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Published in:
Fuel Processing Technology

Link to article, DOI:
[10.1016/j.fuproc.2017.10.005](https://doi.org/10.1016/j.fuproc.2017.10.005)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Anicic, B., Lin, W., Dam-Johansen, K., & Wu, H. (2018). Agglomeration mechanism in biomass fluidized bed combustion – Reaction between potassium carbonate and silica sand. *Fuel Processing Technology*, 173, 182-190. <https://doi.org/10.1016/j.fuproc.2017.10.005>

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1 **Agglomeration Mechanism in Biomass Fluidized Bed**
2 **Combustion – Reaction between Potassium Carbonate and**
3 **Silica Sand**

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ABSTRACT

Agglomeration is one of the operational problems in fluidized bed combustion of biomass, which is caused by interaction between bed materials (e.g. silica sand) and the biomass ash with a high content of potassium species. However, the contribution of different potassium species to agglomeration is not fully understood yet. In the present work, the reaction between K_2CO_3 and silica sand has been studied extensively by thermogravimetric analysis. The reacted samples were analyzed by SEM-EDX to reveal the reaction mechanism. The results indicated that the reaction occurs in a solid-solid phase already at temperatures around 700 °C. The reaction rate increases with increasing temperature, but decreases with an increase of CO_2 partial pressure. Using smaller particle size and well mixed solid reactants results in an increased reaction rate. It is observed that the reaction initiates in the contact area between K_2CO_3 and silica sand, forming a thin product layer. The layer acted as a reactive media further reacting with K_2CO_3 and silica sand. The results provide a basis for understanding of potassium induced agglomeration process in fluidized bed biomass combustion.

Keywords: fluidized bed combustion; biomass; agglomeration; reaction mechanism; potassium carbonate; silica sand.

1. INTRODUCTION

Fluidized bed combustion is a promising technology to utilize biomass for heat and power production [1]. The technology offers a good fuel flexibility and a high combustion efficiency [2–4]. However, a main challenge associated with fluidized bed combustion of biomass is agglomeration, which can influence bed hydrodynamics, change fluidization regime, and eventually result in defluidization, causing unscheduled shutdown of the plant [5–7]. In biomass combustion, agglomeration is to a large extent caused by the interactions between the bed materials (e.g. silica sand) and the potassium species present in biomass [5,8–10].

During combustion, the potassium in the biomass may be released and transformed to gaseous/aerosol phase (e.g. as KCl, K₂SO₄, K₂CO₃) or retained in ash. Knudsen *et al.* revealed that a fraction of 20 to 45 % of the potassium in annual biomass is released to the gas phase via KCl vaporization during combustion below 800 °C [11]. The presence of KCl in biomass ash was confirmed by several studies through XRD analysis [12–15]. At temperatures higher than 850 °C, the potassium release may be associated with decomposition of other potassium salts such as K₂CO₃ and K₂SO₄ [11]. K₂SO₄ has been found in the ashes obtained from straw and wood combustion [16,17]. The formation of K₂CO₃ during biomass combustion has been suggested by several thermodynamic studies [15,18,19], and it has been detected in the fly ash obtained from a full-scale pulverized wood combustion boiler [20], and in the ash obtained from a groundnut shell combustion below 650 °C [12]. In addition, Zhao *et al.* found that a significant amount of the K₂CO₃ can be present in the char from a fast pyrolysis of rice husk in a temperature range of 500–900 °C, based on the measured water soluble potassium and the anions (SO₄²⁻, PO₃³⁻, HCO₃³⁻) [21]. Recently, Chen *et al.* reported the formation of K₂CO₃ from char bonded potassium during pyrolysis of KCl loaded cellulose samples [22]. The potassium retained in the residual ash of a biomass is mainly present as potassium silicates [23,24].

The potassium species formed in fluidized bed biomass combustion may interact in different ways with the bed materials (typically silica sand). Grimm *et al.* suggested that the agglomeration process can be initiated by the formation of a coating layer via reactions between gaseous or liquid K-compound and silica sand bed material [2]. Scala *et al.* suggested that a non-molten or partially molten ash particles can be deposited at silica sand surface [9]. Subsequently, the potassium retained in ash (e.g. as K-silicates or K₂CO₃/K₂SO₄ in aerosol form) can interact with the sand forming various potassium silicates [9]. Moreover, some of the potassium species may condensate on the bed material surface, due to the difference between local combustion and an average bed temperatures [5]. Figure 1 summarizes the possible interactions between potassium species and bed material during biomass combustion.

Recently, Gatternig and Karl investigated the different agglomeration mechanisms relevant for biomass combustion, by performing two-stage experiments [5]. They concluded that the agglomeration is mainly caused by the interactions between the adhered solid ash particles and

the silica sand; resulting in formation of a multi-coating layer responsible for particles binding. The binding neck may consist of the molten ash particles, which was usually observed for herbaceous biomass. However, the gas-solid reaction and the condensation of potassium did not contribute to agglomeration in their experiments [5].

The interactions of different potassium species and silica sand have been studied under fluidized bed and fixed bed conditions to understand their impacts on agglomeration [25–27]. Sevonius *et al.* studied the agglomeration in a laboratory scale fluidized bed, with the silica sand as a bed material, by adding model salts (KCl , K_2CO_3 , K_2SO_4) in a temperature range of 750–900 °C [25]. A defluidization occurred in the case of KCl and K_2CO_3 addition, while no bed agglomeration was observed in the case of K_2SO_4 addition. KCl did not react with the silica sand but acted as a glue agent to bind bed particles, while K_2CO_3 reacted with silica sand to form a molten phase responsible for the bed agglomeration [25]. Narayan *et al.* performed similar experiments in a lab scale fluidized bed, where model salts (KCl and K_2CO_3) were added to the silica sand in order to identify the defluidization temperature [26]. The KCl addition caused defluidization in the temperature range 756–765 °C, while the K_2CO_3 addition caused defluidization between 728–737 °C. SEM-EDX analysis revealed that KCl did not react with the silica sand, while K_2CO_3 reacted with the sand, forming high viscous potassium silicates [26]. Ma *et al.* investigated the interaction between K_2SO_4 and SiO_2 under different atmospheres (air, steam and H_2) below 900 °C at fixed bed conditions [27]. Similar to Sevonius *et al.* work [25], no interaction between K_2SO_4 and SiO_2 in air and steam atmosphere was observed. However, the formation of a potassium silicate was observed in H_2 atmosphere below 900 °C, which was attributed to reaction between K_2SO_4 and silica sand under such conditions [27].

Although it is known that the reaction between K_2CO_3 and silica sand can induce agglomeration, the detailed reaction mechanism and the impact of reaction parameters are not well understood [25–27]. To our knowledge, only Arvelakis *et al.* briefly studied the reaction between K_2CO_3 and silica sand in a TGA [28]. A significant mass loss was observed for a mixture of K_2CO_3 and silica sand heated from 700 °C to 1100 °C. On the other hand, pure K_2CO_3 decomposition **under neutral atmosphere primarily** started at approximately 1050 °C [28], implying that the **significant mass loss measured below 1050 °C is a result of the** reaction between K_2CO_3 and silica sand.

In this work, a systematic investigation on the reaction between K_2CO_3 and the silica sand was performed in a TGA. The influence of the important parameters, such as temperature, CO_2 partial pressure, the mixing of solid particles, and particle size was examined. SEM-EDX analyses of the reaction products, and thermodynamic calculations of the reaction systems, were carried out to understand the reaction mechanism.

2. EXPERIMENTAL

2.1 Materials

Analytic pure potassium carbonate (CAS 584-08-7, 99.9%) with two particle size ranges, *i.e.* a size range of 2.58 to 224 μm (a mean diameter of 18 μm , hereafter denoted as powder K_2CO_3) and a size range of 146 to 489 μm (a mean diameter of 285 μm , hereafter denoted as coarse K_2CO_3), were used. Moreover, potassium silicate, $\text{K}_2\text{O}\cdot n\text{SiO}_2$ ($n=4$, corresponding to $\text{K}_2\text{Si}_4\text{O}_9$) was melted at 850 $^\circ\text{C}$, and grinded to a narrow size between 180 to 355 μm . The silica sand particles used have a size between 255 to 483 μm (a mean diameter of 385 μm), which is within the size range commonly used in fluidized bed boilers [29]. The sand was pretreated at 800 $^\circ\text{C}$ under oxidizing conditions for 2h in order to remove potential organic impurities.

The melting temperatures of the K_2CO_3 and SiO_2 are 891 $^\circ\text{C}$ and 1710 $^\circ\text{C}$, respectively [30]. Any reaction between K_2CO_3 and SiO_2 occurring below the melting points of both reactants indicates that the reaction is initiated in a solid-solid state [28]. Consequentially, mixing of the reactants may be an important parameter. Thus, three different mixing modes were used in the experiments: well-mixed, two layers (segregated layers of salt and sand with the same surface area), localized two layers (a layer of salt localized at the middle of the sand surface). The well-mixed samples were prepared by manual mixing of the particles for 10 mins in a cylindrical TGA crucible with a diameter of 16 mm and a height of 20 mm. The two layers samples were prepared by placing the sand at the bottom of the crucible, while the K_2CO_3 was placed above it to completely cover the upper sand surface. The procedure was similar for preparing the localized two layers samples, but in this case the K_2CO_3 was localized at the middle of the sand layer.

2.2 Experimental setup

The experiments were carried out in a high-heating rate thermogravimetric analyzer (TGA, *Netsch STA 449 F1 Jupiter*), which is capable to heat up the sample up to a maximal heating rate of 1000 K/min. The uncertainty of the TGA is ± 0.001 mg, which is several orders of magnitude lower than the mass of samples placed (approximately 0.7 g in each run) in the TGA, indicating that the instrumental error is negligible. Besides that, the results of the repeatability tests showed that the average deviation of the experiments was less than 2% (provided in the Supporting Information).

The same temperature program was used for all experiments: the sample was firstly heated to 150 $^\circ\text{C}$ and kept for 1 hour to remove moisture. Afterwards, the sample was heated to a final temperature (between 700 and 850 $^\circ\text{C}$) at a heating rate of 500 K/min and kept for 4 hours. The heating rate was chosen to mimic the rapid heating of particles in a fluidized bed. However, due to the high heating rate, the experiments are to a large extent carried out under isothermal conditions. Thus, for presenting the results, the initial time ($t = 0$ s) is chosen to be the time when the final temperature was reached. A gas flow rate of 50 ml/min was used for all experiments.

The experiments were carried out under pure N₂, pure CO₂, and a mixture of 50% CO₂ and 50% N₂ conditions. Considering the typical flue gas composition in a fluidized bed boiler, it would be interesting to study the reaction under H₂O atmosphere. However, our TGA cannot be operated under H₂O atmosphere. Based on thermodynamic equilibrium calculations, the difference of studying the reaction in N₂ atmosphere and in air atmosphere is negligible. Thus, for the convenience of operating the TGA, N₂ is used instead of air.

2.3 Analytical methods

The solid samples obtained from the experiments were analyzed by using a Scanning Electron Microscopy with Energy dispersive X-ray (SEM-EDX) analysis (*JEOL JSM-5910*). Some of the samples were imbedded in an epoxy resin and gradually polished using a fine emery paper and an ethanol solution to reveal the cross section of the agglomerated silica sand grains.

Additionally, XRD analysis was performed to identify the products of reaction using a Huber diffractometer with a characteristic Cu K α radiation and operation conditions of 40 kV and 40 mA. The exposure time was 30 mins.

2.4 Thermodynamic equilibrium calculations

Thermodynamic equilibrium calculations can provide information about the thermodynamically favored products under different operating conditions. In the present work, equilibrium calculations of the reaction systems were performed in the FACTSAGE 7.0 software. The FToxid and the FactPS databases were chosen for the simulation. SlagA model for liquid phase calculation was chosen, since it gave the best fitting between the calculated results of the investigated system and experimentally results reported for a similar K₂O-SiO₂ system [30].

The calculations were done for different SiO₂:K₂CO₃ molar ratios under pure N₂ and pure CO₂ atmospheres. Calculations were performed in the temperature range 500 and 1500 °C, but the range between 700 and 900 °C is most relevant for the present study. The most common SiO₂:K₂CO₃ molar ratio used in experiments was 1:0.013 (equal to 100:3 mass ratio), corresponding to the overall (global) ratio. Moreover, since both reactants were present in the solid state, it is expected that the local concentration differs from the global concentration. Thus, a range of SiO₂:K₂CO₃ molar ratios, from 1:0.013 to 1:1, were used in equilibrium calculations. 1 mol of SiO₂ was used in all calculations and the amount of K₂CO₃ was changing in order to obtain specified ratios. The amount of bulk gas was in large excess and it was set to 100 moles for all calculations. Preliminary calculation showed that when in large excess, the exact amount of bulk gas has no impact on the results of equilibrium calculations.

3. RESULTS AND DISCUSSION

3.1 Equilibrium distribution of potassium species

The distributions of potassium species predicted by thermodynamic equilibrium calculations are shown in Figure 2. Moreover, the calculation results for the pure K_2CO_3 in CO_2 and N_2 atmosphere are given as supporting material.

Thermodynamic equilibrium calculations indicated that at least three different potassium silicates can be formed through the following global reactions:

The results show that the formation of different potassium silicates (K_2SiO_3 , $K_2Si_2O_5$ and $K_2Si_4O_9$) is already thermodynamically favorable at 600°C. At high temperatures, these potassium silicates all convert to a molten phase slag.

The formation of the different potassium silicates depends on the molar ratios of the reactants and the gas atmosphere. For high $SiO_2:K_2CO_3$ molar ratios (1:0.25 or above), the formation of $K_2Si_4O_9$ is favorable, and it converts to a molten slag phase at approximately 770 °C, which is in agreement with the experimentally reported formation of liquid phase for $SiO_2:K_2O$ systems [30]. For a $SiO_2:K_2CO_3$ molar ratio of 1:0.33, both $K_2Si_4O_9$ and $K_2Si_4O_5$ present at low temperatures, and they convert to a molten slag phase at approximately 750 °C. For $SiO_2:K_2CO_3$ molar ratios above 1:0.33, the impacts of the N_2 and CO_2 atmospheres on the equilibrium distribution of potassium species are generally negligible.

The impact of the gas atmospheres is significant when the $SiO_2:K_2CO_3$ ratio becomes 1:1. In pure N_2 atmosphere, the solid phase K_2SiO_3 is the only thermodynamically stable species in the temperature range of 700-900 °C. In CO_2 atmosphere, both $K_2Si_2O_5$ and K_2CO_3 exist at temperatures below 840 °C. Above this temperature, the $K_2Si_2O_5$ and a part of K_2CO_3 convert to a molten slag phase. These results indicate that K_2CO_3 conversion is hindered in presence of CO_2 , probably due to the fact that the equilibrium of reaction (1) is shifted to left due to the Le Chatelier's principle. Consequentially, as the K_2CO_3 amount is increasing the formation of K_2SiO_5 is more favorable compared to K_2SiO_3 ; meaning that some K_2CO_3 remains unconverted.

3.2 TGA results

Aforementioned reaction (1) indicates that conversion of K_2CO_3 can be monitored by the mass loss caused by the release of CO_2 . Since thermal decomposition of the K_2CO_3 is significant only above 1050 °C, all the mass loss below this temperature was attributed to the CO_2 release, and the K_2CO_3 conversion can be calculated accordingly.

3.2.1 Influence of reaction temperature

The conversions of powder K_2CO_3 under N_2 atmosphere, with a $SiO_2:K_2CO_3$ mole ratio of 1:0.013, are plotted at Figure 3. The results show that the reaction rate increased with increasing temperature. The reactants were partially converted before the system reached isothermal

condition. The conversion of K_2CO_3 in the heating-up stage was increased with increasing reaction temperature.

At temperatures above 750 °C, K_2CO_3 can be completely converted. However, at 700 °C, the conversion was only approximately 0.8 with a reaction time of 4h. Considering the typical operation temperatures (800-850 °C) of a fluidized bed boiler and the long residence time of bed particles, the results imply that the reaction between K_2CO_3 and silica sand can occur to a considerable degree, if the K_2CO_3 and silica sand particles are in close contact.

The performed thermodynamical calculations revealed that formation of melt phase is possible above 750 °C. Consequentially, above 750 °C, the overall reaction mechanism can be influenced by the change in physical properties of the formed products. That can provide an explanation why the complete conversion was achieved relatively fast above 750 °C, compared to the 700 °C where only 0.8 conversion was reached.

3.2.2 Impact of particle size of K_2CO_3

Figure 4 illustrates the impact of K_2CO_3 particle size (coarse and powder) at two different temperatures (750 °C and 800 °C), with well-mixed $SiO_2:K_2CO_3$ (mole ratio 1:0.013) samples in the N_2 atmosphere. The results indicate that the K_2CO_3 particle size significantly influenced the initial reaction stages. For the powder K_2CO_3 particles, a complete conversion was achieved at both temperatures. However, the coarse K_2CO_3 particles only reached a stable conversion around 0.8 and 0.9, respectively, at 750 °C and 800 °C.

3.2.3 Influence of CO_2 partial pressure

The influence of the gas environment was evaluated by performing experiments under pure N_2 , pure CO_2 and a mixture of 50% N_2 and 50% CO_2 . All experiments were performed at 800 °C, using well-mixed SiO_2 and powder K_2CO_3 with a mole ratio of 1:0.013. The obtained results are plotted at Figure 5. It is shown that the presence of CO_2 strongly inhibited the reaction, especially at the initial stage. However, the difference between 50% CO_2 and 100% CO_2 was insignificant.

Thermodynamic calculations revealed that the impact of atmosphere is significant with low $SiO_2:K_2CO_3$ molar ratio, where the conversion of K_2CO_3 is less favorable in the presence of CO_2 .

We believe the impact of thermodynamics is dominant in our case. However, the presence of CO_2 may also influence CO_2 desorption from the reaction surface, which was observed in the sodium carbonate/silica sand system [31,32].

3.2.4 Impact of sand to K_2CO_3 mole ratio

Figure 6 shows the impact of mole ratios, for the well-mixed SiO_2 and powder K_2CO_3 samples at 800°C and the N_2 atmosphere. A minor effect of the different K_2CO_3 content can be observed at the initial reaction stage, showing a slightly higher conversion for a lower content of K_2CO_3 . The difference became negligible after the conversion reached approximately 0.95. Overall, all curves were close to each other, implying an insignificant impact of varying $SiO_2:K_2CO_3$ molar ratio from 1:0.009 to 1:0.022.

3.2.5 Impact of mixing

Figure 7 illustrates the effect of mixing on the K_2CO_3 conversion, for SiO_2 and powder K_2CO_3 with a mole ratio of 1:0.013 under N_2 atmosphere, 800°C. Initially, the conversions of the two layers and the localized two layers samples were significantly lower compared to the well-mixture sample. The two-layer sample eventually reached an almost complete conversion after a residence time of 4h. On the other hand, the final conversion of K_2CO_3 , in the localized two layers sample, was only about 0.3.

3.2.6 Comparison of fused glass and silica sand

Figure 8 compares the K_2CO_3 conversion with a fused glass and the silica sand. Powder K_2CO_3 was used in both experiments, and it was localized at the middle of the sand/glass surface (localized two layers). The fused glass was used in order to investigate the impact of the SiO_2 structure on the overall reaction rate. The silica sand has a crystalline structure, while the fused glass is in amorphous phase.

The K_2CO_3 conversion profiles were similar to each other. The initial conversion (up to about 0.15) was almost the same for the two cases. Then a noticeable change in the K_2CO_3 conversion rate occurred for both samples, with the fused glass having a slight higher reaction rate. The small difference between the fused glass and silica sand might be associated to the difference in surface smoothness.

3.2.7 Reaction between K-silicate and K_2CO_3

Figure 9 compares the K_2CO_3 conversions with potassium silicate ($K_2Si_4O_9$) and silica sand. Powder K_2CO_3 was used in both experiments, with a reaction temperature of 800 °C in N_2 atmosphere. The results indicated that the reaction rate was similar for silica sand and the potassium silicate. At high conversion degrees, the reaction rate was slightly lower for potassium silicate. Since $K_2Si_4O_9$ is a possible product from the reaction of silica sand and potassium carbonate, the experiments indicate that the formed intermediate potassium silicate product may further react with the potassium carbonate forming different mixtures of potassium silicates.

3.3 SEM-EDX analyses

SEM-EDX analyses of the reaction products were performed in order to understand the reaction mechanism. Figure 10 represents a grain from the two layers mixture under the CO_2 atmosphere with a K_2CO_3 conversion degree of 0.22. Spot 1 characterizes the unreacted K_2CO_3 , while Spot 3 is the unreacted silica sand surface. Spot 2 represents a layer of produced potassium silicate covering the silica sand surface. The smooth surface implies that the potassium silicate is melted under the experimental temperature (800 °C). Besides, Figure 10 indicates that the reaction can proceed away from the initial contact points between K_2CO_3 and the silica sand, since the formed potassium silicate had invaded the unreacted silica surface. However, at the current conditions, the extent of invasion was limited, since only a part of the sand surface was covered by the product layer.

The observations from Figure 10 lead to a hypothesis that formation of a product coating layer around the sand particle is possible at high conversion degrees and sufficient initial contact areas. The hypothesis is supported by Figure 11, showing that the sand surface is completely covered by a product layer consisting of potassium silicate.

Reacted samples with different K_2CO_3 conversion degrees (0.15/0.55/0.99) were imbedded in an epoxy resin and polished in order to obtain a cross-sectional view of the agglomerated grains. Figure 12 represents the cross-section SEM images of these samples together with an elemental analysis along the lines, as well as the elemental compositions of selected points (e.g. A1). The elemental analysis along the lines provided the intensity of the EDX emission, showing qualitatively the relative distribution of the elements.

Sample A shows the initial stage of the reaction. Spot A1 represents the unreacted potassium carbonate, and Spot A2 represents an initial product layer with a Si:K molar ratio of approximately 1. However, the formed product layer is more heterogeneous compared to the layers in Sample B and Sample C.

In Sample B and Sample C, the product layers are quite homogeneous, with more or less constant Si:K molar ratios. The ratio is approximately 2.2 and 2.5, respectively, for Sample B and Sample C, indicating that the product layer consists of a mixture of $K_2Si_4O_9$ and SiO_2 . It should be pointed out that no unreacted potassium carbonate was observed in the Sample 2 for this particular grain, meaning that its local concentration was relatively low and it was fully converted under the operating conditions.

The obtained results are similar as SEM-EDX analysis of agglomerated samples from straw combustion in a lab scale fluidized bed [8]. Lin *et al.* reported the formation of a continuous product layer covering silica sand surface and acting as a binder of grains. They observed a steep potassium concentration profile at the interphase between the layer and the grain, and concluded that the formation of the layer was main reason for agglomeration [8].

Beside the described SEM-EDX analyses, XRD analysis was also performed to identify the reaction products. The only crystalline phase detected was SiO_2 , indicating that all of the products were present in amorphous form. The results of XRD analysis are given as supporting material.

3.4 Plausible reaction mechanism

A reaction mechanism, which is proposed based on the experimental results and thermodynamic calculations, is schematically presented in Figure 13. The reaction between K_2CO_3 and the silica sand starts at the contact area between the reactants. Initial stage of the reaction depends on the contact areas between reactants, and it results in a relatively homogeneous molten layer of potassium silicates with a comparative low Si:K ratio (e.g. a mixture of $K_2Si_4O_9$ and $K_2Si_2O_5$). The molten potassium silicates layer can further react with both the silica sand and K_2CO_3 ,

1 resulting in an expanding homogeneous product layer with increasing Si:K ratios (e.g. a mixture
2 of $K_2Si_4O_9$ and SiO_2).

3 One of the possible reactions between K_2CO_3 and potassium silicates has been illustrated in
4 Figure 9. The interface between K_2CO_3 and the product layer probably has a relatively low local
5 Si:K ratios. Thus, according to the thermodynamic calculations in Figure 2, the reaction rate at
6 the interface may be inhibited by the presence of CO_2 , resulting in the experimentally observed
7 lower reaction rate under CO_2 atmospheres.

8 **3.5 Practical implication**

9 The investigated mechanism of the reaction between K_2CO_3 and SiO_2 can contribute to the
10 overall understanding of agglomeration mechanisms in biomass-fired fluidized bed boilers.
11 Potassium carbonate may be generated from conversion of char bounded potassium, as indicated
12 by previous research [12,20,21]. At the typical fluidized bed boiler temperatures (around 850
13 °C), formed K_2CO_3 is typically present in form of aerosols. It can come into a contact with the
14 silica sand particles, thus initiating solid-solid state reaction that results in the formation of a
15 molten potassium silicates product layer. The layer can further react with the attached K_2CO_3 . As
16 a consequence, the thickness of the product layer will increase. At the same time, the formed
17 product layer is capable of dissolving SiO_2 , which will further increase the thickness of the
18 formed coating layer. As the layer thickness is increasing, the particle becomes stickier and they
19 will agglomerate when a critical thickness is achieved. This may cause bed defluidization.

21 **4. CONCLUSIONS**

22 Based on the results of this work, the following conclusions can be drawn for the reaction
23 between K_2CO_3 and silica sand:

- 24 1. Potassium carbonate can react with silica sand to release CO_2 at temperatures well below
25 the decomposition temperature of potassium carbonate. The reaction occurs in solid-solid
26 phase with a high reaction rate at temperatures relevant to fluidized bed combustors
27 ($> 800^\circ C$).
- 28 2. The reaction rate increases with increasing temperature, but decreases with an increase of
29 CO_2 partial pressure. Mixing of the two solid reactants has a significant impact on the
30 reaction rate, which is much higher for the well mixed particles than for the segregated
31 particles due to enhanced contact between the solid particles. Moreover, the reaction rate
32 is affected in a same way by the particle size of K_2CO_3 , i.e. smaller particle size results in
33 a higher reaction rate.

3. Based on the SEM/EDS analyses of the samples, a plausible mechanism of the reaction is proposed. The reaction is initiated by surface reaction at the contact area between K_2CO_3 and silica sand, forming a molten homogeneous product layer. The product layer further reacts with K_2CO_3 and silica sand.
4. The results obtained in this work provide a basis for understanding of potassium carbonate induced agglomeration process in fluidized bed biomass combustion.

ACKNOWLEDGMENT

This project is funded by Innovation Fund Denmark (DANCNGAS), Sino-Danish Center for Education and Research, and Technical University of Denmark, which are gratefully acknowledged.

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FIGURES

Figure 1: Interaction between potassium species formed during biomass combustion and bed material.

Figure 2: Thermodynamic equilibrium calculation for different SiO₂:K₂CO₃ molar ratios under different atmosphere

Figure 3: K_2CO_3 conversion rates at different temperatures. Pure N_2 environment; $SiO_2:K_2CO_3$ molar ratio = 1:0.013; well mixed mixtures; powder K_2CO_3 ; total residence time 4h.

Figure 4: K_2CO_3 conversion rates for different sizes of K_2CO_3 . Pure N_2 environment; $SiO_2:K_2CO_3$ molar ratio = 1:0.013; well mixed mixtures; total residence time 4h.

Figure 5: K_2CO_3 conversion rates under different gas atmospheres. $T = 800\text{ }^{\circ}\text{C}$, $SiO_2:K_2CO_3$ molar ratio = 1:0.013; well mixed mixtures; powder K_2CO_3 ; total residence time 4h.

Figure 6: K_2CO_3 conversion rates for K_2CO_3 :sand mixtures with different molar ratio. $T = 800^\circ\text{C}$, Pure N_2 ; well mixed mixtures; powder K_2CO_3 ; total residence time 4h. ($\text{SiO}_2:\text{K}_2\text{CO}_3 = 1:0.009$ mol/mol = 100:2 wt./wt. ; $\text{SiO}_2:\text{K}_2\text{CO}_3 = 1:0.013$ mol/mol = 100:3 wt./wt.; $\text{SiO}_2:\text{K}_2\text{CO}_3 = 1:0.022$ mol/mol = 100:5 wt./wt.)

1
2 **Figure 7: K_2CO_3 conversion rates for different mixtures. $T = 800\text{ }^{\circ}\text{C}$; Pure N_2 ; $SiO_2:K_2CO_3$ molar ratio = 1:0.013; powder**
3 **K_2CO_3 ; total residence time 4h.**

Figure 8: K_2CO_3 conversion rates rate for SiO_2/K_2CO_3 and fused glass/ K_2CO_3 samples. $T = 800\text{ }^{\circ}C$; Pure N_2 ; powder K_2CO_3 ; total residence time 4h.

Figure 9: K_2CO_3 conversion rate of $SiO_2:K_2CO_3$ and $K_2Si_4O_9:K_2CO_3$ mixtures: $T = 800\text{ }^\circ\text{C}$; Pure N_2 ; powder K_2CO_3 ; total residence time 4h.

Elemental composition (mol %)

Spot	K	O	Si	Si:K ratio
1	0.17	0.83	0	0
2	0.12	0.67	0.21	1.85
3	0	0.52	0.48	–

Figure 10: SEM-EDX analysis of a representative reaction product: 0.22 K_2CO_3 conversion; $\text{SiO}_2\text{:K}_2\text{CO}_3$ molar ratio = 1:0.013; $T = 800\text{ }^\circ\text{C}$; pure CO_2 atmosphere; segregated mixture; powder form of K_2CO_3 ; isothermal reaction time 4h.

Elemental composition (mol %)

Spot	K	O	Si	Si:K ratio
1	0.11	0.55	0.34	2.97
2	0.10	0.60	0.30	3.08

- 1
 - 2
 - 3
 - 4
- Figure 11: SEM-EDX analysis of a silica sand grain covered by formed product layer: full K_2CO_3 conversion $\text{SiO}_2\text{:K}_2\text{CO}_3$ molar ratio = 1:0.013; T= 800 °C; pure N_2 atmosphere; well mixed sample; powder form of K_2CO_3 ; isothermal reaction time 4h.

Figure 12: SEM-EDX analysis of imbedded samples. Sample A: K_2CO_3 conversion 0.15; $\text{SiO}_2:\text{K}_2\text{CO}_3$ molar ratio = 1:0.013; $T = 800^\circ\text{C}$; pure CO_2 atmosphere; residence time 10 min. Sample B: K_2CO_3 conversion 0.55; $\text{SiO}_2:\text{K}_2\text{CO}_3$ molar ratio = 1:0.013; $T = 800^\circ\text{C}$; pure CO_2 atmosphere; residence time 2 h. Sample C: K_2CO_3 conversion 0.99; $\text{SiO}_2:\text{K}_2\text{CO}_3$ molar ratio = 1:0.013; $T = 800^\circ\text{C}$; pure N_2 atmosphere; residence time 4 h.

Figure 13: Schematic representation of the reaction mechanisms between K_2CO_3 and silica sand