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# Towards understanding the role of K

# <sup>2</sup> during biomass steam gasification

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# 12 Highlights

- Rice husk steam gasification was conducted with K<sub>2</sub>CO<sub>3</sub> added without direct contact
- A two-compartment thermobalance crucible was used to assess the gas phase
- 15 influence
- The K-catalysis mechanisms involve the gas phase, most likely with formed KOH(g)
- Both pyrolysis and steam gasification steps are catalyzed by K
- The K-catalysis competes with the reaction of K with SiO<sub>2</sub> inherent to biomass

# 19 Abstract

- 20 Steam gasification is known to be catalyzed by K. However, the exact mechanisms are not
- 21 identified to this day. In the present study, the catalytic influence of K on biomass steam

22 gasification and its interaction with Si was investigated. The study was conducted through thermogravimetric analysis (TGA) on rice husks as a Si-rich biomass and  $\rm K_{2}\rm CO_{3}$  as a model 23 24 K-compound. Experiments were conducted in three different configurations: biomass or 25 inorganic compound alone; mixtures of biomass and inorganic powders; biomass and 26 inorganic compound without contact in a two-compartment crucible. It was shown that K has 27 a catalytic effect on both the pyrolysis and the gasification steps. These effects occur even 28 when the K-compound is not in direct contact with the biomass. Therefore, it demonstrates 29 that the mechanisms involve the gas phase through the volatilization of a K-compound, most 30 likely KOH(g). However, the observed catalytic effect on rice husks was weaker than the 31 effect obtained in the case of beech wood, a Si-poor and more generally ash-poor biomass, 32 under the same conditions. It shows that there is a competition between i) the influence of K 33 on the biomass pyrolysis and char gasification kinetics and ii) the interaction of K with SiO<sub>2</sub> 34 inherent to the biomass.

## 35 Keywords

36 steam gasification; reaction kinetics; catalysis; potassium; silica; rice husk

# 37 **1. Introduction**

38 To develop bioenergy production, agricultural residues represent an interesting source as 39 they have an important availability and do not decrease the surface of land available for food 40 production. However, agricultural residues can be problematic during the gasification process 41 due to high inorganic contents compared to woods. Their main inorganic elements are 42 generally Si, K and Ca [1]. Such elements can be detrimental to the gasification process by 43 inducing slag formation and/or agglomeration of the gasifier bed [2,3]. Moreover, they can 44 have a strong effect on the reaction kinetics which may influence the biomass residence time 45 inside the reactor and therefore the gasifier design. In this context, the residence time must 46 be adapted either to reach the highest conversion possible or to purposely have a remaining

47 char that can be burnt in order to bring the required heat to the process, depending on the48 gasifier technology.

Alkali and alkaline earth metals (AAEMs) tend to have a catalytic effect that enhances

50 biomass gasification kinetics. More specifically, alkali metals, and in particular K which is 51 more present in biomass than Na [1], are reported to be more active than alkaline earth 52 metals. The catalytic activity of AAEMs was reported to be, in decreasing order, K, Na, Ca 53 and Mg [4–6]. This ranking has been determined for materials with various ash contents. 54 Catalytic gasification uses this effect to improve the gasification process. Catalysts usually 55 studied are compounds of AAEMs as well as some heavy metal compounds such as Fe-56 compounds and Ni-compounds [7,8]. In the case of K-catalysis, added compounds are mostly K<sub>2</sub>CO<sub>3</sub> and KOH which are compounds naturally found in biomass [7]. KNO<sub>3</sub>, KCl or 57  $K_2SO_4$  have also been studied [9–11]. Authors have found the following relative activity: KOH 58 ~  $K_2CO_3$  ~  $KNO_3$  >  $K_2SO_4$  > KCI [12–14]. They have also demonstrated that under steam the 59

60 intermediate species KOH was formed from all salts [14].

49

61 Several methods have been used in the literature to highlight the catalytic effects of these 62 inorganic elements. Studies have used raw biomass or biomass char [15-24], biomass or 63 char washed with deionized water and/or with acid to remove the inherent inorganic matter 64 [5,10,20,25-28], or biomass or char with added inorganic compounds [6,9-12,20,26,27,29-65 37]. These latter ones were prepared through solid mixing [26,29,30,35,37] or impregnated 66 with a solution containing the inorganic compound [6,9–12,27,30–37]. Impregnation has 67 been the major addition method used in literature since it is simple to carry out and allows a 68 close contact between the inorganics and the biomass.

Few authors have compared the effects of various addition methods. Elliott *et al.* [37] and Bach-Oller *et al.* [30] have observed a slightly stronger catalytic effect of  $K_2CO_3$  in the case of impregnation compared to dry mixing. Authors have supposed an activity through the gas phase and attributed the slight decrease in activity with dry mixing to a lower inorganic

compound volatilization due to mass transfer limitations. However, to our knowledge, no
available investigations have been conducted to identify the gas phase effect of K-catalysts.
In addition, several studies in the literature have examined the catalytic CO<sub>2</sub> gasification of
biomass species having a low inorganic content [9-12, 25, 31, 33, 35-37].
In this context, the present work aims to contribute to the understanding of the K influence on
biomass steam gasification in the case of a Si-rich biomass, in order to better understand the

79 K behavior, its effect through the gas phase and its potential interaction with the inherent

80  $SiO_2$  of the biomass.

# 81 2. Materials and Methods

# 82 **2.1. Materials**

83 The selected biomass for this study was rice husks (RH) from Camargue, France, a Si-rich 84 biomass. Its behavior was compared to sunflower seed shells (SSS) from Bordeaux, France, 85 a Si-poor and K-rich biomass, and beech wood (BW) from France, Si-poor and more 86 generally ash-poor biomass. The samples were ground below 200 µm in a Pulverisette 14 87 rotor mill (FRITSCH, Idar-Oberstein, Germany). The ash content and inorganic element 88 composition of the samples were measured according to solid fuel standards NF EN 14775 89 [38] and NF EN ISO 16967 [39], respectively. The properties of each biomass are 90 summarized in Table 1.

# 91 Table 1. Composition of rice husks and beech wood (in dry basis).

Property	Unit	Rice husks (RH)	RH + 7wt% K <sub>2</sub> CO <sub>3</sub>	Sunflower seed shells (SSS)	Beech wood (BW)
Ash at 550 °C	wt%	14.6	20.3**	3.3	0.6
С	wt%	41.6	39.0	50.2	45.9
Н	wt%	5.2	4.7	6.5	6.2
O*	wt%	45.1	35.6	40.6	47.1
Ν	wt%	0.5	0.50	0.7	0.3

S	wt%	0.1	0.09	0.1	0.058
CI	wt%	0.1	0.09	0.1	0.005
Si	mg.kg <sup>-1</sup>	63955	59518	194	115
К	mg.kg <sup>-1</sup>	5822	44632	9729	910
Ca	mg.kg <sup>-1</sup>	1797	1672	4489	2516
Mg	mg.kg <sup>-1</sup>	659	613	1838	475
Р	mg.kg <sup>-1</sup>	981	913	896	75
Na	mg.kg <sup>-1</sup>	413	384	9	3.6
Al	mg.kg <sup>-1</sup>	228	212	150	12
Fe	mg.kg <sup>-1</sup>	192	179	1099	34
Main inorganic elements		Si – K – Ca	Si – K – Ca	K – Ca –Mg	Ca – K – Mg

\*Total oxygen calculated by difference with all other elements.

\*\*Theoretical, calculated as:  $%K_2CO_3 + (100 - %K_2CO_3) \times Ash of rice husks$ 

92

A model K-compound was selected for the study: potassium carbonate ( $K_2CO_3$ ). It was selected since it can be found naturally in biomass [40]. Merck  $K_2CO_3$  EMSURE® ACS, ISO, Reag. Ph. Eur,  $\geq$  99.0 % was used. The  $K_2CO_3$  powder was ground from around 500 µm to <100 µm with a mortar and pestle, in a N<sub>2</sub> atmosphere to prevent its hydration. It was then kept in a vacuum desiccator.

# 98 **2.2. Experimental installation and procedure**

99 The steam gasification behavior of the samples was investigated through thermogravimetric

100 analysis (TGA). Experiments were carried out at atmospheric pressure using a Setsys

101 thermobalance (SETARAM, Caluire, France) coupled with a Wetsys steam generator

102 described elsewhere [16].

103 A home-made crucible was designed for this present investigation. It is a crucible consisting

104 of a cylindrical platinum crucible of 2 mm height and 10 mm diameter with a partition of the

same height along its diameter made up of platinum with 5% gold (**Figure 1**). The feed gas is

106 injected from below the crucible.



108 Figure 1. Divided crucible (here containing RH and K<sub>2</sub>CO<sub>3</sub>).

109 Experiments were conducted in three different configurations: biomass or inorganic

110 compound alone; mixtures of biomass and inorganic powders; biomass and inorganic

- 111 compound without direct contact in the crucible.
- 112 Inorganic concentrations were expressed as a percentage of the total sample:

$$\% Inorganic = \frac{m_{Inorganic}}{m_{Inorganic} + m_{Biomass}} \tag{1}$$

113 With  $m_{Inorganic}$  the mass of inorganic added and  $m_{Biomass}$  the mass of biomass.

114 Mixtures of biomass and inorganic powders were prepared with approximately 140 mg of

biomass and the necessary mass of inorganic compound to obtain the desired concentration.

116 The two powders were added to a plastic flask with a few glass beads of 3 mm diameter.

117 Homogeneous mixing was obtained by shaking the flask by hand for around one minute.

118 The TGA sample mass was determined through preliminary experiments on pure biomass to

- 119 be in the chemical regime in this configuration.
- 120 Approximately 15 mg of sample were heated at 24 °C.min<sup>-1</sup> until 450 °C under 0.05 L.min<sup>-1</sup>
- 121  $N_2$  and kept for 60 min at this temperature. They were then heated at 24 °C.min<sup>-1</sup> until
- 122 800 °C and kept at this temperature until the end of the experiment. Samples were swept by
- 123 N<sub>2</sub> after the final temperature was reached to ensure pyrolysis completion and mass stability
- 124 (12 min). Gas was then switched to a mixture of 20 vol% H<sub>2</sub>O in N<sub>2</sub> with the same gas flow of

125 0.05 L.min<sup>-1</sup>. This marked the beginning of the gasification step. The experiment was

126 completed when the mass was stabilized, i.e. when gasification was finished and only ashes127 remained.

128 Experiments were conducted at least in duplicates to verify repeatability. Only one of the

129 repetitions is plotted.

130 Results were plotted as the normalized mass:

$$\frac{m(t)}{m_i},\tag{2}$$

131 where  $m_i$  and m(t) are the mass of initial raw biomass and the mass measured at the time t, 132 respectively.

Gasification solid conversion was defined from the mass loss measured as a function of timeduring TGA by using the following expression:

$$X(t) = \frac{m_{ichar} - m(t)}{m_{ichar} - m_f},$$
(3)

where  $m_{ichar}$  and  $m_f$  are the mass of char before gasification (at the time of steam injection) and the mass measured at the end of gasification (remaining ash), respectively.

137 The gasification rate was then defined as the variation of conversion versus time:

$$r(t) = \frac{dX}{dt}.$$
(4)

138 An average reactivity between two values of conversion  $X_1$  and  $X_2$  was also defined:

$$r_{X_1-X_2} = \frac{\int_{t_{X_1}}^{t_{X_2}} \frac{r(t)dt}{1-X(t)}}{t_{X_2}-t_{X_1}}.$$
(5)

There is no standardized definition for the reactivity [41]. In this study, the average reactivity
was calculated between 1 and 80% conversion as in several investigations in literature

141 [16,19,41]. This choice allowed to obtain a trend that was not affected by the particular

142 phenomena that can occur at high conversion values.

Additionally, the derivative thermogravimetric (DTG) curve was obtained with the followingequation:

$$DTG(t_n) = -\frac{m_{n+1} - m_{n-1}}{t_{n+1} - t_{n-1}}.$$
(6)

145 where  $t_{n-1}$ ,  $t_n$  and  $t_{n+1}$  are consecutive time steps,  $m_{n-1}$  is the mass measured at time  $t_{n-1}$ 146 and  $m_{n+1}$  is the mass measured at time  $t_{n+1}$ .

To allow comparison between the different samples, results from pyrolysis and gasification of samples with added  $K_2CO_3$  (mixtures and without contact) were corrected by subtracting the equivalent mass profiles of pure  $K_2CO_3$  to the measured mass profiles. An example is given in **Figure 2**. The black curve is the mass as directly measured in TGA. The orange curve is the pure  $K_2CO_3$  profile that is subtracted. Finally, the blue curve is the equivalent char mass with the  $K_2CO_3$  subtracted. It is this last mass that is used in further data treatments and interpretations.



- 155 **Figure 2. Measured mass, equivalent char mass (as used in further interpretations)**
- 156 and corresponding pure  $K_2CO_3$  mass.
- 157 **2.3. Characterization techniques**
- 158 **2.3.1. Optical microscopy**
- 159 Optical microscopy was used to observe the sample morphology before and after reaction.
- An Olympus SZX12 microscope was used with a ToupTek Photonics ToupCam camera andthe associated ToupView software.
- 162 **2.3.2. Scanning electron microscopy coupled to energy dispersive X-ray**
- 163spectroscopy
- 164 Scanning electron microscopy coupled to energy dispersive X-ray spectroscopy (SEM–EDX)
- 165 was used to study the morphology and the surface elemental composition of the TGA
- 166 residues. A Philips XL30 microscope was used with a 15 kV electron beam. Back-scattered
- 167 electrons (BSE) detection was used. It creates a contrast related to atomic number. Samples
- 168 were placed on graphite tape and graphitized before analysis.
- 169 **2.4. Thermodynamic equilibrium simulation method**
- 170 Calculations at thermodynamic equilibrium were performed to simulate the behavior of  $K_2CO_3$ 171 under steam at 800 °C.
- 172 They were performed by minimization of the Gibbs free energy of the total system with the
- 173 FactSage 7.2 software and the databases FTsalt and FactPS [42,43].
- 174 The steam gasification procedure applied to pure K<sub>2</sub>CO<sub>3</sub> was simulated at thermodynamic
- equilibrium. The initial data are listed in **Table 2**. K<sub>2</sub>CO<sub>3</sub> initial mass was slightly different from
- 176 the experimental initial mass put in the TGA since calculations dealt with the gasification step
- 177 and there was a slight mass loss before gasification (**Figure 4**).
- 178 The gas flow is constant, therefore the effect of time is simulated by the effect of the initial
- 179 gas mass [44].

Temperature	800 °C		
Initial solid	K <sub>2</sub> CO <sub>3</sub> 0.54 mg 0.70 mg 1.23 mg 1.73 mg 2.99 mg		
Initial gas	0 to 1.5 g N <sub>2</sub> + 0 to 0.241 g H <sub>2</sub> O (0.5 L.min <sup>-1</sup> , 0 to 30 min)		

### 180 **Table 2. Initial data for the thermodynamic equilibrium calculations.**

# 181 3. Results and Discussion

# 182 **3.1. Pure biomass steam gasification**

183 The results obtained during the pyrolysis and steam gasification of the pure biomass

184 samples are plotted in **Figure 3**.



Figure 3. TGA of rice husks (RH), sunflower seed shells (SSS) and beech wood (BW)
 presented as a. normalized mass versus time and b. gasification solid conversion rate
 versus gasification solid conversion.

The three biomass species show similar behaviors during pyrolysis. Significant mass loss
occurs below 450 °C, in agreement with literature [45]. Then significantly different behaviors

191 are observed during gasification. More than six hours are required to gasify rice husks

192 (average reactivity  $r_{1-80\%} = 1.4\%$ .min<sup>-1</sup>) while gasification of sunflower seed shells require less 193 than 20 minutes (average reactivity  $r_{1-80\%} = 30.3\%$ .min<sup>-1</sup>). Rice husks gasification rate is 194 continuously decreasing whereas sunflower seed shells has a constant and then decreasing 195 conversion rate. Beech wood has an intermediate behavior with a gasification time of around 196 40 minutes (average reactivity  $r_{1-80\%} = 4.9\%$ .min<sup>-1</sup>) and a gasification rate that is constant and 197 then increases. Another work showed that these significant differences are mainly due to the 198 inorganic composition of the biomass species, and not to the char physical properties [46].

# 199 **3.2.** Pure K<sub>2</sub>CO<sub>3</sub> thermogravimetric analysis (TGA)

The pyrolysis and gasification procedure was applied to various mass samples of K<sub>2</sub>CO<sub>3</sub>.
Figure 4 shows the mass evolution versus time.



Figure 4. Mass evolution versus time of various initial masses of K<sub>2</sub>CO<sub>3</sub> alone during
 the pyrolysis and gasification procedure. Full line: measurement. Dotted line:
 thermodynamic equilibrium simulation. Dashed line: mathematical model fitting
 experimental data.

A very low volatilization of  $K_2CO_3$  is observed during the pyrolysis step. On the contrary, the sample is completely volatilized when steam is injected. This behavior is in accordance with

209 literature [47–49]. The volatilization time depends on the initial mass varying from 40 min to
210 2h for samples between 0.68 and 3.20 mg.

In order to explain this behavior, a thermodynamic equilibrium simulation with pure  $K_2CO_3$ was conducted. Under thermodynamic equilibrium conditions, in the case where  $K_2CO_3$  is in an inert atmosphere, it is slightly volatilized as K(g) and  $CO_2(g)$ . On the opposite, in the case where  $K_2CO_3$  is in a steam atmosphere, it is largely volatilized as KOH(g). These volatilized species can be explained by the following reactions [50,51]:

 $K_2 C O_3(s) = 2 K(g) + C O_2(g) + 0.5 O_2(g)$ (7)

$$K(g) + H_2 O(g) = KOH(g) + 0.5 H_2(g)$$
(8)

The simulated mass evolution of  $K_2CO_3$  during the gasification step is plotted in dotted lines in **Figure 4**. The simulation predicts that the whole amount of  $K_2CO_3$  volatilizes in 2 to 20 minutes in thermodynamic equilibrium conditions. It shows mass transfer limitations during  $K_2CO_3$  volatilization. They could be due to the configuration of the crucible in the carrier gas and/or to the  $K_2CO_3$  particle size.

221 The mass evolution of K<sub>2</sub>CO<sub>3</sub> as a function of time and initial mass was modeled through a 222 second-degree polynomial of general equation as shown in Figure 4. The model is 223 presented in Supplementary Material. Here, the objective was only to fit experimental results 224 in the TGA configuration to be able to extrapolate the results to other initial masses in the 225 studied range. It has not been attempted in the present work to give a signification to these 226 coefficients as in the literature [48]. For example, Knudsen et al. [48] have modelled the 227 evaporation of pure K-compounds based on mass transfer for a carrier gas sweeping the 228 crucible parallel to its surface, on the contrary to the TGA configuration where the gas is 229 perpendicular. Authors have assumed K transport was controlled by diffusion through an 230 external gas film. They have used mass transfer correlations to obtain the coefficients.

### **3.3.** Interactions between materials

232 Pyrolysis and gasification of rice husks-slow-gasifying biomass-were carried out with 233 K<sub>2</sub>CO<sub>3</sub> added in two configurations: mixed and without contact in a divided crucible. Both configurations had approximately the same proportion of added K<sub>2</sub>CO<sub>3</sub>, i.e. 7 wt%. This 234 235 proportion corresponds to 4 wt% of K in the initial mixture (Table 1). Such a high content 236 (see natural contents < 1 wt% of K in raw biomass, in **Table 1**) was selected to clearly 237 observe the phenomena. Results were compared to rice husks and sunflower seed shells 238 alone. The evolution with time of the normalized mass of the samples-including ashes-and 239 the DTG curves are presented in Figure 5. As stated in the Materials and Methods section 240 (section 2.2), the measured mass profiles were corrected by subtracting the equivalent mass 241 profiles of pure inorganic compound.



The apparent difference between the two biomass species during low temperature pyrolysis is due to the difference of ash content. When looking at the DTG curves it can be seen that all samples with and without  $K_2CO_3$  have the same behavior during low temperature pyrolysis, i.e. a first very high peak below 450 °C (**Figure 5**.b). It corresponds to the degradation of the biomass macromolecular constituents [52].

249	Above 450 °C, the curves indicate that $K_2CO_3$ addition has an effect on both pyrolysis and
250	gasification steps. This effect is discussed in the following sections.

# 3.3.1. Influence of K<sub>2</sub>CO<sub>3</sub> addition on the pyrolysis reaction

Though the present study focuses on the gasification reaction, an effect of K addition already appeared during the pyrolysis step at high temperature, before steam injection. Since the char formed during pyrolysis is the starting material of the gasification reaction, it is important to also investigate these phenomena.

256

# 3.3.1.1. High temperature pyrolysis phenomena observation

Figure 6 is a zoom of the high temperature pyrolysis from Figure 5. It shows the evolution of
the normalized mass and DTG of the samples during the 30 minutes preceding steam
injection, i.e. during heating from 450 to 800 °C.



Figure 6. a. TGA and b. DTG of RH with and without added K<sub>2</sub>CO<sub>3</sub> and of SSS. Zoom on the high temperature pyrolysis. Full line: alone. Dotted line: mixed. Dashed line: without contact. Oscillations observed in b. are due to the experimental set-up and are considered as not significant.

Above 450 °C, a second DTG peak is observed around 82 min and 500 °C for all samples with and without added  $K_2CO_3$ . It corresponds to the typical mass loss observed when heating the samples between 450 and 800 °C, as seen with pure biomass, and is due to a residual char devolatilization.

269 However, when K<sub>2</sub>CO<sub>3</sub> is added to rice husks (mixed and without contact), a third DTG peak 270 is observed close to the beginning of the 800 °C holding time. An additional experiment 271 where heating is conducted up until 1000 °C instead of 800 °C shows that the peak is maximum around 860 °C (see Supplementary materials). The effect is stronger when  $K_2CO_3$ 272 273 is mixed with rice husks. Nevertheless, it appears even if rice husks are not in contact with the added K<sub>2</sub>CO<sub>3</sub> which means it is related to the gas phase and probably attributed to K 274 275 volatilization. The stronger effect in the case of the mixture can then be explained by a higher 276 concentration of K-compound in the gas layer around the biomass in this case.

277

#### 3.3.1.2. Third DTG peak investigation during pyrolysis step

In order to determine the origin of this third DTG peak, the same experiment was conducted on rice husks with  $K_2CO_3$  added without contact but it was stopped after the pyrolysis step at 800 °C, i.e. before steam injection. Optical microscope observations of the crucible before and after the experiment are presented in **Figure 7**.



282

Figure 7. RH with K<sub>2</sub>CO<sub>3</sub> added without contact a. before and b. after pyrolysis until
 800 °C in the TGA, i.e. procedure stopped before steam injection.

Rice husk chars have no visual particularity at this scale. On the K2CO3 side, grains which 285 286 were initially white are covered with a black layer after pyrolysis until 800 °C and material 287 under each grain suggests a partial fusion. The black layer most likely is carbon deposited on 288 top of the inorganic residue. These observations are in agreement with literature where 289 higher char yields have been observed with K impregnation due to condensation of tars [53-290 55]. However, a competition between this char formation and tar cracking have been noted [54]. Regarding the residue under the black layer, it cannot be pure K<sub>2</sub>CO<sub>3</sub> (whose melting 291 292 point is 901°C [42] i.e. above the pyrolysis temperature) but a material with a lower melting 293 point. Since liquid formation is associated to a higher volatilization, it is in agreement with the 294 fact that the third DTG peak also occurs before the pure K<sub>2</sub>CO<sub>3</sub> melting point. These results indicate that a reaction occurs on the  $\rm K_{2}\rm CO_{3}$  side when it is in presence of biomass, even 295 296 without contact.

297 It is known that pyrolysis gases (CO<sub>2</sub>, H<sub>2</sub>O, CO, H<sub>2</sub>) and inorganic gases (H<sub>2</sub>S, NH<sub>3</sub>, HCI, 298 KCI, etc.) are released during biomass devolatilization [56,57]. Therefore, the liquid observed 299 at 800 °C could be due to the reaction of  $K_2CO_3$  with one of these gases.

The residue at 800 °C on the  $K_2CO_3$  side was analyzed by SEM-EDX and only K, C and O were detected. H cannot be detected by this methods.

Therefore  $K_2CO_3$  most likely reacts with  $H_2O(g)$  originating from biomass devolatilization. The residue is then a mixture of  $K_2CO_3$  and KOH where a core of  $K_2CO_3$  is at equilibrium with a liquid phase (solidified at ambient temperature).

The  $K_2CO_3$ -KOH phase diagram (see Supplementary Material) predicts that, at 800 °C, solid K<sub>2</sub>CO<sub>3</sub> is in equilibrium with a liquid for compositions up to 23.5mol% KOH. This is a reasonable composition that could have been obtained from the reaction with H<sub>2</sub>O(g) from the biomass devolatilization. It also predicts that a liquid phase can appear at 450 °C, the temperature of the first plateau of the TGA procedure. This behavior has been confirmed by an additional experiment where a higher mass loss of K<sub>2</sub>CO<sub>3</sub> was observed during high

temperature pyrolysis after it had been in contact with steam during the 450 °C plateau than
when it had only been in a N<sub>2</sub> atmosphere (see Supplementary Material).

Therefore, from these results, the third DTG peak can be attributed to the devolatilization of the carbon matrix catalyzed by a K-compound, probably, KOH(g), released to the gas phase from the K<sub>2</sub>CO<sub>3</sub> side of the crucible.

316 In literature, authors do not usually conduct pyrolysis at such high temperatures. Indeed, as

317 previously stated, the main mass loss occurs below 450 °C so studies are focused on that

318 temperature range. However, studies in the carbon activation literature [58] are in

accordance with the results from the present work where pyrolysis at high temperature in the

320 presence of a K-compound induces an additional mass loss, i.e. third DTG peak. However, in

321 the case of activated carbons the K-compound is added through impregnation of an aqueous

solution, or occasionally through dry mixing (Amoco process) [58], whereas in the present

323 study the effects are observed including when  $K_2CO_3$  is not in contact with the biomass.

For the first time it is here demonstrated that the effect occurs through the gas phase. The main explanation given in literature regarding the mechanism of action involves the intercalation of K followed by its explosive removal to form the pores [58].

327

# 3.3.2. Influence of $K_2CO_3$ addition on the gasification reaction

328

# 3.3.2.1. Gasification phenomena observation

Figure 8 shows the gasification solid conversion and conversion rate of rice husks with and without added  $K_2CO_3$  compared to that of sunflower seed shells. It is clearly seen that,  $K_2CO_3$ has an effect on the gasification step.



Figure 8. Gasification at 800°C of RH with and without added  $K_2CO_3$  and of SSS. a. Solid conversion as a function of time (for RH alone, three replicates are plotted which explains the apparent large line). b. Solid conversion rate as a function of the conversion.

337 As stated in the Materials and Methods section (see 2.2), the results were corrected by 338 subtracting the equivalent mass profiles of pure K<sub>2</sub>CO<sub>3</sub> to the measured mass profiles of the total sample. Therefore, if the rice husks and K2CO3 behaviors were independent, their mass 339 340 profiles would have been additive and the presented equivalent mass profile of rice husks 341 would have been similar to rice husks alone. Yet, the conversion profile of the sample of rice 342 husks and K<sub>2</sub>CO<sub>3</sub> mixed goes above 100%. These high values, which are not physically possible, occur around the time where the profile of pure  $K_2CO_3$  is subtracted. It means that it 343 344 is an effect of the mathematical treatment of the data, i.e. of the K<sub>2</sub>CO<sub>3</sub> profile subtraction, 345 and not a measured effect. In addition, both samples with added K<sub>2</sub>CO<sub>3</sub>, mixed and without 346 contact, have a sudden slope change approximately 50 min after steam injection, which 347 corresponds to the completion of the pure K<sub>2</sub>CO<sub>3</sub> volatilization that is subtracted to the 348 results. Moreover, both curves are above the curve of rice husks alone. This last difference compared to the curve of rice husks alone is significant even in the case where  $K_2CO_3$  is 349 350 added without contact. Indeed, Figure 8.a shows three replicates of the experiments on rice

husks alone that are all grouped compared to curves with added  $K_2CO_3$ . All the above observations show that there is an interaction between the biomass and the inorganic sample both when  $K_2CO_3$  is mixed and without contact. The behaviors of the samples cannot be assessed through the simple addition of the behaviors of the pure rice husks and  $K_2CO_3$ . This means that the equivalent rice husks profiles presented do not represent the real mass loss on the rice husks side. Therefore, quantitative assumptions cannot be drawn from these data but trends still can be analyzed.

When comparing the addition mode of  $K_2CO_3$ , it can be seen that mixing induces a stronger catalytic effect during gasification. However, even if it is weak, the effect of  $K_2CO_3$  without contact with rice husks is present. This demonstrates that it acts, at least partially, through the gas phase. The stronger effect in the case of the mixture can then be explained by a higher concentration of K-compound in the gas layer around the biomass in this case.

363

#### 3.3.2.2. Influence of the pyrolysis step on gasification

An additional experiment was designed in order to check if a reaction during pyrolysis influences the behavior during gasification. Pyrolysis of rice husks with added  $K_2CO_3$  without contact was carried out and the resulting char was gasified alone, after the residue on the  $K_2CO_3$  side was removed. Results are shown in **Figure 9**.





During this experiment, only char was gasified, therefore no subtraction of a K<sub>2</sub>CO<sub>3</sub> profile 371 372 was required. This explains that the curve does not have the sudden slope change like the 373 previous ones. It is seen directly that the gasification rate of rice husks is higher than for pure 374 RH alone while K<sub>2</sub>CO<sub>3</sub> is not present anymore during gasification. Its average reactivity 375 between 1 and 80% conversion increased from 1.4 to 2.2 %.min<sup>-1</sup>. To our knowledge, this 376 result has never been demonstrated in the literature. It indicates that the interaction between K<sub>2</sub>CO<sub>3</sub> and char during the pyrolysis step catalyzes a subsequent gasification. Moreover, this 377 378 effect occurs without contact between the biomass and the inorganic compound, therefore 379 through the gas phase during pyrolysis step by the volatilization of K compounds and their 380 condensation on the biomass char.

#### 3.3.3. Ash characterization

### 382 **3.3.3.1.** Effects of K<sub>2</sub>CO<sub>3</sub> addition on ash yield and ashes appearance

383 From the normalized mass profiles presented in **Figure 5**, it can be observed that when

- 384 K<sub>2</sub>CO<sub>3</sub> is added to rice husks, mixed or without contact, the mass stabilizes at a higher ash
- yield (19.7 and 15.2wt% respectively) than rice husks alone (13.6wt%) (**Table 3**).

<b>Table 3. Gasification ash yield measured in TGA and associated</b>	theoretical	yields.
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	Rice husks	Rice husks + K <sub>2</sub> CO <sub>3</sub> without contact	Rice husks + K <sub>2</sub> CO <sub>3</sub> mixed
Added K <sub>2</sub> CO <sub>3</sub> (wt%)	—	7.0 ± 0.3	
Experimental (wt%)	13.6 ± 0.5	15.2 ± 0.7	19.7 ± 1.3
Theoretical if all K <sub>2</sub> O remains* (wt%)	—	17.4 ± 0.8	
Theoretical if all K <sub>2</sub> CO <sub>3</sub> remains** (wt%)		19.6 ± 0.8	

\*  $Ash_{with \ K2O} = \%K_2CO_3 \times \frac{M_{K2O}}{M_{K2CO_3}} + (100 - \%K_2CO_3) \times Ash_{rice \ husks}$ \*\*  $Ash_{with \ K2CO_3} = \%K_2CO_3 + (100 - \%K_2CO_3) \times Ash_{rice \ husks}$ 

387

This higher ash yield suggests that at least a part of the added K<sub>2</sub>CO<sub>3</sub> is incorporated to the 388 389 biomass char and therefore to the biomass ash at the end of the gasification step. The 390 increase is observed including in the case of addition without contact. Therefore, this proves 391 that K<sub>2</sub>CO<sub>3</sub> is incorporated after its volatilization during the pyrolysis step. As a result, the Kspecies in the ash can be in another form than directly  $K_2CO_3$ , such as  $K_2O$ . The higher ash 392 393 yield value corresponds to the theoretical ash yield calculated if all the added K<sub>2</sub>CO<sub>3</sub> is 394 incorporated to the ashes, either directly as  $K_2CO_3$  (19.6wt%) or as  $K_2O$  (17.4wt%). 395 In order to investigate this supposed reaction of a K-species with the rice husk ashes, the 396 ashes from the previous experiments were characterized through optical microscope and SEM-EDX. 397

- 398 Pictures from microscope observation of ashes from rice husks alone and mixed with K<sub>2</sub>CO<sub>3</sub>
- are presented **Figure 10**.



Figure 10. Ashes from pyrolysis and gasification of RH a. alone and b. with mixed  $K_2CO_3$  (same aspect without contact).

403 Ashes in the presence of K<sub>2</sub>CO<sub>3</sub> show some black glassy agglomerates on top of the white 404 ashes (Figure 10.b) that are absent from rice husks alone (Figure 10.a). It suggests the 405 formation at the process temperature of a liquid that solidified at ambient temperature. The 406 SiO<sub>2</sub>-K<sub>2</sub>O phase diagram (see Supplementary Material) confirms that liquid can be present at the process temperature of 800 °C. The SiO<sub>2</sub>/(K<sub>2</sub>O+SiO<sub>2</sub>) ratio for a mixture of rice husks and 407 7wt% of K<sub>2</sub>CO<sub>3</sub> is of 0.79 (from rice husks composition in **Table 1**). However, local 408 409 concentrations could vary largely to reach lower or higher ratios. The change in appearance 410 in the presence of K<sub>2</sub>CO<sub>3</sub>—including without contact—confirms that a reaction occurs between the added K<sub>2</sub>CO<sub>3</sub> or one of its decomposition products and the inorganic 411 412 compounds naturally contained in biomass-most likely SiO<sub>2</sub> which represents 94 wt% of the 413 inorganic content of rice husks.

414 The same ashes were characterized through SEM-EDX, as presented in **Figure 11**.



Figure 11. SEM observation of ashes from pyrolysis and gasification of RH a. alone
and b. with K<sub>2</sub>CO<sub>3</sub> added without contact (same aspect mixed).

Again with SEM, the typical rice husk ashes and the glassy agglomerates can be
distinguished. The EDX analysis confirms that the typical rice husks ashes contain mainly
SiO<sub>2</sub>. In the glassy agglomerates, the detected elements are K, Si and O. This supports the
idea of K-silicates formation.

This demonstrates that, in addition to influencing the pyrolysis and gasification of the carbonaceous matrix, the added  $K_2CO_3$  also reacts with the inorganic elements inherent to the rice husks. This behavior is supported by literature observations of the reaction between K-compounds and SiO<sub>2</sub> to form K-silicates [20,21,59]. However, our study suggests that the reaction involves the gas phase, which has not been proved in literature.

427 This leads to a limitation of the catalysis of the gasification by  $K_2CO_3$  due to its reaction on

428  $SiO_2$  inherent to the rice husks.

# 429 **3.3.3.2.** Competing interactions of K with carbon and silica

430 To demonstrate these competing interactions, the same experimental procedure was applied 431 to beech wood with  $K_2CO_3$  added without contact. Beech wood had a very low  $SiO_2$  content 432 so it was expected that  $K_2CO_3$  would have induced a stronger catalysis than for rice husks. 433 The normalized mass evolution and the gasification conversion profiles are shown in Figure





Figure 12. TGA of BW with and without added K<sub>2</sub>CO<sub>3</sub> and of RH and SSS during a. the
high temperature pyrolysis step and b. the steam gasification step.

The additional mass loss during high temperature pyrolysis (Figure 12.a) occurs for beech in
the same way as for rice husks (third DTG peak).

440 Regarding gasification (**Figure 12**.b) when  $K_2CO_3$  is added without contact, beech wood

441 reactivity greatly increases (average reactivity increasing from  $r_{1-80\%} = 4.9$  to 42.4%min<sup>-1</sup>). It

442 reaches sunflower seed shells level ( $r_{1-80\%} = 30.3\%$ .min<sup>-1</sup>). The catalysis is very strong

443 compared to what is observed in the case of rice husks (average reactivity increasing from r<sub>1-</sub>

- 445 rice husks is a Si-rich biomass. Therefore it confirms that the competing reaction of  $K_2CO_3$
- 446 decomposition product on the inherent  $SiO_2$  prevents it to catalyze the gasification.

# 447 **4.** Synthesis of the several effects of K along biomass pyrolysis

# 448 and steam gasification

During the present investigation, we have observed that the addition of K during the pyrolysis
and gasification of rice husks has significant effects at several levels. It influences the
kinetics of both pyrolysis and gasification steps and it interacts with the inorganic compounds
inherent to the biomass.

It is important to note that all these effects occur whether K2CO3 is in contact or not with the 453 biomass. This behavior highlights the fact that K2CO3 mechanisms of action are through the 454 455 gas phase, with the formation of KOH(g). This is permitted by the fact that experiments use a 456 low gas flow that enables the mass transfers and reactions to occur at the proximity of the 457 crucible. Conducting experiments with a high gas flow would then be expected to reduce or 458 suppress the catalytic effect which would confirm this result. Effects observed in the case of 459 mixtures are stronger than without contact which can be explained by a higher concentration 460 of K-compound in the gas layer around the biomass in this case.

The effects of  $K_2CO_3$  on biomass pyrolysis and gasification demonstrated in the present study are summarized in **Figure 13**. During the pyrolysis, steam is produced and reacts with  $K_2CO_3$  to form a mixture of  $K_2CO_3$  and KOH where a core of  $K_2CO_3$  is at equilibrium with a liquid phase. When the pyrolysis reaches a high temperature, KOH<sub>(g)</sub> is volatilized from this mixture and catalyzes an additional devolatilization of the char. Then, when steam is added, the mixture completely volatilizes as KOH<sub>(g)</sub>. This formed KOH<sub>(g)</sub> catalyzes the gasification and reacts with the biomass inherent SiO<sub>2</sub> to form K-silicates.





# Figure 13. Scheme of the effects of K<sub>2</sub>CO<sub>3</sub> on biomass pyrolysis and gasification, in the case of K<sub>2</sub>CO<sub>3</sub> added without contact.

471 It is demonstrated that the interaction of  $K_2CO_3$  with the biomass during the pyrolysis is 472 decisive for the subsequent gasification. Indeed, when the two materials are in presence only 473 during pyrolysis but not during gasification, catalysis is still observed.

474 However, the catalytic effect remains weaker than what has been observed in literature in the 475 case of impregnation or occasionally mixing [32,35,60]. This is attributed to the fact that the 476 present work intends to catalyze rice husks that have a high content in Si, while most 477 literature studies work with materials with a low ash content [4,6,9-12,33,34,36]. Hence, we 478 have confirmed this fact by experiments on beech wood that has a very low Si content. Along 479 with the ash characterization during the TGA experiments, these results highlight a 480 competition between on the one hand the influence of K<sub>2</sub>CO<sub>3</sub> on the biomass pyrolysis and 481 char gasification kinetics and on the other hand its interaction with SiO<sub>2</sub> inherent to the rice 482 husks.

# 483 **5. Conclusions**

484 The present work contributes to the understanding of the K role in biomass steam

485 gasification. It has demonstrated the competition between  $SiO_2$  and the carbonaceous matrix

486 to react with a K-catalyst. On the one hand, the K-compound catalyzes the high temperature

pyrolysis and the steam gasification of the carbonaceous matrix of biomass. On the other
hand, its decomposition product reacts with the SiO<sub>2</sub> inherent to biomass. In both cases,
effects are observed including when the K-compound is not in direct contact with the
biomass which demonstrates that the mechanisms of action involve the gas phase.

During the pyrolysis at high temperature, an additional mass loss occurs in presence of  $K_2CO_3$ . This observation is in accordance with the carbon chemical activation literature. It has been demonstrated in the present work that it is related to an additional volatilization of the carbon matrix in relation with the formation of KOH(g). The latter is formed from the reaction of  $K_2CO_3$  with  $H_2O(g)$  released from the devolatilization of the carbon matrix.

496 Regarding the gasification step itself,  $K_2CO_3$  increases the reaction rate both with and without 497 contact with the biomass. It has been demonstrated in the present study that the interaction 498 of  $K_2CO_3$  with the biomass during the pyrolysis step is decisive for the ulterior gasification.

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