

Impact of KCI impregnation on single particle combustion of wood and torrefied wood

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1	Impact of KCl Impregnation on Single Particle Combustion of Wood and
2	Torrefied Wood
3	
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12 Highlights

- 13 We study combustion of raw and torrefied wood spheres with varying K content.
- 14 Ignition time and devolatilization time depend mostly on fuel particle mass.
- 15 Both char yield and reactivity influence char conversion time.
- Potassium promotes char yield and char reactivity of raw and torrefied wood.
- 17 Torrefaction increases char yield but does not influence char reactivity.

Abstract 18

19	In this work, single particle combustion of raw and torrefied 4mm wood particles with different
20	potassium content obtained by KCl impregnation and washing was studied experimentally under a
21	condition of 1225°C, 3.1% O ₂ and 26.1% H ₂ O. The ignition time and devolatilization time
22	depended almost linearly on the fuel particle mass. The char conversion time was influenced by
23	both the char mass and char reactivity. Both KCl impregnation and torrefaction promoted char
24	yield, while washing slightly inhibited char formation. The char reactivity was increased by KCl
25	impregnation, decreased by washing, and unchanged by torrefaction. Compared to the raw wood
26	particle, the char conversion time was increased by torrefaction, decreased by washing, and almost
27	unchanged by KCl impregnation due to its promoting effect on both char yield and reactivity.

Keywords: Biomass; Torrefaction; Potassium; Combustion; Char yield; Char Reactivity 28

29 **1. Introduction**

30 Over the last decade, there has been an increasing interest in using torrefaction as pretreatment of 31 biomass because of its ability to increase hydrophobicity, grindability and energy density of biomass [1-3]. Torrefied biomass, also known as bio-coal, is a suitable coal substitute with lower SOx and net 32 33 CO₂ emissions [4]. It can be handled and combusted in a similar way as coal in pulverized-fuel power 34 plants without additional modifications of the plants [5]. Its potential of application in pulverizedfuel power plants and metallurgical processes has been evaluated [5-7]. However, unlike the 35 torrefaction process and its effect on upgrading of biomass fuels which have been extensively 36 37 investigated, studies on the combustion or gasification characteristics of torrefied biomass are still 38 limited [8-20]. 39 Char conversion is usually the rate limiting step in biomass combustion and gasification. It is 40 generally agreed that torrefaction can increase the char yield of biomass [9,13,14,21]. However, the effect of torrefaction on the char reactivity is still in discussion. Using a thermogravimetric analyzer 41 42 (TGA), Jones and coworkers reported that torrefaction reduced the reactivity of willow and 43 Eucalyptus chars produced in a drop tube reactor [9,22,23], with the chars produced from the torrefied biomass less reactive than the chars produced from the untreated biomass. Karlström et al. [21] 44 45 showed that after torrefaction, the char reactivity was increased, decreased and unchanged for straw, olive stones and pine shell, respectively. Our previous work [13] revealed that the chars from raw and 46 47 torrefied Schima wood had almost the same reactivity.

48	The observed discrepancy of the effect of torrefaction on char reactivity may be related to the ash
49	content and composition in biomass. The existing studies indicate that torrefaction does not influence
50	the char reactivity of biomass with low ash content [13, 21], while for biomass with high ash content,
51	it may either reduce or promote the char reactivity [9,21-23]. Among the ash forming species in
52	biomass, potassium species, such as KCl, can effectively increase both char reactivity [24,25] and
53	char yield [26,27-39]. In order to better understand the effect of torrefaction on char reactivity, it is
54	therefore of interest to evaluate how torrefaction can influence the char reactivity of biomass with
55	different potassium content. In addition, since potassium promotes both char yield and char reactivity,
56	it is of interest to investigate the effect of potassium on char conversion time under high temperature
57	conditions relevant for pulverized fuel combustion.
58	In the present work, we prepared wood particles with different potassium content by water washing,
59	impregnation with KCl, impregnation with KCl after washing, and washing after impregnation. The
60	raw and the torrefied wood particles with different potassium content were combusted in a single
61	particle reactor to evaluate the time for ignition, devolatilization and char conversion. In addition,
62	selected char particles were extracted from the single particle reactor to determine the char yield and
63	to analyze the char reactivity by thermogravimetric analysis.

2. Experimental

65 2.1 Feedstock

Spherical Schima wood particles with a diameter of ~4mm were used as feedstock. The particle size
was chosen to represent the largest particles used in pulverized fired biomass boilers [13,30]. The
gross calorific value, proximate analysis and ultimate analysis of the fuel are listed in Table 1. As can
be seen, Schima wood is low in ash and alkali and alkaline earth metal content.

The wood particles were machine-produced to ensure uniformity. Each particle was drilled with a 0.4mm driller, and then weighed on a microbalance (\pm 0.01 mg). The weight of the particles was averaging out at 20.0mg with a standard deviation of 1.5mg. The dimensions in three principal axes were measured using a handheld micrometer (\pm 0.05 mm) and the mean diameter was 3.94 mm with a standard deviation of 0.04 mm.

75 2.2 Sample pretreatment and torrefaction

76 Four ways of pretreatment consisting of washing, impregnation and their different combinations were applied to the Schima wood particles: (a) washing by deionized water at 333K for 3h under stirring; 77 (b) impregnation with 1.07 % (weight basis) KCl solution at room temperature for 3h; (c) washing 78 79 by deionized water at 333K for 3h under stirring, followed by impregnation with 1.07% KCl solution 80 at room temperature for 3h; (d) impregnation with 1.07 % KCl solution at room temperature for 3h, 81 followed by washing by deionized water at 333K for 3h under stirring. For all the treatments, less 82 than 0.3g wood sample was soaked in 150ml water or KCl solution. After washing/impregnation, all pretreated samples were dried in an oven at 333 K for about 12h. 83 Part of the raw and pretreated samples were torrefied in a tube oven in the presence of nitrogen at 84

85 290°C or 350°C for 1h, following the procedures described in [13].

86 All prepared particles were stored in sample bags before being tested in the single particle combustion 87 reactor. The samples, which were washed but not torrefied, were denoted as "washed raw". Similarly, 88 the sample "KCl+washed 290°C" denotes the Schima wood particles that were first impregnated by 89 KCl solution, and then washed and torrefied at 290°C for 1h, and so on.

90

2.3 Single particle combustion experiments

91 The combustion experiments were conducted in a single particle combustion (SPC) reactor shown in 92 Figure 1. The SPC reactor was designed to simulate the combustion conditions in a pulverized fuel-93 fired boiler. The setup mainly consists of a tube reactor, a burner, a gas supply system and a video 94 recording system. A burner with ninety-four injection nozzles were used to achieve good gas mixing 95 and led to a uniform flow distribution and a flat temperature profile in the center of the reactor, where 96 the biomass particles were placed. Four mass flow controllers (MFCs) controlled the flow to the burner, maintaining flow rates of 8.45 Nl/min, 5.20 Nl/min and 22.80 Nl/min for hydrogen, oxygen 97 and nitrogen, respectively. Before and after the experiment, the temperature and the oxygen 98 99 concentration (dry basis) in the center of the reactor were measured by a suction pyrometer and a 100 NGA2000 gas analyzer to be 1225±30°C and 4.1±0.05% O₂, respectively. Based on the stoichiometry, 101 the average O₂ concentration in the flue gas before and after water condensation were calculated to 102 be 3.1% and 4.2%, respectively. The difference between the calculated O₂ concentration (4.2%) and 103 the measured value (4.1%) is small. Thus the atmosphere that the particles were exposed to was then 104 taken to be the calculated 3.1% O₂ and 26.1% H₂O. A detailed description of the reactor and the experimental procedures can be found elsewhere [13,31]. 105

To start the combustion experiment, a ceramic protection tube was placed in the SPC reactor. Then a single fuel particle held by a small Al₂O₃ rod (0.3mm in diameter) was inserted coaxially into the ceramic protection tube. The video recording was initiated, and the protection tube was rapidly withdrawn, exposing the particle to combustion environment. The combustion process was recorded by a camera with a speed of 67 frames/second.

111 The time-interval between the withdrawal of the protective tube and the first visible light flash is 112 taken to be the ignition time, which is believed to be governed by the time required for moisture 113 evaporation and heating up of the particle to start devolatilization and produce a visible volatile flame 114 [32]. The devolatilization time is defined as the time duration of the visible volatile flame. After the 115 devolatilization stage, the remaining char was combusted until complete burnout, indicated by the 116 end of the shrinkage and a brightness change of the remaining residue. This time period is defined as 117 the char burnout time. We neglected a possible overlap of the devolatilization and char combustion stages, as the video images in the present study and previous studies [13,32] show a clear separation 118 119 between these two processes. For selected experiments, after the extinction of the volatile flame, the 120 char particle was quickly removed to the water cooled chamber of the SPC reactor and quenched by 121 1 Nl/min nitrogen. The char particles were weighted to determine the char yield.

122 **2.4 Thermogravimetric analysis (TGA)**

123 The char reactivity was analyzed in a TGA instrument (Netzsch STA 449F1 Jupiter). A small amount 124 of pulverized char sample (~2 mg) was first dried at 110°C for 10 minutes and then heated at

125 10° C/min to 800°C in an atmosphere of 5% O₂ and 95% N₂.

126 **3. Results and discussion**

127 **3.1 Ignition time**

128 Figure 2 shows the ignition time versus the fuel particle mass. The considerable scatter in ignition 129 time is attributed mainly to the experimental uncertainties. Nevertheless, there seems to be a 130 correlation between the ignition time and the sample mass, i.e. torrefied particles with smaller mass 131 appear to ignite more rapidly than raw particles. We believe this is primarily due to the higher heating 132 rate of the particles with smaller mass. In addition, compared to the raw wood particles, the torrefied samples have a darker surface and a lower moisture content, which would further shorten the ignition 133 134 time through promoting the radiation heat transfer and reducing the drying time. The impact of KCl 135 addition on ignition time is not obvious. However, for the raw wood particles, it seems that the ignition time is slightly shortened by the addition of KCl, possibly because devolatilization starts at 136 137 lower temperatures when KCl is added to biomass [27].

138 **3.2 Devolatilization time**

Figure 3 shows that the devolatilization time increases nearly linearly with increasing fuel particle mass, similar to our earlier findings in the same reactor [13]. The KCl impregnated particles seem to have slightly shorter devolatilization time, independent of whether they are washed or not before the impregnation. For the raw fuel, the effect of washing is insignificant on the devolatilization time, probably due to the low potassium content in the raw fuel. However, washing after impregnation is effective for restoring the devolatilization behavior to that observed for the raw and washed samples. In a previous study on single particle combustion, Jones et al. [32] concluded that the devolatilization time followed the sequence of K-impregnated <raw< water-washed. The present study shows that the catalytic effect of KCl remains even after the torrefaction pretreatment. However, samples with a high torrefaction degree, such as the "KCl 350C", "350C" and "washed 350C" samples, have similar devolatilization time for particles with similar masses.

3.3 Char yield

The char particles extracted from the SPC reactor were weighed, and the mass ratio of the residue over the untreated raw fuel particle was taken as the char yield and plotted in Figure 4. Based on the TGA results, the ash content in the residues is generally below 10 wt%. Thus, the tendencies shown in Figure 4 would be the same if the char yield was determined on ash-free basis.

155 Figure 4 indicates that the char yield of raw and KCl doped raw particles follows the expected order and increases with the potassium content in the samples, i.e., "KCl" (13.2%) > "washed+KCl" 156 (12.8%) > "raw" (9.6%) > "KCl+washed" (8.8%) > "washed" (6.9%). This finding is in agreement 157 158 with previous studies on biomass char formation [33-36], showing the promotion effect of potassium 159 on char formation. For samples torrefied at 290°C, the char yield follows the same order, i.e. KCl 160 (20.7%) > "washed+KCl" (18.5%) > "raw" (12.7%) > "KCl+washed" (12.3%) > "washed" (10.2%). 161 The char yield increased significantly after torrefaction, which is in agreement with our previous study [13] and a number of other studies on low-temperature thermal treatment [37-39]. Compared 162 to the non-torrefied samples, the increases of char yield after torrefaction at 290°C are 3.3%, 3.5%, 163 3.2%, 5.6%, 7.6% for the "Washed", "KCl+washed", "raw", "washed +KCl", and "KCl" samples, 164

respectively, correlating well with the expected order of potassium content in the samples. This indicates a synergistic effect of KCl addition and torrefaction on cross-linking and charring reactions to increase the char yield. In other words, increased torrefaction severity and increased potassium content would both lead to increased char yield. This synergistic effect resulted in a significant increase of char yield from 6.9% for washed raw sample to 25.4% for KCl impregnated sample torrefied at 350°C.

171 **3.5 Char reactivity**

172 Figure 5 shows the TG results of oxidation of selected chars. The results are given in dry ash free (daf) basis in order to facilitate a direct comparison of the char reactivity. The reactivities of KCl 173 174 doped chars, i.e. "Washed KCl 290C", "Washed KCl" and "KCl 290C", are quite similar, implying 175 that the effect of torrefaction and initial washing on char reactivity, compared to the effect of 176 potassium doping, is small. The reactivities of the "raw" char and "290C" char are almost identical, in agreement with our previous finding that torrefaction does not influence the char reactivity of 177 Schima wood [13]. This trend is also observed from the chars doped with KCl. Compared to the KCl 178 179 doped chars, the reactivities of the "raw" char and "290C" char are much lower, supporting the 180 significant catalytic effect of potassium on char oxidation, as reported extensively in literature 181 [32,40,41].

The washed samples, i.e. "Washed", "Washed 290C" and "KCl washed 290C", also exhibit similar char reactivities. However, their char reactivities are considerably lower than those of "raw" char and "290C" char. A possible explanation is that washing removes ash forming elements (e.g. potassium)

in biomass that can catalyze char oxidation, resulting in lower char reactivity. Similar results havebeen observed for straw and washed straw [27].

187 **3.6 Char burnout time**

- 188 Figure 6 provides an overview of the char burnout time versus the char mass for different samples.
- To facilitate the evaluation of the results, the samples are grouped into: 1) samples produced from raw Schima wood, including "raw", "290C", "350C"; 2) samples produced from KCl impregnated Schima wood, including "KCl raw", "KCl 290C", "KCl 350C", "washed+KCl", "washed+KCl
- 192 290C"; 3) samples produced from washed Schima wood, including "washed raw", "washed 290C",
- 193 "washed 350C", "KCl+washed", "KCl+washed 290C".
- For each group of samples, it is observed that the char oxidation time increases with the degree torrefaction, i.e. in the order of non-torrefied sample, sample torrefied at 290°C, and sample torrefied at 350°C. This is primarily because torrefaction can promote the char yield, resulting in heavier char particle that requires longer combustion times. A similar tendency has been observed in our earlier work [13].
- Comparing different groups of samples with similar char mass, it is observed that the char burnout time generally increases in an order of group 2, group 1 and group 3. This tendency is consistent with the expected char reactivity in these groups, as illustrated in Figure 5. For char samples with similar mass, the burnout time decreases with increasing char reactivity, indicating that the char conversion is kinetically influenced under the experimental condition ($1225^{\circ}C$, 3.1% O₂ and 26.1% H₂O). This

further suggests that gasification by H₂O would play an important role, as the char+O₂ reaction is
 expected to be diffusion controlled under the experimental condition.

206 Comparing the group 1 and group 2 samples, it can be seen that although KCl impregnation increases 207 the char mass considerably both for raw samples and torrefied samples, the char conversion time is 208 almost unchanged due to the increased char reactivity. On the other hand, a comparison of group 1 209 and group 3 implies that although washing reduces slightly the char mass/yield, the conversion time 210 is considerably increased due to the reduced char reactivity.

211 **4. Conclusion**

212 Single particle combustion of wood particles pretreated by KCl impregnation, washing, torrefaction and their different combinations was studied experimentally under a condition of 1225°C, 3.1% O₂ 213 214 and 26.1% H₂O. The ignition time and devolatilization time depend almost linearly on the fuel particle 215 mass. The char conversion time is influenced both by the mass and the reactivity of char particles. 216 The char yield is promoted by KCl impregnation and torrefaction, while slightly inhibited by washing. 217 The char reactivity is increased by KCl impregnation, decreased by washing, and almost unchanged 218 by torrefaction. Compared to the raw wood particle, the char conversion time under the current 219 experimental condition is increased by torrefaction, decreased by washing, and almost unchanged by 220 KCl doping due to the combined effect of promoting both char yield and reactivity.

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Parameter	Unit	value
Gross calorific value	MJ/kg (as received)	18.7
Moisture	wt% (as received)	5.6
Ash	wt% (as received)	1.2
Volatiles	wt% (as received)	75.6
Fixed carbon	wt% (as received)	17.7
Carbon (C)	wt% (dry basis)	49.6
Hydrogen (H)	wt% (dry basis)	6.1
Nitrogen (N)	wt% (dry basis)	< 0.2
Sulphur (S)	wt% (dry basis)	< 0.1
Chlorine (Cl)	wt% (dry basis)	< 0.2
Aluminum (Al)	mg/kg(dry basis)	260
Calcium (Ca)	mg/kg(dry basis)	590
Iron (Fe)	mg/kg(dry basis)	110
Potassium (K)	mg/kg(dry basis)	850
Magnesium (Mg)	mg/kg(dry basis)	210
Sodium (Na)	mg/kg(dry basis)	< 10
Phosphorus (P)	mg/kg(dry basis)	2500
Silicon (Si)	mg/kg(dry basis)	1100

322 Table 1. Gross calorific value, proximate and ultimate analysis of Schima wood.





Figure 1. Schematic diagram of the SPC reactor.





326 Figure 2. Ignition time of raw and pretreated particles as a function of the fuel particle mass in the

327 SPC reactor (1225°C, 3.1% O₂ and 26.1% H₂O). Red, blue and black symbols denote the washed





329

330 Figure 3. Devolatilization time of raw and pretreated particles as a function of the fuel particle mass

331 in the SPC reactor (1225°C, 3.1% O₂ and 26.1% H₂O). Red, blue and black symbols denote the

332 washed samples, KCl impregnated samples, and sample without these two pretreatment, respectively.





335 Figure 4. The char yield of pretreated and untreated fuel particles. Each value is the mean of five

individual experiments in the SPC reactor (1225°C, 3.1% O₂ and 26.1% H₂O), and error bars

337 indicate standard deviation.



340 Figure 5. TG results of the oxidation of selected chars obtained from the SPC reactor. The results





342

343 Figure 6. Char burnout times versus the char mass obtained in the SPC reactor (1225°C, 3.1% O₂

and 26.1% H₂O). Red, blue and black symbols denote the washed samples, KCl impregnated

345 samples, and sample without these two pretreatment, respectively.