the temperature of the flue gases or their chemical composition by using  
122 a gas sampling probe. The chemical composition of the oxidizer agent, injected into the  
123 IPFR reactor, can be adjusted by changing the flow rates of natural gas and air fed to the  
124 pre-combustor located on the top of the reactor. Once the velocity of the oxidizing gases is  
125 fixed, the desired residence time of biomass particles inside of the IPFR is achieved by

126 changing the feeding port and the position of the sampling probe at the bottom of the  
127 reactor. The solid sampling probe consists of a water-cooled jacket where the collected  
128 particles are quenched with nitrogen in few milliseconds at a temperature below 300°C to  
129 stop all the reactions. The qualification of the IPFR and the procedures applied to biomass  
130 characterization are presented by Biagini et al.[17], whereas the quantification of the  
131 experimental uncertainties (mass loss and residence time) was discussed by Li et al.[11].

132

133 <Figure 1.>

134

135 In real biomass combustion systems, volatile combustion consumed a considerable part of  
136 the oxygen, resulting in the char oxidation occurs at a lower oxygen concentrations below  
137 21%. In this work, the char oxidation tests are carried out by varying the oxygen  
138 concentration from 3% to 9%, and the residence time from 30 to 600 ms. A total of 20  
139 tests were carried out under various conditions, as shown in Table 2.

140

141 <Table 2>

142

143 During every char combustion test, the partially and/or completely burnt char particles are  
144 collected and then analyzed to determine the value of mass conversion according to the ash  
145 tracer method, which assumes that the biomass ash is inert and thermally stable. Eq.(1)is  
146 used to determine the weight loss on a dry-ash-free basis.

$$147 \quad X = 1 - \frac{ash_0}{ash} \cdot \left( \frac{1-ash}{1-ash_0} \right) \quad \text{Eq.(1)}$$

148 A morphological analysis was also performed on the char samples. As an example, the  
149 particle size distribution of the produced RB-char was analyzed, and compared to that of  
150 its parent fuel, as shown in Figure 2. It can be noted that produced char particle sizes are

151 smaller than the parent ones, and the particle size distributions of chars produced from  
152 torrefied biomass and the parent material show a similar trend.

153

154 <Figure 2 >

### 155 3. Kinetic determination approach

#### 156 3.1 Char combustion model

157 The char combustion rate is controlled by the chemical kinetics and the external diffusion  
158 of oxygen. A uniform temperature inside of the particle is assumed due to its micro size. It  
159 is suitable to model the char combustion occurring under Regime II condition. The  
160 variation of particle mass is described by Eq. (2).

$$161 \quad \frac{dm_p}{dt} = S_p D (P_{O_2, \infty} - P_{O_2, s}) = k (P_{O_2, s})^n \quad \text{Eq.(2)}$$

162 The kinetic constant  $k$  is expressed in the Arrhenius form, whereas the oxygen diffusion  
163 coefficient varies with the temperature according to Eq.(3).

$$164 \quad D = C \frac{\left(\frac{T_p + T_g}{z}\right)^{0.75}}{d_p} \quad \text{Eq.(3)}$$

165 The temperature of the char particle is calculated from the heat balance of the particle. The  
166 particles are considered to be spherical, and the change of their diameter during char  
167 oxidation is also taken into account according to Eq.(4).

$$168 \quad d_p = d_{p,0} (1 - X)^\alpha \quad \text{Eq. (4)}$$

169 The burning mode is identified by the parameter  $\alpha$ , which varies between 0 and 1/3, where  
170  $\alpha = 0$  corresponds to a constant particle size with decreasing density (Regime I), and  $\alpha =$   
171  $1/3$  corresponds to a decreasing particle size with constant density (Regime III). Since  
172 phenomena occurring during the latest stages of combustion are not considered in this  
173 study, i.e. char annealing and changes in particle structure,  $\alpha$  is fixed at 0.25.

174 By manipulating Eq.(2), the unknown partial pressure of oxygen at the surface of the  
175 particle can be eliminated, and Eq.(5) is obtained.

$$176 \quad \frac{dm_p}{dt} = S_p k \left( P_{O_2, \infty} - \frac{dm_p}{dt} \frac{1}{S_p D} \right)^n \quad \text{Eq.(5)}$$

177 Analytical solutions can be found for apparent reaction order of 0.5 or 1, whereas in this  
178 study Eq.(5) is solved numerically.

179 It is important to highlight a few limitations of this model, which does not take into  
180 account phenomena occurring at high conversion levels, thus overestimating conversion  
181 for  $X > 0.7$  [18]. Therefore, it is a “single film” model that does not consider secondary  
182 reactions occurring around the particle surface. For this reason CO is considered to be the  
183 only product of carbon oxidation, even if a not negligible amount of  $CO_2$  should be  
184 formed. More detailed discussion on this model and its limitations can be found in [18].

### 185 3.2 Determination of apparent kinetics

186 The determination of the reaction order and the kinetic parameters follows the approach  
187 suggested by [19]and[20]. The apparent reaction order and kinetic parameters are  
188 determined by minimizing the root square mean error (RSME) between modeled and  
189 experimental conversions, described by Eq.(6), over a dataset of  $N$  experimental values.

$$190 \quad RSME = \sqrt{\frac{1}{N} \sum_{i=1}^N (X_{mod} - X_{exp})_i^2} \quad \text{Eq.(6)}$$

191 A brute force method is employed to get the optimization parameters, constraining the  
192 activation energy to be between 10 and 200 kJ/mol and the pre-exponential factor to be  
193 positive. Finally, the joint optimization of the two parameters is repeated for reaction  
194 orders between 0.05 and 2.00. Char oxidation models are usually based on either apparent  
195 or intrinsic kinetics. The intrinsic approach considers the particle reaction rate as a function  
196 of the intrinsic reactivity, pore surface area, and local oxygen concentrations, whereas the  
197 apparent kinetics consider an overall reaction rate and the reaction rate is based on the



198 external surface area and on oxygen concentration at particle surface[21]. The evolution of  
199 the surface area of biomass is very complicated, in this work, the apparent activation energy  
200 is applied, considering the elementary char oxidation steps are lumped into a single one.

201

## 202 **4. Results and discussions**

203

### 204 4.1 High-temperature char oxidation tests

205 Char oxidation characterization, performed in semi-industrial facility-IPFR, leads to more  
206 reliable kinetic parameters than studies performed in traditional analyses, e.g. TGA. First of  
207 all, the char particles produced under high heating rate in the IPFR are more similar to  
208 those found in industrial furnaces. Then, their combustion rate is controlled by both the  
209 chemical kinetics of carbon oxidation and the diffusion of oxygen around the particle. In  
210 contrast, char oxidation tests performed in a TG balance usually occur under kinetically  
211 controlled Regime I conditions.

212 Figure 3 (a) shows the results of char oxidation tests performed on the raw PKS, at 900°C  
213 with two oxygen concentrations (4%, 8%) and at 1200°C with 4% oxygen. It is concluded  
214 that both oxygen diffusion and kinetics play an important role on biomass char oxidation at  
215 900 °C, while at the elevated temperature of 1200 °C, the biomass char burns completely  
216 even at diluted oxygen concentration conditions within 500 ms. This result could further  
217 support the volumetric combustion concept applied in large-scale boilers[22], which  
218 supposed to create a good complete combustion atmosphere at elevated temperature but  
219 diluted oxygen concentrations realized by internal recirculation of flue gas, achieving  
220 uniform temperature profile and gas species distributions. In fact, the difference between  
221 the char burnout profiles obtained at 900°C with varying oxygen concentrations( $\approx 10\%$ ) is  
222 less relevant than the difference between the char burnout profiles obtained at varying

223 temperature with constant 4% oxygen concentration ( $\approx 30\%$ ). However, at 900°C, a longer  
224 residence time is required to reach such a conversion level even at an enhanced oxygen  
225 concentration of 8%. Combustion tests of torrefied biomass char were performed as well.  
226 Figure 3(b) shows the results of char oxidation tests performed at 900°C with oxygen  
227 concentrations ranging from 3% to 9%, to understand the impact of torrefaction on the  
228 char oxidation process. A high oxygen concentration leads to an increase of mass  
229 conversion of the TB-char by 15% and 20% for 6% and 9% oxygen concentrations  
230 respectively.

231 When comparing the mass conversions of RB-char and TB-char oxidizations at 900 °C  
232 with varying oxygen concentrations, apparently, the mass conversion rate of RB-char is  
233 faster than the TB-char even oxidized at a lower oxygen concentration, for instance,  
234 35.29% of TB-char is converted at 6% oxygen concentration compared to 40.79% of RB-  
235 char conversion at 4% oxygen concentration. In addition, Figure 3 (b) shows that the  
236 impact of torrefaction on char conversion is significant in the early-stage char oxidation  
237 process, while torrefaction shows less effect on the final mass conversions of char. Oxygen  
238 concentration has a considerable effect on the final mass conversion when operating at the  
239 same temperature. A similar result was reported from a TGA study on raw and torrefied  
240 biomass, aimed at studying their reactivity in air. In this TGA tests, the torrefaction process  
241 influences the parameters of the first stage, whereas those corresponding to the second  
242 remained unaffected[9]. This is desired, since torrefaction favors the formation of a stable  
243 flame during combustion in a pulverized-fuel burner. First, according to the previous work  
244 on biomass flame[14], biomass normally has a wider flame volumes when compared to that  
245 of coal, and the volume of biomass flame reduces after torrefaction and similar to coal  
246 flames, and therefore a combustion stability can be expected when co-firing torrefied  
247 biomass with coal. Additionally, this could be also explained as the change of cellulose

248 structure during the torrefaction process because of the decomposition of hemicellulose,  
249 which further influences the char structure formed after high-temperature devolatilization,  
250 benefitting a stable combustion.

251

252 <Figure 3(a)>

253 <Figure 3(b)>

#### 254 4.2 High-temperature char combustion kinetics

255 The kinetic parameters of char oxidation for the studied raw and torrefied biofuels,  
256 determined by minimizing the differences between modeled and experimental results, are  
257 finally presented in Table 3. It can be noted that the accuracy of the model prediction is  
258 acceptable, with a Root Square Mean Error of 4.50% and 8.60% for RB-char and TB-char,  
259 respectively.

260 <Table 3>

261 Due to the TB-char oxidation tests were only performed at one temperature 900 °C, it was  
262 not possible to determine the appropriate activation energy, because particle temperatures  
263 will not differ in the different experimental runs. Here, the apparent activation energy for  
264 TB-char is chosen to be 60 kJ/mol, while the pre-exponential factor and reaction order are  
265 determined by same approach. In addition, the oxygen reaction order is significantly higher  
266 for TB-char than for RB-char, which agrees with the experimental data that show a more  
267 relevant contribution of oxygen to the overall conversion for the former than for the latter  
268 biomass char. Accordingly, it is impossible to compare the char reactivity of RB-char and  
269 TB-char by the activation energy only, but a good prediction can be expected by applying  
270 the determined kinetics.

271 However, the obtained kinetics of the studied chars are compared by Arrhenius plot with  
272 referenced biomass and coal kinetics, as shown in Figure 4. The referenced biomass and

273 coal kinetics are selected from literature[23], in which Karlström et al. studied anthracite  
274 chars and char from beech tree, their kinetics were obtained based on experiments at  
275 varying temperatures (950 °C, 1200 °C, and 1400 °C) and varying oxygen conditions (4%,  
276 6%, 8%, and 12%). In Figure 4, the O<sub>2</sub> concentration is fixed as 4% for comparison. It is  
277 clear that the reactivity of RB-char is high, and the reactivity of TB-char is comparable with  
278 the tree-char from Karlström's work, while the reactivity of all the biomass chars are  
279 significantly higher than that of anthracite char. The slope of the line in Arrhenius plots  
280 represents the activation energy, the selected activation energy for TB-char is in the similar  
281 ranges of referenced biomass char while still significant lower than that of anthracite char,  
282 this could be concluded that the chosen activation energy of 60 kJ/mol for TB-char is  
283 reasonable, and the predicted mass conversions of studied char oxidations based on the  
284 obtained all kinetic parameters will be examined and validated later.

285

286 <Figure 4>

287

#### 288 4.3 Examination of determined kinetics

289 Figure 5 shows the comparison between the predicted and the experimental mass  
290 conversion for char combustion of the raw (a) and torrefied (b) PKS, which demonstrates  
291 the ability of the model to predict the conversion trend with a sufficient degree of accuracy.  
292 The kinetic parameters of char oxidation of raw and torrefied PKS determined in this work  
293 are thus examined and validated. From Figure 5(a), it can be concluded that, at the  
294 relatively low temperature of 900 °C, the mass conversions of RB-char are under-predicted  
295 in the early stage of char oxidation, while the final mass conversions are slightly over-  
296 predicted when compared to experimental data. When the temperature rises up to 1200 °C,  
297 a good agreement is achieved, although the predicted mass conversion is in a small degree

298 lower than the experimental data, and a good prediction for the final mass conversion is  
299 obtained. According to the char oxidation model, the oxidation rate is governed by both  
300 kinetic and oxygen diffusion. When the operating temperature reaches 1200 °C, the char is  
301 combusted under Regime III, in which reaction rate is dominantly controlled by diffusion.  
302 Figure 5(b) shows a similar mass conversion trend for TB-char, the mass conversions of  
303 TB-char are slightly under-predicted in the early stage of char oxidation, while the final  
304 mass conversions are over-predicted when compared to experimental data, and the  
305 predicted mass conversions show good agreements with experimental data. A big gap  
306 between experiments and prediction is shown in TB-char oxidized at 900 °C and 9%  
307 oxygen concentration case in late oxidation stage, this might be caused by the experimental  
308 errors, and the errors could be made experimentally either by uncertainties of mass loss or  
309 by uncertainties of residence time, the uncertainties caused by experiments have been  
310 comprehensively discussed in our previous work[11]. Another reason might be the small  
311 ash content when compared to the fixed carbon content in studied char samples, while the  
312 mass conversion during char oxidation is calculated based on the Eq.(1), a small uncertainty  
313 on the ash content measurement may cause a significant difference in mass conversion,  
314 however unfortunately, there is still lack an measurement method to accurately track the  
315 mass conversion of solid thermal conversions in plug flow reactor. In general, it can be  
316 concluded the determined kinetics of RB-char and TB-char can be used to predict the mass  
317 conversions during the char oxidation processes.

318 <Figure 5(a)>

319 <Figure 5(b)>

320

## 321 **5. Conclusions**

322 The promising properties of torrefied biomass provide a co-utilization option to  
323 incorporate large percentage biomass co-firing ratio in existing coal-fired boilers without  
324 major modifications. Torrefied biomasses are supposed to be a coal-like fuel used in  
325 industrial furnaces. Torrefied biomass is expected to have a better combustion stability  
326 than raw biomass and similar to that of coal. In this work, the studied two chars were  
327 produced from both raw and torrefied biomass in conditions similar to real combustion  
328 systems, i.e., high temperature and heating rate. The char samples were then combusted in  
329 the IPFR reactor by varying temperature, oxygen concentration and residence time.  
330 According to the results, the char produced from torrefied biomass was less reactive than  
331 the one from raw biomass. The impact of torrefaction on char conversion was significant  
332 in the early-stage char oxidation process, while torrefaction showed no effect on the final  
333 mass conversion. Oxygen concentration gives a relevant contribution when the char is  
334 oxidized at the same temperature. Finally, the char oxidation kinetic parameters were  
335 determined using a parameter optimization method, which minimizes a least squares-based  
336 objective function of the difference between model and experimental results. The predicted  
337 mass conversion showed a good agreement with experimental data, especially at high  
338 temperatures.

339

#### 340 **Acknowledgements**

341 The authors would like to thank the EU-Biofuels Research Infrastructure for Sharing  
342 Knowledge (BRISK) project and EU/EIT-KIC Innoenergy for the financial support of  
343 this work.

344

#### 345 **Nomenclature**

##### *Symbols*

$A$	Pre-exponential factor in Arrhenius expression, (1/s)
$C$	Diffusion constant, (m <sup>2</sup> /s)
$D$	Diffusion rate coefficient, (m <sup>2</sup> /s)
$d_p$	Particle diameter, (m)
$E$	Activation energy, (J/kmol)
$HR$	Heating rate, (K/min)
$k$	Kinetic constant, (kg/m <sup>2</sup> -Pa-s)
$m$	Mass, (kg)
$n$	Reaction order, (-)
$P$	Pressure (Pa)
$R$	gas universal constant, 8.3143 J/(mol-K);
$S$	Char specific surface, (m <sup>2</sup> /kg)
$T$	Temperature, (K)
$X$	Mass conversion, (-)
$a$	Particle size evolution exponent, (-)

### ***Abbreviations***

$ash$	Ash content of residue, (% <sub>db</sub> )
$daf$	Dry ash free basis
$db$	Dry basis
$FC$	Fixed Carbon content
IPFR	Isothermal Plug Flow Reactor
MC	Moisture content
PKS	Palm Kernel Shell, the parent material of torrefied biomasses
RB	Raw biomass, in this work RB refers PKS
RSME	Root Square Mean Error
TB	Torrefied biomass ( PKS after 30 min torrefaction at 300 °C)
VM	Volatile Matters

### ***Subscripts***

0	Initial value
$\infty$	Bulk gas
exp	Experimental
g	Gas phase
mod	Modeled
p	Particle
s	Surface

347 **References**

- 348 1. <http://www.irena.org/DocumentDownloads/Publications/IRENA-ETSAP%20Tech%20Brief%20E21%20Biomass%20Co-firing.pdf>.  
349
- 350 2. Li, J., et al., *Co-firing based on biomass torrefaction in a pulverized coal boiler with aim of 100% fuel switching*. Applied Energy, 2012. **99**(0): p. 344-354.  
351
- 352 3. Biagini, E. and L. Tognotti, *A generalized correlation for coal devolatilization kinetics at high temperature*. Fuel Processing Technology, 2014. **126**(0): p. 513-520.  
353
- 354 4. Lin, L., E. Gustafsson, and M. Strand, *Aerosol-based method for investigating biomass char reactivity at high temperatures*. Combustion and Flame, 2011. **158**(7): p. 1426-1437.  
355
- 356 5. Campbell, P.A., R.E. Mitchell, and L. Ma, *Characterization of coal char and biomass char reactivities to oxygen*. Proceedings of the Combustion Institute, 2002. **29**(1): p. 519-526.  
357
- 358 6. Jiménez, S., et al., *Kinetics of devolatilization and oxidation of a pulverized biomass in an entrained flow reactor under realistic combustion conditions*. Combustion and Flame, 2008. **152**(4): p. 588-603.  
359
- 360 7. Tapasvi, D., et al., *Kinetic Behavior of Torrefied Biomass in an Oxidative Environment*. Energy & Fuels, 2013. **27**(2): p. 1050-1060.  
361
- 362 8. Fisher, E.M., et al., *Combustion and gasification characteristics of chars from raw and torrefied biomass*. Bioresource Technology, 2012. **119**(0): p. 157-165.  
363
- 364 9. Arias, B., et al., *Influence of torrefaction on the grindability and reactivity of woody biomass*. Fuel Processing Technology, 2008. **89**(2): p. 169-175.  
365
- 366 10. Lin, L. and M. Strand, *Investigation of the intrinsic CO<sub>2</sub> gasification kinetics of biomass char at medium to high temperatures*. Applied Energy, 2013. **109**(0): p. 220-228.  
367
- 368 11. Li, J., et al., *High-temperature rapid devolatilization of biomasses with varying degrees of torrefaction*. Fuel, 2014. **122**(0): p. 261-269.  
369
- 370 12. Branca, C. and C. Di Blasi, *Combustion Kinetics of Secondary Biomass Chars in the Kinetic Regime*. Energy & Fuels, 2010. **24**(10): p. 5741-5750.  
371
- 372 13. Biagini, E., M. Simone, and L. Tognotti, *Characterization of high heating rate chars of biomass fuels*. Proceedings of the Combustion Institute, 2009. **32**(2): p. 2043-2050.  
373
- 374 14. Li, J., et al., *Flame characteristics of pulverized torrefied-biomass combusted with high-temperature air*. Combustion and Flame, 2013. **160**(11): p. 2585-2594.  
375
- 376 15. Li, J., et al., *Process simulation of co-firing torrefied biomass in a 220 MWe coal-fired power plant*. Energy Conversion and Management, 2014. **84**(0): p. 503-511.  
377
- 378 16. Sheng, C. and J.L.T. Azevedo, *Estimating the higher heating value of biomass fuels from basic analysis data*. Biomass and Bioenergy, 2005. **28**(5): p. 499-507.  
379
- 380 17. Biagini E., B.F., Bonvicini G., Coraggio G., Tognotti L., *Advanced Characterization of Biofuels for Combustion and Gasification Plants*. CHEMICAL ENGINEERING TRANSACTIONS, 2014. **37**: p. 6.  
381
- 382
- 383 18. Karlström, O., et al., *Multivariable optimization of reaction order and kinetic parameters for high temperature oxidation of 10 bituminous coal chars*. Combustion and Flame, 2011. **158**(10): p. 2056-2063.  
384
- 385
- 386 19. Murphy, J.J. and C.R. Shaddix, *Combustion kinetics of coal chars in oxygen-enriched environments*. Combustion and Flame, 2006. **144**(4): p. 710-729.  
387
- 388 20. Ballester, J. and S. Jiménez, *Kinetic parameters for the oxidation of pulverised coal as measured from drop tube tests*. Combustion and Flame, 2005. **142**(3): p. 210-222.  
389
- 390 21. Toporov, D.D., *Chapter 4 - Mathematical Modelling and Model Validations*, in *Combustion of Pulverised Coal in a Mixture of Oxygen and Recycled Flue Gas*, D.D. Toporov, Editor. 2014, Elsevier: Boston. p. 51-97.  
391
- 392
- 393 22. Li, J., et al., *Volumetric combustion of biomass for CO<sub>2</sub> and NO<sub>x</sub> reduction in coal-fired boilers*. Fuel, 2012. **102**(0): p. 624-633.  
394



- 395 23. Karlström, O., et al., *Comparing reaction orders of anthracite chars with bituminous coal chars at high*  
396 *temperature oxidation conditions*. Proceedings of the Combustion Institute, 2013. **34**(2): p.  
397 2427-2434.  
398
- 399

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**Table 1. Analysis of pulverized biomass.**

	Proximate analysis, wt%					Ultimate analysis, wt%			
	$MC^{ur}$	$VM^{db}$	$FC^{db}$	$Asb^{db}$	$LHV^{db}$ (MJ/kg)	$C^{db}$	$H^{db}$	$O^{db}$	$N^{db}$
RB	7.20	72.78	22.99	4.23	17.28	51.83	6.28	37.22	0.44
RB-char	/	21.44	62.18	16.38	/	53.60	2.25	27.17	0.60
TB	5.10	49.92	41.58	8.50	25.00	60.67	4.33	25.93	0.57
TB-char	/	16.27	68.59	15.14	/	67.54	2.53	14.17	0.62

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**Table 2. Resume of the char combustion tests performed in the IPFR.**

Temp. (°C)	O <sub>2</sub> (vol. %)	Residence time (ms)						
		30	50	100	150	300	500	600
900	3	/	/	/	/	/	/	TB-char
900	4	RB-char	RB-char	/	RB-char	RB-char	RB-char	/
900	6	/	/	/	/	TB-char	/	TB-char
900	8	/	/	/	RB-char	RB-char	RB-char	/
900	9	/	/	TB-char	/	TB-char	/	TB-char
1200	4	RB-char	RB-char	RB-char	RB-char	RB-char	RB-char	/

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Table 3. High temperature char combustion: kinetic parameters.

	$A$ [kg/m <sup>2</sup> sPa <sup>n</sup> ]	$E$ [kJ/mol]	$n$ [-]	RSME [-]
RB-char	0.3900	47.5	0.29	4.50%
TB-char	0.0037	60.0	0.80	8.60%

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**Figure captions:**

407 Figure 1. Scheme of the Isothermal Plug Flow Reactor (IPFR).

408 Figure 2. Particle size distributions of RB (PKS) and RB-char.

409 Figure 3. Mass conversion during char oxidation tests at different oxygen concentrations (a. RB-  
410 char; b. TB-char).

411 Figure 4. Arrhenius plots for studied RB-char and TB-char and compared with referenced chars.

412 Figure 5. Comparison between modeled and measured mass conversions (a. RB-char; b. TB-char).