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1 **Effect of bauxite additive on the ash sintering characteristics during**

2  **$K_2CO_3$ -catalyzed steam gasification of lignite**

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10 This paper is aimed to investigate the ash sintering characteristics of LLI lignite with bauxite  
11 additive during  $K_2CO_3$ -catalyzed steam gasification. In this paper, the ash samples were  
12 prepared using a catalytic gasification system at 1123 K under steam atmosphere with carrier  
13 gas  $N_2$ . The ash sintering temperature was determined using a pressure-drop sintering device  
14 with inert  $N_2$ . The ash mineralogy and morphology were analyzed using an X-ray  
15 diffractometer (XRD) and a scanning electron microscope-energy dispersive X-ray  
16 spectrometer (SEM-EDS). The results showed that  $K_2CO_3$  decreased the sintering  
17 temperatures of ash samples and made the ash molten degree become more serious.  
18 Kaliophilite was the main cause to facilitate the formation of liquid phases and trigger the  
19 occurrence of sintering, resulting in a lower ash sintering temperature. In addition, the  
20 addition of bauxite could ease the molten degree of ashes and lead to a higher ash sintering  
21 temperature. The main cause is that bauxite including sufficient  $SiO_2$  and  $Al_2O_3$  could react  
22 with other minerals to generate more refractory silicon oxide and diminish the fluxing

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23 arcanite and amorphous materials in ashes. At last, from the view of mineralogy, the addition  
24 of bauxite also can decrease the gasification rate of lignite by reacting with potassium to  
25 generate water-insoluble kaliophilite and deactivating the potassium catalyst.

26 Keywords: Ash sintering temperature; Bauxite; Potassium carbonate; Catalytic gasification;  
27 Lignite

28

## 29 1. INTRODUCTION

30 Currently, coal is the main energy resource in China, which occupies about 70% of the total  
31 energy consumption<sup>1,2</sup>. About 12.7% of the total coal reserves are covered by lignite<sup>3,4</sup>. As  
32 a efficient and clean lignite utilization method, the catalytic gasification technology has been  
33 paid much attention and is widely employed<sup>5,6</sup>. It is well known that alkali and alkaline earth  
34 metal (AAEM) elements of lignite acting as a catalyst play a significant role in the lignite  
35 gasification process<sup>7,8</sup>. However, AAEM species can potentially give rise to some  
36 undesirable effects and issues relating with the ash in gasifiers<sup>9,10</sup>. These issues including  
37 bed agglomeration, slagging, corrosion, erosion and so on majorly originate from the  
38 sintering behavior<sup>11,12</sup>. Hence, it is necessary to study the sintering characteristics of lignite  
39 ash produced by catalytic gasification.

40

41 Ash sintering refers to the process in which some partial melting particles become sticky and  
42 bond together with adjacent solid particles. These bonded particles will potentially grow up  
43 and finally form a bulk of ash deposits<sup>13</sup>. Literature reports have reached consensus that the  
44 ash sintering behavior is mainly controlled by the ash chemistry and other factors such as  
45 atmosphere, temperature, pressure, and particle size<sup>8,10,14</sup>. Jing et al.<sup>15</sup> investigated the  
46 effect of ash composition on the sintering behavior during pressurized combustion and

47 gasification process using SEM and XRD technique. The result showed that the addition of  
48  $\text{Fe}_2\text{O}_3$  can obviously reduce the sintering temperatures under gasification atmospheres and  
49 only slightly affect the sintering temperature under combustion atmosphere. Matjie et al.<sup>16</sup>  
50 studied the behavior of coal mineral matter in sintering and slagging of ash during the  
51 gasification process using quantitative XRD and automated electron beam image analysis.  
52 The results indicated that the minerals and inorganic elements in the coal have undergone  
53 significant transformations during gasification, the nature of which depends not only on the  
54 mineralogy but also the mineral association. Minerals and mineral associations were  
55 responsible for ash sintering behavior.

56

57 Generally, the AAEM (e.g. potassium) is easily to react with Si and Al compounds in coal  
58 ash, and then somewhat resulting in the formation of lower melting point products<sup>17-19</sup>.  
59 Potassium can be incorporated into the structures of silicates to form eutectics with low  
60 melting temperatures of about 813 - 873 K in the  $\text{K}_2\text{O}$ - $\text{SiO}_2$  binary system<sup>20</sup>. Potassium can  
61 also facilitate the formation of low temperature eutectics (973 - 1273 K) in the  $\text{K}_2\text{O}$ - $\text{SiO}_2$ -  
62  $\text{Al}_2\text{O}_3$  ternary systems<sup>21</sup>. In addition, bauxite, a naturally occurring heterogeneous ore, is the  
63 world's main source of aluminum<sup>22</sup>. One of conventionally commercial applications of  
64 bauxite is refractory, which is an active additive for preventing the formation of problematic  
65 ash components<sup>23</sup>. The bauxite can trap the alkali (particularly potassium) into the solid<sup>24,25</sup>.  
66 Barisano, D et al.<sup>26</sup> reported that at gasification steady state condition, the addition of bauxite  
67 as a sorbent can remove the potassium vapor and a gradual and significant decrease in the K  
68 concentration was observed. After high temperature treatment, the bauxite including  
69 aluminum-bearing minerals can capture the potassium to generate some higher melting point  
70 of alumina with different crystal structures<sup>27,28</sup>. However, although the bauxite additive  
71 gives rise to increase the ash fusion temperature, it somewhat leads to the deactivation of

72 potassium catalyst. Thus, it needs to be better understand in ash minerals related problems of  
73 lignite with the addition of bauxite during  $K_2CO_3$ -catalyzed steam gasification.

74

75 However, studies on the ash sintering characteristics of lignite with different concentrations  
76 of bauxite additive produced by different concentrations of  $K_2CO_3$  catalytic gasification are  
77 scarce. Accordingly, a systematic research effort is needed to better understand the  
78 interactions among lignite minerals,  $K_2CO_3$  and bauxite during catalytic gasification  
79 condition and how the ash sintering characteristics are impacted upon. To this end, the  
80 current study investigated the effect of bauxite additive on the ash sintering characteristics  
81 during  $K_2CO_3$ -catalyzed gasification of lignite.

82

## 83 **2. EXPERIMENTAL SECTION**

84

85 In this work, a lignite named LLI from China was selected. The lignite sample was  
86 pulverized and sieved to less than 0.2 mm in size. According to the Chinese standard  
87 (GB/T212-2001), the lignite ash was prepared by heating the lignite sample in air in a Muffle  
88 furnace to 1088 K for 2 hours. The ash chemical compositions of LLI lignite were analyzed  
89 using X-ray fluorescence (XRF) and the results as well as the proximate and ultimate analysis  
90 data of LLI lignite are presented in Table 1. The ash fusion temperatures of ash samples were  
91 tested under air atmosphere according to the Chinese standard (GB219-74) and the results are  
92 also shown in Table 1.

93

94 To investigate the influence of additive on the ash sintering behavior, the bauxite was chosen  
95 for this study in respect of its high content of refractory  $Al_2O_3$  and  $SiO_2$ . The ingredients of  
96 bauxite were tested by XRD technique and the results are presented in Table 2. Besides, as

97 for catalytic gasification,  $K_2CO_3$  regarded as one of the most promising catalyst for coal  
98 gasification was selected in this work. The mass fractions of  $K_2CO_3$  or bauxite, i.e.,  $K_2CO_3$   
99 (or bauxite)/lignite were set to 0%, 1%, 5% and 10%. The bauxite and  $K_2CO_3$  both were  
100 added to the lignite sample using an impregnation method. After thorough mixing by  
101 vigorous stirring, the samples were dried in an oven at 378 K for 24 hours. At last, the dried  
102 samples were mechanically stirred adequately in a crucible again in order to mixing the  
103 additives and lignite evenly.

104

105 During the process of catalytic gasification, the gasification agent gas was steam. The steam  
106 volume flow rate was controlled by a water pump. The carrier gas was  $N_2$ , which had the  
107 same rate of volume flow of  $500\text{ cm}^3\text{ min}^{-1}$  as steam. The carrier gas could give impetus to  
108 the steam to flow from bottom to top of the fixed-bed gasification reactor (500mm length and  
109 50mm OD and 36mm ID). The whole gasification reactor was heated by a vertical electric  
110 furnace to guarantee that steam and reactor maintained a desired temperature. Firstly, a  
111 sample of approximately 4g was placed in the gasification reactor. Secondly, let the  $N_2$  get  
112 into the reactor and increased the furnace temperature to 1123K and then kept the  
113 temperature for 5 mins for lignite pyrolysis before gasification process. At last, opened the  
114 water pump to give a source to generate steam for steam gasification and then kept the whole  
115 system for 4 hours to make sure that the samples were gasified fully.

116

117 After the ash preparation process, a pressure-drop sintering device was used to determine the  
118 ash sintering temperature in inert  $N_2$  atmosphere. A schematic diagram of the pressure-drop  
119 sintering device is shown in Figure 1. Briefly, an ash pellet (8mm diameter and height) of  
120 approximately 0.4g, prepared using an ash pellet compaction device with a compaction  
121 pressure of 25 MPa, was inserted in the middle of alumina mullite tube (1000mm length and

122 8mm OD and 5mm ID) in an electric furnace. A stream of inert N<sub>2</sub> passed through the pellet  
123 at a constant flow rate of 4 cm<sup>3</sup> min<sup>-1</sup> controlled by a mass flow controller. The furnace was  
124 heated from ambient temperature at 8 K min<sup>-1</sup> and the pressure-drop across the pellet was  
125 recorded as a function of the temperature. In the current experimentation, the ash sintering  
126 temperature was defined as the temperature when the pressure-drop across the pellet reached  
127 to the maximum <sup>29</sup>. The sintering temperatures thus determined using this technique had a  
128 repeatability of ± 10 K.

129

130 In order to understand the reasons for the changes in the ash sintering behavior and clarify the  
131 cause of the occurrence of ash sintering due to the different ash preparation procedures, the  
132 morphological and mineralogical transformation of the ash samples were investigated. The  
133 morphological characteristics and spot composition analysis were performed using a  
134 TESCAN-Vega-3-XM scanning electronic microscopy (SEM) analyzer aided with an Oxford  
135 X-ray energy dispersive spectroscopy (EDS). The spot location is represented on the  
136 provided SEM images by a star symbol. To gain a better understanding of the ash  
137 mineralogical transformations and characteristics, ash samples were studied using a  
138 PANalytical X-ray diffractometer analyzer (EMPYREAN) with copper K $\alpha$  radiation. The  
139 qualitative powder XRD analysis employed an accelerating voltage of 40 kV, a current of 40  
140 mA and a scan speed of 0.0847 °s<sup>-1</sup> between 5° and 70° of the 2 $\theta$ .

141

### 142 **3. RESULTS AND DISCUSSION**

#### 143 **3.1 Effect of K<sub>2</sub>CO<sub>3</sub> and bauxite on the ash sintering temperature**

144

145 In order to study the effect of  $K_2CO_3$  and bauxite on the ash sintering temperature, Figure 2  
146 compared the ash sintering temperature of LLI lignite with different concentrations of bauxite  
147 additive produced by different concentrations of  $K_2CO_3$  catalytic gasification.

148

149 For the effect of  $K_2CO_3$  on the ash sintering temperature, with a same concentration of  
150 bauxite additive, it is seen that the sintering temperatures of ash samples decreased by  
151 increasing the concentration of  $K_2CO_3$  from 0 to 10 wt%; the ashes from LLI without  $K_2CO_3$   
152 catalyst showed the highest sintering temperatures, whereas the ashes from LLI with 10 wt%  
153  $K_2CO_3$  had the lowest sintering temperatures. Besides, it is also noted that, without bauxite  
154 additive, the ash sintering temperature difference between LLI with and without 10 wt%  
155  $K_2CO_3$  was relatively larger than others, and the decreased degree was about 149 K. At last,  
156 these phenomena demonstrated that  $K_2CO_3$  could play a significant role in reducing ash  
157 sintering temperature.

158

159 Meanwhile, for the effect of bauxite additive on the ash sintering temperature, Figure 2 also  
160 showed that, with a same concentration of  $K_2CO_3$  catalyst and the concentration of bauxite  
161 raised from 0 to 10 wt%, the sintering temperatures of ash samples got increased; the ashes  
162 from LLI without bauxite additive showed the lowest sintering temperatures, whereas the  
163 ashes from LLI with 10 wt% bauxite additive had the highest sintering temperatures. In  
164 addition, it is also illustrated that, with 10 wt% concentration of  $K_2CO_3$  catalyst, the ash  
165 sintering temperature difference between LLI with and without bauxite additive was  
166 relatively larger than others, and the increased sintering temperature was about 82 K. These  
167 phenomena verified that bauxite could play an important role in promoting ash sintering  
168 temperature.

169



## 170 **3.2 Ash morphology**

### 171 3.2.1 Effect of $K_2CO_3$

172

173 Figure 3 illustrated the ash surface morphology change of LLI lignite with different  
174 concentrations of bauxite additive produced by different concentrations of  $K_2CO_3$ . In Figure  
175 3, the second row including four images presents four ash samples from LLI with 1 wt%  
176 bauxite additive. On the left of first row, it is shown that the ash samples from LLI without  
177  $K_2CO_3$  catalyst present some irregularly shaped and dispersed particles, in which no obvious  
178 melting or agglomeration phenomena occurred. By increasing the concentration of  $K_2CO_3$   
179 catalyst to 5 wt%, still no clear molten phenomenon occurred on the ash particle surfaces.  
180 However, when the concentration of  $K_2CO_3$  was up to 10 wt%, the ash particles hold together  
181 and became agglomerated, the surface of which was obviously molten and smooth, which  
182 indicated that some liquid phases had already formed and the ash sintering had occurred. On  
183 the whole, the morphology changes validated the trend of ash sintering temperature results in  
184 Figure 2. Besides, from the analysis of EDS, the ash samples from LLI without  $K_2CO_3$   
185 catalyst, the chosen spot on the particle was mainly composed of O, Ca, Si and Al, implying  
186 that the particle may contain Ca-bearing aluminosilicate including feldspar minerals. With the  
187 increase of  $K_2CO_3$ , higher content of K element presented in the elemental analysis. When  
188 the concentration of  $K_2CO_3$  was 10 wt%, the EDS results showed that those melting surfaces  
189 were mainly comprised of O, K, Si, and Al, indicating that the melting surface may have been  
190 comprised of K-bearing aluminosilicate. It has been reported that K-bearing aluminosilicate  
191 could react with other minerals to form the low temperature eutectics, which facilitated the  
192 formation of liquid phases. Those liquid phase could potentially act as a glue that bonded the  
193 ash particles together in a mechanism called the viscous flow sintering<sup>13</sup>.

194

195 Likewise, from third or fourth row of Figure 3, it is shown that with 5 wt% or 10 wt% bauxite  
196 additives, the morphology change and elemental analysis of ash particles showed  
197 correspondingly similar trend with the four ash samples from LLI with 1wt% bauxite as the  
198 rise of  $K_2CO_3$  concentration, respectively. The trend was that irregularly shaped and  
199 dispersed particles tended to be agglomerated particles with molten and smooth surfaces, and  
200 the molten degree became more severe. In addition, with a higher concentration of  $K_2CO_3$ ,  
201 the EDS results showed that those melting surfaces were mainly comprised of O, Si, K and  
202 Al, implying K-bearing aluminosilicate played an important role in facilitating the melting  
203 surface. Overall, the increase of  $K_2CO_3$  promoted the content of K-bearing aluminosilicate in  
204 ash, which facilitated the formation of liquid phases and the occurrence of ash sintering.

205

### 206 3.2.2 Effect of bauxite

207

208 In Figure 3 also illustrated the effect of bauxite additive on the ash surface morphology  
209 change. The first column including four images presents four ash samples from LLI without  
210  $K_2CO_3$  catalyst. All these ash samples showed irregularly shaped particles without melting  
211 surface, which confirmed the results that these ash samples had high ash sintering  
212 temperatures which were above 1133 K and exceeded the ash preparation temperature of  
213 1123 K shown in Figure 2. Thus, it is difficult to distinguish and compare the melting degree  
214 of these ash samples by surface morphology. By the analysis of EDS, the elemental  
215 compositions on the surface of these unmelted particles were mainly O, Si, Al and Ca,  
216 indicating that these particles may be composed of Ca-containing feldspar minerals. Similarly,  
217 the second column including four images presents four ash samples from LLI with 1 wt%  
218  $K_2CO_3$  catalyst. From Figure 3, it is shown that with the concentration of 1 wt%  $K_2CO_3$   
219 catalyst, the morphology change and elemental analysis of ash particles was correspondingly

220 similar with the four ash samples from LLI without  $K_2CO_3$  catalyst as the rise of bauxite  
221 concentration, respectively. This can be explained by the  $K_2CO_3$  proportion was only 1 wt%,  
222 which was not enough to largely impact on ash mineral transformation and morphology  
223 change.

224

225 Additionally, with the same concentration of 5 wt%  $K_2CO_3$ , the surface texture of four kinds  
226 of ash particles in the third column of Figure 3 were still irregularly shaped and unmelted as  
227 the augment of bauxite additive from 0 wt% to 10 wt%. At last, when the concentration of  
228  $K_2CO_3$  was added up to 10 wt%, the four kinds of ash particles in the fourth column of Figure  
229 3 were obvious agglomerated and stucked together with molten surfaces. The occurrence of  
230 molten surface indicated that some liquid phases had formed. Those liquid phases could act  
231 as glues bonding particles together for the viscous flow sintering<sup>30</sup>. Meanwhile, the melting  
232 degree of ashes from LLI without the addition of bauxite which presented the neck of  
233 sintered ash particles was much more serious than the others. In other words, as the augment  
234 of bauxite additive, it is also illustrated that the molten degree of ash samples was eased,  
235 which was consistent with increasing sintering temperature of ash samples shown in Figure 2.  
236 In addition, due to the addition of 10 wt%  $K_2CO_3$ , the EDS result showed that the major  
237 elemental compositions of melting surface of all four ash samples were composed of O, K, Si,  
238 Al and Fe, in which high content of K and Fe elements existed. The existence of iron element  
239 was originated from the addition of bauxite. It is suggested that the melting surface may have  
240 been comprised of K-bearing aluminosilicate and Fe-containing compounds. These K-bearing  
241 aluminosilicate and Fe-containing compounds were capable of forming low melting  
242 temperature eutectics and then facilitated the occurrence of ash sintering<sup>31</sup>.

243

244

### 245 3.3 Ash mineralogy

#### 246 3.3.1 Effect of $K_2CO_3$

247

248 Figure 4 presents the XRD patterns of the ashes of LLI lignite with 1 wt% bauxite additive  
249 produced by different concentrations of  $K_2CO_3$  catalytic gasification at 1123 K. In Figure 4,  
250 the results showed that the main minerals were silicon oxide ( $SiO_2$ ), nosean ( $Na_{8.08}$   
251  $(Al_6Si_6O_{24})(SO_4)_{0.98}$ ), iron oxide ( $Fe_3O_4$ ), anorthoclase  $((Na,K)(Si_3Al)O_8)$  and albite  
252  $(NaAlSi_3O_8)$  in the ash from LLI lignite. Except silicon oxide, these are fluxing minerals <sup>31</sup>  
253 which are prone to produce low-temperature co-fusion with other minerals <sup>15</sup>. As the increase  
254 of the  $K_2CO_3$  concentration, new K-containing phases arcanite ( $K_2SO_4$ ), leucite ( $KAlSi_2O_6$ )  
255 and kaliophilite ( $KAlSiO_4$ ) appeared while the content of silicon oxide became less and  
256 feldspars such as nosean disappeared. The arcanite was formed as a product from the reaction  
257 that potassium was adsorbed by  $SO_3$  <sup>32</sup>. The kaliophilite started to appear in the ash sample  
258 from LLI lignite produced by catalytic gasification with 5 wt%  $K_2CO_3$ , then increased in the  
259 content when the proportion of  $K_2CO_3$  enhanced up to 10 wt%. The kaliophilite which is a  
260 kind of K-bearing aluminosilicate was formed as a reaction product from K element which  
261 partly from arcanite,  $SiO_2$  and  $Al_2O_3$  <sup>33</sup>. The kaliophilite and leucite which are members of  
262 the feldspathoid group of minerals and arcanite all can react with other minerals to form low  
263 temperature eutectics <sup>34</sup>, leading to the decrease of the ash sintering temperature. Meanwhile,  
264 this verified the analysis of SEM-EDS in the Figure 3 that the melting surface of ash samples  
265 was comprised of K-bearing aluminosilicate. And these K-bearing aluminosilicate may  
266 include the kaliophilite and some co-fusion mixtures. Besides, when the proportion of  $K_2CO_3$   
267 enhanced up to 10 wt%, it is illustrated that there was a broad hump existing at  $2\theta=33^\circ$  in the  
268 diffraction pattern, which suggests that some amorphous materials existed in the ash sample.  
269 The XRD technique can not detect which kind of mineral is in the amorphous materials, but

270 can estimate the content of amorphous materials. Those amorphous materials mainly  
271 contained some low temperature co-fusions<sup>35</sup>. Overall, the presence of K-containing  
272 compounds (arcanite and kaliophilite) and amorphous materials led to a lower ash sintering  
273 temperature. The similar phenomena were also observed for the other ash samples of LLI  
274 lignite with 5 wt% bauxite additive produced by different concentrations of K<sub>2</sub>CO<sub>3</sub> catalytic  
275 gasification.

276

277 In addition, Figure 5 demonstrates that the XRD patterns of the ashes of LLI lignite with 10  
278 wt% bauxite additive produced by different concentrations of K<sub>2</sub>CO<sub>3</sub> catalytic gasification. It  
279 is evident that the major minerals of ashes produced from LLI lignite without K<sub>2</sub>CO<sub>3</sub> at 1123  
280 K were silicon oxide, nosean, iron oxide and gehlenite (Ca<sub>2</sub>Al(AlSi)O<sub>7</sub>). Similarly, by  
281 increasing the K<sub>2</sub>CO<sub>3</sub> concentration to 10 wt%, the major mineral in the ash was fluxing  
282 kaliophilite while feldspars such as gehlenite disappeared. Compared with the results in  
283 Figure 4, it is noted that less arcanite presented in the ash samples from LLI lignite 10wt%  
284 K<sub>2</sub>CO<sub>3</sub> in Figure 5. This is because the bauxite had a strong affinity to K<sub>2</sub>CO<sub>3</sub>. The potassium  
285 could start to be captured to generate the kaliophilite by the kaolin which was a part of  
286 bauxite even at 673K<sup>36</sup>. As the analysis from Figure 4, kaliophilite could react with other  
287 minerals to form low temperature eutectics<sup>34</sup>. On the whole, the existence of massive  
288 kaliophilite was the main cause to lead to a lower ash sintering temperature.

289

290 3.3.2 Effect of bauxite

291

292 Figure 6 illustrates the XRD patterns of the ashes of LLI lignite with different concentrations  
293 of bauxite additive produced by gasification. The results showed that the main minerals were  
294 silicon oxide, nosean and iron oxide in the ash from LLI lignite. As increasing the bauxite

295 addition, the peak intensity of refractory silicon oxide in the pattern was significantly  
296 increased, suggesting that the content of silicon oxide became richer in the ash samples. In  
297 addition, some feldspar minerals such as nosean and albite-calcian appeared and significantly  
298 increased in the content in the ashes. These are because the fact that the increased bauxite  
299 including sufficient  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  could react with other minerals in the ashes to generate  
300 those feldspar minerals<sup>37</sup>. These results correlated with the analysis of SEM-EDS that some  
301 irregularly shaped particles were composed of feldspar minerals. Therefore, it is concluded  
302 that the increased content of refractory silicon oxide reduced the proportion of fluxing  
303 minerals in the ashes, which somewhat promoted the ash sintering temperature. The similar  
304 phenomena were also detected for the other ash samples of LLI lignite with different  
305 concentrations of bauxite additive produced by catalytic gasification with 1 wt% or 5 wt%  
306  $\text{K}_2\text{CO}_3$ .

307

308 Furthermore, this study also investigated the XRD patterns of ashes of LLI lignite with  
309 different concentrations of bauxite additive produced under catalytic gasification with 10wt%  
310  $\text{K}_2\text{CO}_3$ . As it can be observed in Figure 7, with the concentration of 10 wt%  $\text{K}_2\text{CO}_3$ , the  
311 major minerals in the ash from LLI lignite without bauxite addition were silicon oxide,  
312 kaliophilite, arcanite and potassium calcium silicate ( $\text{K}_4\text{CaSi}_3\text{O}_9$ ). Likewise, as the rise of  
313 bauxite addition from 1 to 10 wt%, it is noted that the contents of iron oxide and silicon oxide  
314 were slightly increased while arcanite became less in the ashes. This is because the fact that  
315 the increased bauxite brought in increasing silicon oxide and iron oxide. The iron oxide was  
316 transformed from ferric oxide containing in bauxite during reducing steam atmosphere<sup>38</sup>,  
317 which could not largely impact on the sintering temperature due to the degree of variability of  
318 iron oxide was slightly. The potassium was captured to generate the kaliophilite instead of  
319 arcanite by the bauxite addition, which is similar with the XRD analysis above. These

320 phenomena are consistent with the results in the fourth column of Figure 3. Moreover, it is  
321 also observed that there was a broad hump existing at  $2\theta=33^\circ$  in the diffraction pattern of four  
322 ash samples, respectively, implying that each ash sample contained some amorphous  
323 materials. The area under the hump depends on the content of amorphous materials in the  
324 sample. It is believed that bigger area means higher content of amorphous materials in the  
325 sample<sup>35</sup>. However, it is illustrated that the area became smaller as the addition of bauxite  
326 increased from 0 to 10 wt%, demonstrating that the amount of amorphous materials  
327 containing low temperature co-fusions in the samples was reduced. Therefore, together these  
328 factors including increased refractory silicon oxide, less fluxing arcanite and decreased  
329 amorphous materials promoted the ash sintering temperature.

330

331 In addition, it is stated that a key factor of catalytic gasification is to make sure the activity of  
332 catalyst, which majorly determines the carbon conversion and gasification rate of lignite<sup>39</sup>. In  
333 this study, the existence of potassium catalyst which can possess the catalytic function for  
334 gasification mainly are water-soluble  $K_2CO_3$  and arcanite<sup>40</sup>. However, due to the presence of  
335 bauxite, it can react with the active  $K_2CO_3$  to form water-insoluble compound kaliophilite  
336 instead of arcanite, leading to the deactivation of potassium catalyst<sup>41</sup>. Thus, with a same  
337 concentration of  $K_2CO_3$ , the less content of arcanite indicates lower activity of catalyst and  
338 gasification rate of lignite, and vice versa. In Figure 7, as the rise of bauxite addition, it is  
339 illustrated that the content of arcanite were decreased and the proportion of kaliophilite  
340 increased in ashes, which suggests that the addition of bauxite can decrease the gasification  
341 rate of lignite.

342

343 The ash sintering was triggered by the formation of viscous liquid phases on the ash particles  
344 surface<sup>13, 42</sup>. The viscous liquid phases further lead to rearrangement and agglomeration of

345 ash particles <sup>43</sup>. Therefore, the key factor of the occurrence of sintering is the presence of  
346 liquid phases. Usually, the liquid phases originated from some low-temperature co-fusions. In  
347 this study, these low-temperature co-fusions were produced by some interactions between  
348 additives and lignite minerals. Based on the above analysis in this study, due to the presence  
349 of potassium, on the one hand, it could react with  $\text{SO}_3$  from lignite to generate fluxing  
350 arcanite ( $\text{K}_2\text{SO}_4$ ); on the other hand, it is easy to react with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  from bauxite and  
351 lignite to produce some K-containing phases leucite ( $\text{KAlSi}_2\text{O}_6$ ) and kaliophilite ( $\text{KAlSiO}_4$ ).  
352 Leucite and kaliophilite which are members of the feldspathoid group of minerals and fluxing  
353 arcanite could react with other minerals to form low temperature eutectics and then resulted  
354 in the generation of liquid phases and the occurrence of ash sintering. The main reactions  
355 involving with LLI lignite minerals,  $\text{K}_2\text{CO}_3$  and bauxite during catalytic gasification  
356 discussed before are shown as Table 3.

357

358 As a whole, as increasing the bauxite concentration, the addition bauxite can retard the  
359 occurrence of sintering and lead to a higher ash sintering temperature by the way of  
360 generating more refractory silicon oxide and diminishing the fluxing arcanite and amorphous  
361 materials in ash. In addition, the addition of bauxite can decrease the gasification rate of  
362 lignite by forming water-insoluble kaliophilite with  $\text{K}_2\text{CO}_3$  and deactivating the potassium  
363 catalyst.

364

#### 365 4. CONCLUSIONS

366

367 In this work we have investigated the ash sintering characteristics and ash minerals  
368 transformation of LLI lignite with bauxite additive during  $\text{K}_2\text{CO}_3$ -catalyzed steam  
369 gasification at 1123 K using SEM-EDS and XRD. As increasing the  $\text{K}_2\text{CO}_3$  concentration,



370  $K_2CO_3$  decreased the sintering temperatures of ash samples and made the ash molten degree  
371 become more serious. The kaliophilite generated by the interactions between potassium and  
372 aluminosilicate was the main cause to facilitate the formation of liquid phases and trigger the  
373 occurrence of sintering, resulting in a lower ash sintering temperature. On the other hand,  
374 with increasing the concentration of bauxite additives from 0 to 10 wt% the sintering  
375 temperatures of ash samples got promoted. Besides, the melting surfaces of ash particles were  
376 comprised of kaliophilite and iron oxide. The addition of bauxite can ease the molten degree  
377 of ashes and lead to a higher ash sintering temperature. The main cause is that bauxite  
378 including sufficient  $SiO_2$  and  $Al_2O_3$  could react with other minerals to generate more  
379 refractory silicon oxide and diminish the fluxing arcanite and amorphous materials in ashes.  
380 At last, from the view of mineralogy, the addition of bauxite also can decrease the  
381 gasification rate of lignite by reacting with potassium to generate water-insoluble kaliophilite  
382 and deactivating the potassium catalyst. These results could provide a useful support for the  
383 practical application of  $K_2CO_3$ -catalyzed steam gasification.

384

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386

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392

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Table 1

Table 1 Proximate and ultimate analysis and ash composition as well as ash fusion temperatures of LLI lignite

Proximate analysis / wt %			Ultimate analysis / wt %				
(dry basis)			(dry basis)				
V	A	FC	C	H	O	N	S
32.54	15	52.46	67.18	1.76	17.66	0.68	4.27
Ash composition / wt %							
SiO	Al <sub>2</sub> O	Fe <sub>2</sub> O	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	
44.3	17	10.2	11.4	1.51	1.61	10.8	
Ash fusion temperatures (K) (oxidizing atmosphere)							
DT		ST	HT		FT		
1305		1576	1614		1628		

Table 2

Table 2 Ingredients of bauxite

Ingredients	wt %
Silica crystalline – quartz	<3
Kaolinite	1 – 20
Ferric oxide	1 – 20
Aluminium hydroxide	40 – 85

Table 3

Table 3 The main reactions involving with LLI lignite minerals,  $K_2CO_3$  and bauxite during catalytic gasification under steam atmosphere at 1123 K

$K_2CO_3 + SO_3 \rightarrow K_2SO_4$ (Arcanite)	(1)
$Al_2O_3 + SiO_2 + Na_2O + K_2O \rightarrow (Na, K)Al(Si_3, Al)O_8$ (Anorthoclase)	(2)
$Al_2O_3 + SiO_2 + Na_2O + CaO \rightarrow (Na, Ca)Al(Si, Al)_3 O_8$ (Albite – Calcian)	(3)
$K_2CO_3 + Al_2O_3 + SiO_2 \rightarrow KAlSiO_4$ (Kaliophilite)	(4)
$K_2SO_4$ (Arcanite) + $Al_2O_3 + SiO_2 \rightarrow KAlSiO_4$ (Kaliophilite)	(5)



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- Figure 1 A schematic diagram of the pressure-drop sintering device (1: Gas cylinder; 2: Mass flow controller; 3: Data taker; 4: Thermocouple measuring furnace temperature; 5: Mullite tube; 6: Control panel; 7: Electric furnace; 8: Thermocouple measuring sample temperature; 9: Pressure transmitter; 10: Ash pellet)
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Figure 1

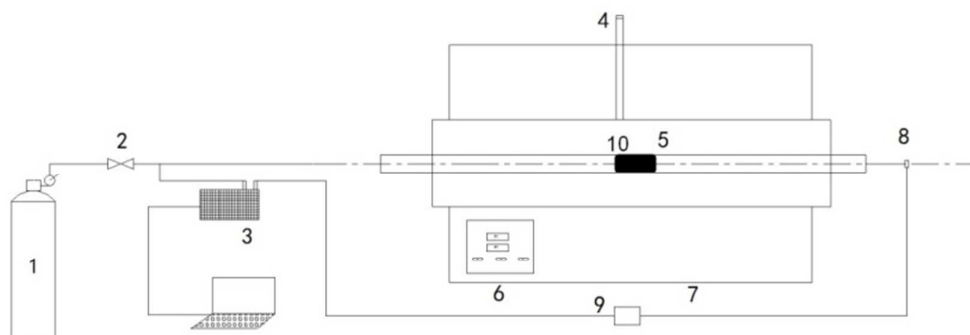


Figure 1 A schematic diagram of the pressure-drop sintering device (1: Gas cylinder; 2: Mass flow controller; 3: Data taker; 4: Thermocouple measuring furnace temperature; 5: Mullite tube; 6: Control panel; 7: Electric furnace; 8: Thermocouple measuring sample temperature; 9: Pressure transmitter; 10: Ash pellet)

Figure 2

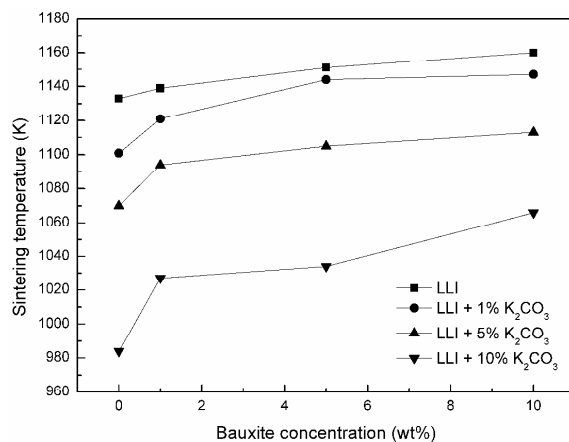


Figure 2 The ash sintering temperature of LLI lignite with different concentrations of bauxite additive produced by different concentrations of K<sub>2</sub>CO<sub>3</sub> catalytic gasification at 1123 K under steam atmosphere

Figure 3



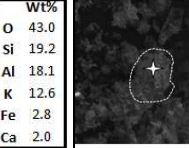
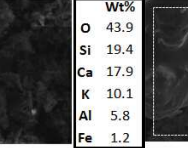

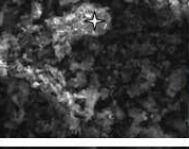
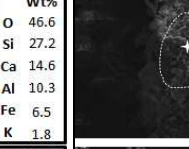
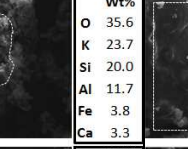

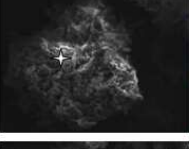
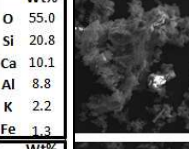
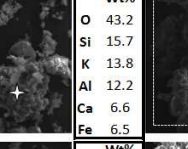
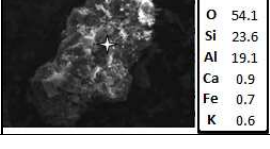

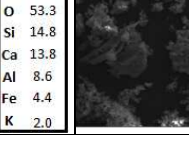
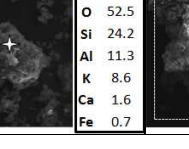
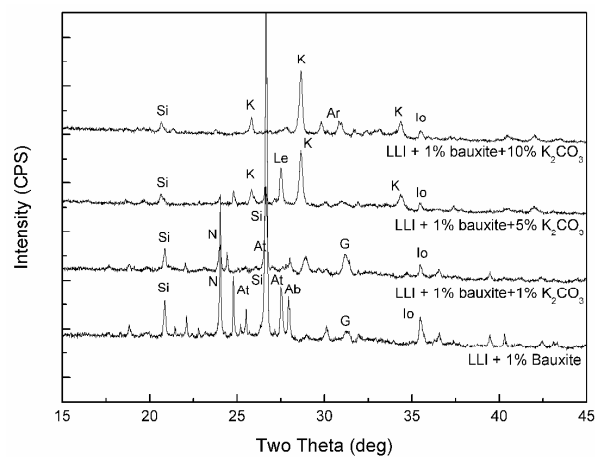
LLI	0 wt% K <sub>2</sub> CO <sub>3</sub>	1 wt% K <sub>2</sub> CO <sub>3</sub>	5 wt% K <sub>2</sub> CO <sub>3</sub>	10 wt% K <sub>2</sub> CO <sub>3</sub>
0 wt% bauxite				
	Wt% O 39.0 Ca 28.7 Si 15.6 Al 7.4 Fe 3.6 Mg 2.5	Wt% O 43.0 Si 19.2 Al 18.1 K 12.6 Fe 2.8 Ca 2.0	Wt% O 43.9 Si 19.4 Ca 17.9 K 10.1 Al 5.8 Fe 1.2	Wt% O 57.4 K 16.2 Si 14.8 Al 6.9 Na 1.7 Fe 1.3
1 wt% bauxite				
	Wt% O 53.8 Ca 16.4 Si 16.1 Al 7.0 Fe 2.6 Mg 1.1	Wt% O 46.6 Si 27.2 Ca 14.6 Al 10.3 Fe 6.5 K 1.8	Wt% O 35.6 K 23.7 Si 20.0 Al 11.7 Fe 3.8 Ca 3.3	Wt% O 41.4 K 21.3 Si 15.8 Fe 9.1 Al 8.0 Ca 2.2
5 wt% bauxite				
	Wt% O 40.9 Si 27.0 Al 17.5 Ca 4.5 K 3.9 Fe 3.6	Wt% O 55.0 Si 20.8 Ca 10.1 Al 8.8 K 2.2 Fe 1.3	Wt% O 43.2 Si 15.7 K 13.8 Al 12.2 Ca 6.6 Fe 6.5	Wt% O 40.0 Fe 26.1 K 15.9 Si 7.9 Al 5.5 S 2.0
10 wt% bauxite				
	Wt% O 54.1 Si 23.6 Al 19.1 Ca 0.9 Fe 0.7 K 0.6	Wt% O 53.3 Si 14.8 Ca 13.8 Al 8.6 Fe 4.4 K 2.0	Wt% O 52.5 Si 24.2 Al 11.3 K 8.6 Ca 1.6 Fe 0.7	Wt% O 46.3 Si 19.4 K 17.8 Al 8.1 Fe 4.5 Ca 2.2

Figure 3 The SEM-EDS of the ashes of LLI lignite with different concentrations of bauxite additive produced by different concentrations of K<sub>2</sub>CO<sub>3</sub> catalytic gasification at 1123 K under steam atmosphere (The magnification is 2 kx and scale bar for each image is 20 μm, the melting surface was surrounded by dotted line)

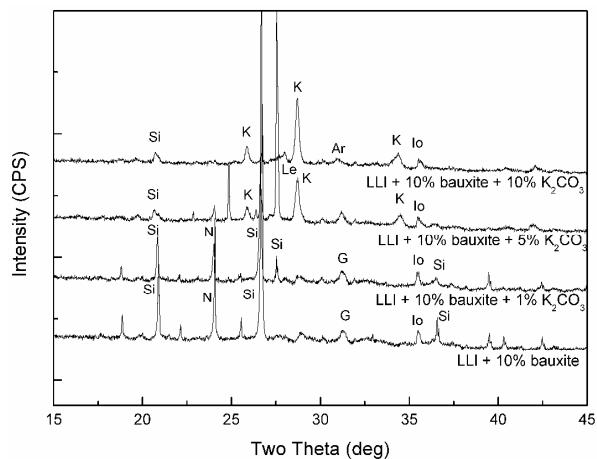
Figure 4



(Si - Silicon oxide (SiO<sub>2</sub>); Io - Iron oxide (Fe<sub>3</sub>O<sub>4</sub>); K – Kaliophilite (KAlSiO<sub>4</sub>); N - Nosean (Na<sub>8.08</sub>(Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>)(SO<sub>4</sub>)<sub>0.98</sub>); G - Gehlenite (Ca<sub>2</sub>Al(AlSi)O<sub>7</sub>); Ar – Arcanite (K<sub>2</sub>SO<sub>4</sub>); At - Anorthoclase ((Na,K)(Si<sub>3</sub>Al)O<sub>8</sub>); Ab - Albite (NaAlSi<sub>3</sub>O<sub>8</sub>); Le - Leucite (KAlSi<sub>2</sub>O<sub>6</sub>))

Figure 4 The XRD patterns of the ashes of LLI lignite with 1 wt% bauxite additive produced by different concentrations of K<sub>2</sub>CO<sub>3</sub> catalytic gasification at 1123 K under steam atmosphere

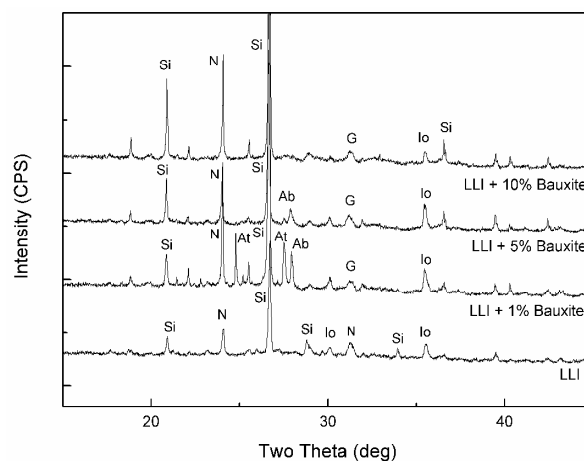
Figure 5



(Si - Silicon oxide ( $SiO_2$ ); Io - Iron oxide ( $Fe_3O_4$ ); K – Kaliophilite ( $KAlSiO_4$ ); N - Nosean ( $Na_{8.08}(Al_6Si_6O_{24})(SO_4)_{0.98}$ ); G - Gehlenite ( $Ca_2Al(AlSi)O_7$ ); Ar – Arcanite ( $K_2SO_4$ );  
Le - Leucite ( $KAlSi_2O_6$ ))

Figure 5 The XRD patterns of the ashes of LLI lignite with 10 wt% bauxite additive produced by different concentrations of  $K_2CO_3$  catalytic gasification at 1123 K under steam atmosphere

Figure 6



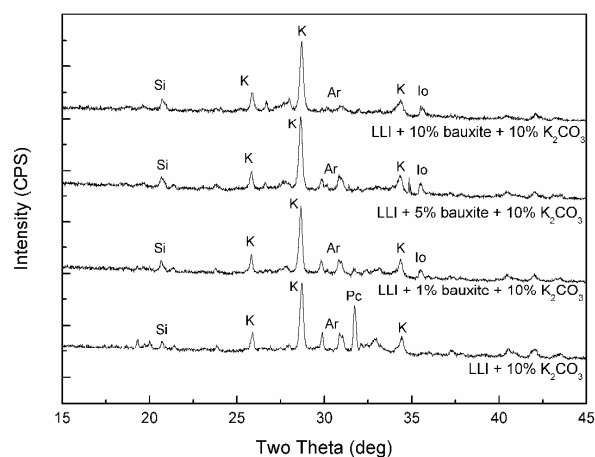
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G - Gehlenite ( $\text{Ca}_2\text{Al}(\text{AlSi})\text{O}_7$ ))

Figure 6 The XRD patterns of the ashes of LLI lignite with different concentrations of bauxite additive produced by gasification at 1123 K under steam atmosphere

Figure 7



(Ar – Arcanite (K<sub>2</sub>SO<sub>4</sub>); Si - Silicon oxide (SiO<sub>2</sub>); Io - Iron oxide (Fe<sub>3</sub>O<sub>4</sub>);

K – Kaliophilite (KAlSiO<sub>4</sub>); Pc – Potassium calcium silicate (K<sub>4</sub>CaSi<sub>3</sub>O<sub>9</sub>))

Figure 7 The XRD patterns of the ashes of LLI lignite with different concentrations of bauxite additive produced by catalytic gasification with 10wt% K<sub>2</sub>CO<sub>3</sub> at 1123 K under steam atmosphere