PARTICLE AGGLOMERATION IN FLUIDIZED BEDS: MECHANISMS, EARLY DETECTION AND POSSIBLE COUNTERMEASURES

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Abstract – Particle agglomeration in fluidized bed systems has been observed in several industrial processes. Bed particles tend to agglomerate when the cohesive force between the particles is strong enough to compare with the other acting forces (gravitational, drag). This cohesive force may arise because of different types of interactions: van der Waals, electrostatic, capillary, viscous, sintering, adhesive, chemical reaction, and so on. The most extensively reported case in the literature is concerned with the fluidized bed combustion of biomass, waste or low-rank coals, containing significant amounts of low-melting compounds (typically alkali metals) in the ash. The occurrence of bed agglomeration in such systems implies the unscheduled shut down of the reactor and costly maintenance operations. Therefore, a great deal of research has been devoted to understand and characterize agglomeration during fluidized bed combustion. This review is focused on this specific system and tries to summarize the present status of understanding of the mechanisms leading to agglomeration, as well as the influence of the different operating variables on this phenomenon. In addition, because of their great practical importance, the possible early detection techniques and operational countermeasures are also briefly described.

INTRODUCTION

Fluidized bed agglomeration in combustion and gasification systems has been reviewed in the literature in the past decade. Bartels et al. (2008) first tried to summarize the current understanding on this problem with a specific emphasis on the development of agglomeration detection techniques. Subsequently, Mettanan et al. (2009) and Khadilkar et al. (2016) reviewed this issue, the latter giving special emphasis on possible agglomeration models development. Niu et al. (2016) also devoted a small section of their review on ash-related issues during biomass combustion on agglomeration in fluidized beds. Billen et al. (2014a) focused their review on equilibrium calculations directed to predict melt formation and, in turn, agglomeration in fluidized bed combustion (FBC). Finally, though not being strictly a review paper, the recent work of Gatterning and Karl (2015) summarizes the current understanding of the agglomeration mechanisms during biomass FBC.

Since the early eighties, operational experience was reported of FBC of low-grade coals, mostly lignite, giving rise to bed agglomeration problems (Goblirsch et al., 1980 and 1982; Rice et al., 1980; Bobman et al., 1985). In the most severe cases agglomeration resulted in the total bed defluidization and combuster shutdown. These problems were recognized to be connected to the large amounts of alkali metals (sodium and/or potassium) included in the fuel ash. At the typical FBC operating temperatures, alkali were found to build up on the inert bed particles surface (typically silica sand and/or limestone) where low-melting-point eutectics with silica and calcium were formed, as soon as the alkali concentration reached a large enough value. Melting of material at the surface of the inert particles enhanced their stickiness, leading to the attachment of an increasing number of bed particles together, and to the formation of large agglomerates. Alkali form and content in the fuel ash, nature of the inert bed material, combustion time and temperature were all found to be key parameters in the agglomeration process (Rizeq and Shadman, 1989; Atakül and Ekinci, 1989). Manzoori and Agarwal (1992, 1993 and 1994) studied the FBC of high-sodium lignite and shed new light on the agglomeration mechanism. They found that, independently of the fuel particle size and temperature, sodium vaporization was limited under FBC conditions while inorganic elements in the ash tended to form a molten matrix on the char surface. This ash transferred to the surface of the inert bed particles most likely as a result of random collisions in the bed. No evidence was found to suggest that ash deposition was caused or initiated by chemical reaction or by vapor condensation. Interestingly, the bed temperature was found not to affect significantly the composition of the ash coating, but only to alter its physical properties (e.g. viscosity). The rate of ash deposition on the bed particles was typically constant during the combustion runs, only dependent on the fuel ash alkali content and bed temperature. Moreover, a critical thickness of the ash coating was necessary to start the agglomeration process.
In the last two decades the declining of conventional energy supplies and pressing environmental constraints have directed a growing interest to the exploitation of biomass resources as a renewable and CO₂-neutral energy source. The attractiveness of biomass has prompted, in turn, research on technologies suitable for converting this class of fuels. Among the others, FBC was indicated as one of the most promising ones, because of its fuel flexibility, high combustion efficiency and low environmental impact. However, agglomeration/defluidization problems were often reported (Albertson, 1989; Davies et al., 1989; Nordin, 1995; Bapat et al., 1997; Wu et al., 1999; Ryabov et al., 2003), even at operating temperatures as low as 650°C (Grubor et al., 1995), especially when crops cultivated with a high degree of fertilization were burned, as these residues generally contain higher amounts of alkali in their ash (Fig. 1). Operational experience showed that bed defluidization was accompanied by a sharp drop in the differential pressure across the bed, as a result of channeling through the bed by fluidizing air (Salour et al., 1993). In addition, a substantial decrease of the in-bed temperatures (because of the lack of combustion in the bed), and a significant increase of the temperature in the lower freeboard section (due to the biomass combustion on the top of the agglomerated bed) was observed upon bed defluidization, making the operation uncontrollable.

**MECHANISMS OF BED AGGLOMERATION AND EFFECT OF OPERATING VARIABLES**

A considerable research effort has been devoted to this subject to date, and now the mechanisms of biomass ash-bed material interaction leading to bed agglomeration are reasonably well understood. Ghaly et al. (1993 and 1994) simulated in a muffle furnace the high temperature interaction between straw ash and either silica or alumina sand. They found that at temperatures above 850°C the straw ash interacted with silica sand forming a melt, because of the presence of a low-temperature eutectic in the potassium-silica system. On the other hand, at the same temperatures alumina sand was found not to interact significantly with the straw ash. Nevertheless, at such temperatures the straw ash melted and covered the alumina particles with a sticky layer. Latva-Somppi et al. (1998) and Valmari et al. (1999) studied the mechanisms of ash deposition on quartz sand particles in full-scale fluidized bed boilers firing different biomass fuels. Results suggested that ash deposition was dominated by two parallel mechanisms: 1) the adhesion (promoted by particle collisions) of micron-sized ash particles on sand surface and their consecutive sintering, forming a porous layer around the particles; and 2) the diffusion of alkali species (especially potassium) to the quartz interface where a compact layer was formed. This latter mechanism was imputed both to solid-state diffusion of alkali from the ash layer to the quartz core and to the direct attack of quartz by volatilized alkali species. Skrifvars et al. (1998 and 1999) stressed the importance of the sintering tendency by partial melting of biomass ash as a cause of bed agglomeration. They proposed a combined method for predicting the sintering tendency of the ash, based on compression strength tests and thermodynamic multicomponent multiphase equilibrium analysis. The main limit of this procedure was that the interaction of the ash with the inert bed material was not taken into account. They also tested the usefulness of standard ASTM ash fusion test, which failed to predict the experimental bed agglomeration temperatures. On the whole, the results suggested that ex-situ methods, not recreating the real environment experienced by the ash in a fluidized boiler, are likely to be unsuitable to correctly predict the agglomeration tendency of biomass fuels.
Öhman and Nordin (1998) proposed a controlled fluidized bed agglomeration method for biomass fuels. This method consisted in the preliminary ashing of a certain quantity of biomass in a fluidized bed followed by a temperature increase (by external heating) of the inert bed-ash system until bed defluidization was achieved (as detected by a drop of the differential bed pressure). The method was applied to a number of biomass fuels to rank their agglomeration tendencies during FBC (Natarajan et al., 1998; Öhman et al., 2000; Zevenhoven-Onderwater et al., 2006). The measured agglomeration temperatures were fairly accurate and reproducible, but uncertainties remained on how well bed agglomeration in full-scale units compare to the results of simulated experiments. In particular, the local overheating near burning char particles and the progressive accumulation of ash in the bed during steady combustion were not taken into account with this method. Further analysis of bed samples collected throughout the tests indicated that all the bed particles were coated with a relatively homogeneous ash layer mainly composed of silica, calcium and potassium in variable amounts. The outermost layer of the coating appeared to be heterogeneous, suggesting that small ash particles deposited on the partially molten coating and gradually homogenized with time. The melting behaviour of the coating was very sensitive to the potassium content and was ultimately responsible for bed agglomeration. The presence of an inner layer around the bed particles mainly consisting of alkali and silica, and of an outer layer resembling the fuel ash composition was confirmed by extensive SEM-EDX analysis on bed samples collected during biomass FBC both in lab-scale and in full-scale tests (Nuutinen et al., 2003 and 2004; Brus et al., 2004 and 2005). The presence of high amounts of phosphorus in selected fuels was also recently shown to enhance agglomeration during FBC, possibly due to the formation of low-melting alkali phosphates or to the influence of phosphates on the availability of calcium in the system (Fryda et al., 2006; Boström et al., 2009; Grimm et al., 2011; Eriksson et al., 2012; Billen et al., 2014b and 2016).

A further contribution to the understanding of the agglomeration mechanism came from the work on straw FBC carried out by Lin et al. (1997, 1999, 2001, 2003a and 2003b). Systematic experiments in a lab-scale fluidized bed combustor showed that the variable which exerted the largest influence on agglomeration was the operating temperature, and that the bed defluidization time decreased exponentially with the temperature. A gradual build-up of potassium in the bed was measured during the run and, interestingly, the data showed that bed temperature had no significant influence on the potassium accumulation rate. This result, together with Simultaneous Thermal Analysis data on ash (Arvelakis et al., 2004), indicated that little potassium compounds were evaporated during combustion. During purposely carried out batch experiments, it was noted that several agglomerates were already formed a few minutes after straw feeding had started, and that they presented a blackish ash core and a shape similar to the straw pellets. This observation suggested that agglomerates had likely originated from potassium rich ash transferred by collisions from the burning char particles to the sand particles. The high temperatures experienced near burning char might have further promoted potassium transfer and subsequent melting. Two mechanisms for bed defluidization were proposed: 1) at low operating temperatures, an increasing number of agglomerates (consisting of a number of bed particles joined together by necks) is formed in the bed during combustion. These agglomerates would progressively build up a defluidized layer at the bottom of the bed, which would eventually lead to the total bed defluidization; 2) at high operating temperatures, instead, the stickiness of the bed particles would increase to a certain level where sudden defluidization occurs. In these conditions the fluidization gas cannot balance drag, gravity, buoyant and adhesive forces. Evidences reported in later studies (Olofsson et al., 2002; Visser et al., 2003) seemed to somewhat justify the above framework.

Recent research has demonstrated that FBC of most biomass fuels takes place with extensive generation of carbon fines (Salatino et al., 1998; Scala et al., 2000 and 2006). This is a consequence of the tendency of these fuels to yield highly porous or even incoherent chars after pyrolysis that are rather fragile and very susceptible to attrition and/or fragmentation during combustion. Attrited char may experience, upon further burn-off, peak temperatures largely exceeding the bed temperature, while coarse particles burn at temperatures only slightly above the bed one (Chirone et al., 2000; Scala et al., 2003). As a consequence, modifications of the ash constituents, like softening, melting or even vaporization, might occur even at nominal bed temperatures at which no such change in mineral matter would take place. Transportation of the fuel ash to the bed particles surface by random collisions between burning fines and inert particles was proposed to be a relevant mechanism responsible for the formation of ash-layered bed material. Upon impact with bed particles the formation of a softened or fluid phase at the contact point may be responsible for fines adhesion on the bed particles surface. In the event that the bed temperature is itself higher than the relevant eutectic temperature, fused potassium-silicate is permanently formed yielding a sticky surface layer responsible for bed agglomeration and defluidization. If the bed temperature is, instead, below the eutectic melting temperature, fines adhesion can still take place, but the formation of a surface melt on the bed solids is prevented.
Fig. 2. SEM micrographs of a typical agglomerate sample (A), the interior of a broken agglomerate (B), a detail of the external surface (C), and ash debris attached on the external surface (D). (Scala and Chirone, 2008).

Scala and Chirone (2006) questioned the importance of the alkali vaporization path on bed agglomeration. They reported that there is evidence in the literature that vaporization of alkali during biomass combustion is rather limited. On the other hand, accumulation of ash alkali onto inert bed was reported to be almost quantitative. In addition, the composition of the outermost coating layer around the sand was found to be very similar to the fuel ash composition, with only limited enrichment of alkali compounds. Finally, bed temperature was found not to influence appreciably both the alkali accumulation rate and the ash coating composition. Based on the above considerations they concluded that the vaporization–condensation mechanism was likely to have only a limited importance, if any, on alkali transfer onto the sand particles. However, they also noted that though limited, alkali vaporization is not negligible, and may be a significant cause of fouling and corrosion problems on the superheaters surfaces (Miettinen Westberg et al., 2003). It is likely that while the short gas residence time and the high temperature in the bed zone lead to little condensation of the gas-phase alkali species on the sand particles, in the low temperature zones of the combustor, where longer residence times are available for the gas, alkali condensation is favored. This reasoning has recently received support by evidence obtained in dedicated experimental tests carried out by Gatterning and Karl (2015). These authors demonstrated that negligible deposition of volatilized alkali species onto bed particles occurs under typical FBC conditions and proposed to neglect the alkali vaporization–condensation/reaction mechanism among the possible alkali-induced agglomeration mechanisms.

Scala and Chirone (2006) suggested that the most likely alkali transfer mechanism on the bed particles relies on collisions of char particles with sand. After depositing on the sand surface the alkali species migrate to the quartz interface by solid-state diffusion through the ash layer and then interact with silica leading to the possible formation of an eutectic. The alkali transfer by collisions is promoted by the high temperatures experienced near burning char, so that it is reasonable to assume that bed agglomerates may start to form around burning char particles. The higher temperatures experienced near burning char enhance the formation of melt and, in turn, the particles stickiness. Two different cases were suggested by these authors:
1) the bed temperature is higher than the relevant eutectic temperature. In this case, after the time necessary to accumulate enough alkali in the bed to reach the eutectic composition at the sand surface (or, from another point of view, the time necessary to reach a critical coating thickness around the sand), the bed suddenly defluidizes as a consequence of the permanent increase of stickiness of the whole sand bed;

2) the bed temperature is lower than the relevant eutectic temperature. In this case, even if alkali progressively accumulate on the sand the formation of a surface melt on the bed solids would be prevented. However, near the burning char, where the temperatures may be much higher than the bed temperature, agglomerates can still form by local surface melting. If these agglomerates are strong enough to withstand collisions within the dense bed, their number would progressively increase, building up a defluidized layer in the bed which would eventually lead to the total bed defluidization.

The above mechanism was further supported by evidence provided in Chirone et al. 2006 and Scala and Chirone (2008), who noted that agglomerates collected after bench-scale and pilot-scale FB combustion tests typically showed internal cavities, indicating that burning fuel particles were likely located inside and possibly initiated the agglomeration process (Figs. 2 and 3). These authors also showed that agglomeration was enhanced by increased bed temperature, smaller bed particle size and presence of internals. In particular, the effect of particle size was explained by considering that larger bed particles have more inertia and consequently are associated to more energetic collisions, so that adhesion of the particles to each other should be more difficult. By analyzing a large number of agglomerates with a SEM/EDX procedure (Fig. 4), Scala and Chirone (2006 and 2008) noted that a high fraction of low-melting point compounds (K, Na) and a low fraction of high-melting point compounds (Ca, Mg) in the fuel ash favours agglomeration. In addition, an initial fuel ash composition close to the low-melting point eutectic composition appears to enhance agglomeration (Fig. 5). This last observation justifies the following result: if the fuel ash is originally rich of both alkali and silica, ash melting may start before the ash encounters the sand particles. This circumstance leads to the so-called melt-induced agglomeration mechanism, which typically leads to extensive agglomeration when firing specific fuels like straw of herbaceous biomass (Gatterning and Karl, 2015).

One final issue that deserves further discussion is the distinction between the “coating-induced mechanism” and the “melt-induced mechanism” for bed agglomeration (Bartels et al., 2008; Liu et al., 2009; Mettanant et al., 2009; Gatterning and Karl, 2015). This distinction appears to be somewhat labile. In fact, the steps leading to bed agglomeration for the two mechanisms are similar: the ash coming from the burning char particles deposits on the surface of the bed particles by collisions, where it builds up until a critical thickness is reached leading to agglomeration. The difference between the two cases is that in the “melt-induced” mechanism the ash is already molten before it deposits onto the bed particles, while in the coating-induced mechanism the ash is solid and a melt is only formed after a suitable eutectic composition is reached in the innermost layer of the coating (which is responsible of the sticky behavior of the particle). However, in both cases the surface of the particles is completely covered by an ash layer: in fact, in the “melt-induced” mechanism it seems unreasonable that few ash particles could be able to form molten necks strongly binding two bed particles, but the build-up of a sufficiently thick molten layer around the particles appears to be necessary to lead to particle agglomeration (Gatterning and Karl, 2015). Clearly, in the “melt-induced” case agglomeration would occur much more rapidly and catastrophically than in the “coating-induced” case.

Fig. 3. Photograph of a fuel particle (A), a char particle (B), and a small sand agglomerate (C) (Chirone et al., 2006).
Fig. 4. SEM micrograph and EDX elemental maps of an agglomerate cross-section. (Scala and Chirone, 2006).

Fig. 5. Ternary diagram of the system K$_2$O-CaO-SiO$_2$ showing the measured composition of different zones on the surface of agglomerated samples, obtained by semiquantitative SEM/EDX spot analyses. (Scala and Chirone, 2008).
DETECTION OF BED AGGLOMERATION AND POSSIBLE COUNTERMEASURES

Apart from understanding the ash-bed material interaction and the agglomeration mechanisms, the possibility of an early detection of incipient bed agglomeration during biomass FBC would be of extreme importance. In this way, appropriate countermeasures to prevent total bed defluidization and boiler shutdown could be taken in due time. Bertels et al. (2008) have excellently reviewed this topic in detail, so that in the following we will only briefly outline the main achievements. As already noted before, *ex situ* methods based on different kinds of characterization of the fuel ash have not been successful in predicting bed agglomeration. In addition, these methods are not suitable for an “on-line” detection of agglomeration during FBC. On the other hand, the simplest available “on-line” measurements are temperature and pressure at different reactor locations, so that techniques involving these two kinds of measurements would be highly desirable. In addition, also acoustic emissions have been suggested as a possible means to monitor the fluid-dynamic status of the bed, though application of this technique appears to be more cumbersome.

The simple measurement of temperature and pressure profiles inside the bed is not appropriate for agglomeration prediction, being the change of these variables significant only upon bed defluidization. On the other hand, a suitable indicator of the quality of fluidization should detect the formation of agglomerates in the bed early enough to give the boiler operator the possibility to intervene on the process conditions. The temperature difference between two bed locations and the variance of either the temperature or the pressure signals in the bed have been proposed as possible early warning quantities able to predict the onset of agglomeration events, since they are strongly influenced by a change of bed fluid-dynamic and mixing conditions in the bed (Scala and Chirone, 2006; Chirone et al., 2006). Though lab-scale and pilot-scale tests were quite successful, the robustness of these techniques with respect to a change of load or of fluidization velocity during FBC was not demonstrated (Figs. 6 and 7).

![Graphs showing temperature, temperature variance, and relative temperature difference between two points at different height profiles at steady state.](image)

Fig. 6. Bed temperature (A), temperature variance (B) and relative temperature difference between two points at different height (C) profiles at steady state. (Scala and Chirone, 2006.)
A technique for the early detection of agglomeration in fluidized beds was more recently presented (Schouten and van den Bleek, 1998; van Ommen et al., 1999, 2000 and 2001; Korbee et al., 2003) based on non-linear pressure fluctuations time-series statistical analysis (attractor comparison analysis). After extensive testing at the lab-scale, and a number of improvements, this technique was successfully tested at the industrial scale (Nijenhuis et al., 2007; Bartels et al., 2009 and 2010) under the name of Early Agglomeration Recognition System (EARS). To date this technique appears to be the most reliable and robust for the on-line detection of agglomeration events during FBC.

Different possible methods for counteracting bed agglomeration have been proposed in the literature, as reviewed by Bertels et al. (2008), Mettanant et al. (2009) and Niu et al. (2016). The simplest action could be to lower the bed temperature and/or increase the gas velocity, since these two variables have been shown to be the most influential on agglomeration. However, these actions are highly undesirable in FBC operation since they involve a change in fluid-dynamics, heat and mass transfer, combustion efficiency, elutriation rate, pollutant emissions, etc. that may lead to an unacceptable combustor performance. On the other hand, a simple and feasible method that is often successful in avoiding bed agglomeration is to control the bed particle size by continuously draining spent bed material and feeding fresh sand. Another possible method implies pre-treatment of the fuel by leaching out the alkali metals before combustion. These methods are effective in preventing agglomeration, at the expense of an increased operating cost of the process.

Other effective methods rely on changing the ash composition in the bed and increasing its melting point. This can be accomplished in three different ways. The first possibility is to co-combust the high-alkali fuel with a low-alkali one. In particular, an auxiliary fuel with a significant ash content mostly made by high-melting point elements should be used. The aim is that of diluting the alkali metals in the bed and fixing them into high-melting point compounds. For example, the use of coal or sewage sludge as auxiliary fuels has been reported to successfully prevent agglomeration during FBC of high-alkali fuels. The second possibility is that of injecting in the bed solid additives that preferentially capture alkali compounds with respect to the bed particles. A large number of materials have been tested, mostly alumino and magnesium silicates and alkaline earth carbonates/oxides. This technique is also effective, and the cost of the additive appears to be the primary issue for applicability. In addition, the possible effect of the additive on the drained bed composition and on the convective pass deposits should be taken into account. Finally, the third possibility is to change the bed material from a silica-containing one (sand) into alternative ones without silica. Again different bed materials have been successfully tested (mostly made of aluminum, magnesium, calcium or iron oxides or their mixtures). Again, material cost and availability as well as its attrition tendency and the spent material disposal issues should be carefully considered for applicability. For all the
above three techniques it is important to note that if a fuel giving a “melt-induced” agglomeration mechanism is fired, the technique might not be able to avoid agglomeration, but only to delay its occurrence. In fact, such fuels contain in their ash all the necessary components to reach a low-melting eutectic, and molten ash is already formed before interacting with bed or additive material.

In summary, several possible effective countermeasures exist that can be used to avoid bed agglomeration. The choice of the best one requires a thorough cost optimization analysis, and would be dependent on the specific plant characteristics and especially on the ash composition of the biomass to be fired.

REFERENCES


