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AGGLOMERATION AND DEFLUIDIZATION IN FBC OF BIOMASS FUELS - MECHANISMS AND MEASURES FOR PREVENTION

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ABSTRACT

The use of biomass fuels in fluidized bed combustion (FBC) and gasification (FBG) is becoming more important because of the environmental benefits associated with these fuels and processes. However, severe bed agglomeration and defluidization have been reported due to the special ash forming constituents of some biomass fuels. Previous results have indicated that this could possibly be prevented by intelligent fuel mixing. In the present work the mechanisms of bed agglomeration using two different biomass fuels as well as the mechanism of the prevention of agglomeration by co-combustion with coal (50/50 %_w) were studied. Several repeated combustion tests with the two biomass fuels, alone (Lucerne and olive flesh), all resulted in agglomeration and defluidization of the bed within less than 30 minutes. By controlled defluidization experiments the initial cohesion temperatures for the two fuels were determined to be as low as 670 °C and 940 °C, respectively. However, by fuel mixing the initial agglomeration temperature increased to 950°C and more than 1050°C, respectively. When co-combusted with coal during ten hour extended runs, no agglomeration was observed for either of the two fuel mixtures. The agglomeration temperatures were compared with results from a laboratory method, based on compression strength measurements of ash pellets, and results from chemical equilibrium calculations. Samples of bed materials, collected throughout the experimental runs, as well as the produced agglomerated beds, were analysed using SEM EDS and X-ray diffraction. The results showed that loss of fluidization resulted from formation of molten phases coating the bed materials; a salt melt in the case of Lucerne and a silicate melt in the case of the olive fuel. By fuel mixing, the in-bed ash composition is altered, conferring higher melting temperatures, and thereby agglomeration and defluidization can be prevented.

INTRODUCTION

The use of traditional and "new" biomass fuels for both heat and electricity production is becoming more important because of the environmental benefits associated with these fuels. The most promising energy conversion technologies are based on fluidized bed combustion (FBC) or gasification (FBG). These processes enable higher electrical and total efficiency as well as greater flexibility concerning the use of various fuels. In addition, the relatively low combustion temperatures reduces the risk of operating problems due to the special ash forming constituents of the biomass fuels. A large number of FBC boilers in Sweden and Finland are presently using biomass fuels with very little or no problem. However, the ash characteristics vary considerably between different biomass fuels [Nordin 1994, Skrifvars and Hupa 1995] and severe bed agglomeration has been reported from FBC and FBG of several types of biomass fuels [Nordin 1995, Salour et al. 1993, Viktorén 1991, Bitowft and Bjerle 1986, Gulyurtlu et al. 1991].

In a recent work the importance of fuel mixing to prevent both harmful emissions and agglomeration was indicated [Nordin 1995]. When coal was co-combusted with an agricultural fuel (Lucerne) in a small pilot scale FBC, an optimal inherent sulphur retention of more than 90 % was obtained. No signs of agglomeration were observed whereas combustion tests of Lucerne alone, resulted in agglomeration and defluidization of the bed within less than one hour of normal operation. Control of in-bed agglomeration by fuel blending therefore seems to be an interesting approach and has also previously been demonstrated by Salour et al [1993]. However, despite some research work made in recent years, of which most has concerned coal combustion, the mechanisms of agglomeration and defluidization are not fully understood. The purpose of the present work was to present a closer study of the mechanisms of both bed agglomeration using two different biomass fuels and prevention of bed agglomeration by co-combustion of these fuels with coal.

EXPERIMENTAL

Fuels and bed material used

The fuels chosen for the present study were the previously studied agricultural fuel (Lucerne), an imported biomass fuel (olive flesh) and coal. Large scale test runs using the olive fuel in a pulverized fuel boiler showed extreme slagging [Höglund et al. 1995] and interest was shown in using the fuel in a FBC instead. The biomass fuels were pelletised to a diameter of 8-10 mm and the coal was crushed and sieved to sizes of 5-15 mm. The characteristics of the fuels and fuel ashes are presented in Table 1. Ashing of the fuels preceding elemental analysis was performed at 550 °C to reduce the loss of volatile ash elements. Molar compositions of the ashes, in forms as predicted by chemical equilibrium calculations for ashing conditions, are illustrated in Fig 1. All fuels were sieved before the experiments so that the fraction of fines could be kept to less than 2 % after the feeding. The bed material (quartz sand, 99.9%) was initially sieved to sizes between 200 and 250 μm .

Table 1 Fuel characteristics (wt%)

	Lucerne	Olive flesh	Coal	Lucerne/Coal	Olive/Coal
Dry substance	92.1	85.6	92.9	92.5	89.3
Ash ^a	8.5	9.9	6.6	7.5	8.2
HV (MJ/kg _{Fuel})	16.1	16.0	27.2	21.6	21.6
C ^a	46.7	50.2	77.3	62.0	63.8
H ^a	5.9	6.3	4.9	5.4	5.6
N ^a	3.1	1.4	1.3	2.2	1.4
S ^a	0.16	0.14	0.74	0.45	0.44
Cl ^a	0.35	0.15	0.08	0.22	0.12
O ^a	35.6	32.1	6.6	21.1	19.4
SiO ₂ ^b	3.9	36.2	43.6	23.8	39.9
Al ₂ O ₃ ^b	0.4	3.6	32.9	16.7	18.3
Fe ₂ O ₃ ^b	0.3	4.25	11.0	5.7	7.6
MgO ^b	3.2	12.4	1.8	2.5	7.1
CaO ^b	28.2	18.2	4.3	16.3	11.3
K ₂ O ^b	26.5	18.2	1.8	14.2	10.0
Na ₂ O ^b	0.8	1.7	0.8	0.8	1.3
P ₂ O ₅ ^b	8.2	4.0	1.9	5.1	3.0

^awt% dry matter^bwt% of ash **Figure 1** Illustration of the ash composition (550°C), as predicted by chemical equilibrium calculations

Pilot scale FBC tests

A pilot scale FBC reactor is used to study bed agglomeration and defluidization in a highly controlled way and under homogeneous conditions. The objects of the tests are; i) to quantify agglomeration tendencies of biomass fuels, as well as for blends of different fuels; and ii) to study the mechanisms of both agglomerate formation and prevention of agglomeration by co-combustion. The reactor is utilised in either of two operational modes. By normal combustion operation, a relatively accurate simulation of a full-scale case is accomplished. However, these tests are not suited for comparisons as the conditions are generally inhomogeneous and the actual temperature of the agglomeration cannot be determined. Our other mode of operation is therefore initiated by loading of the bed with a certain ash to bed material ratio, during normal combustion at a sufficiently low temperature. Then the fuel feeding is stopped and the bed is externally heated in a homogeneous and controlled way. The agglomeration/defluidization tendency for that specific fuel or fuel blend. Samples of bed and ash material for evaluation of mechanisms are collected periodically during the operation.

The pilot FBC reactor

A small pilot scale FBC reactor (5kW), previously constructed in order to facilitate well designed experiments under highly controlled conditions, is used (Fig. 2). The reactor was constructed from stainless steel, being 2 m high, 100 mm and 200 mm in bed and freeboard diameters, respectively.

Figure 2 Schematic view of the pilot scale fluidized bed reactor

Bed temperatures at four locations in the bed are measured by shielded thermocouples (type S) and four differential bed pressures are determined by differential pressure transmitters. To minimise the significant influence of cold walls in such a small scale unit, the reactor is equipped with electrical wall heating elements. To allow for a constant increase of the bed temperature with a homogeneous temperature profile,

much effort was spent on improving the bed section of the reactor as well as the controlling system (Fig. 3). A preheater, allowing primary air temperatures of more than 1050 °C, was constructed. Forced convection is utilised in a cyclone-like stainless steel cylinder equipped with Kanthal electric heating elements. All temperatures are controlled by Eurotherm temperature controllers and the maximum temperature deviations within the bed were found to be less than ± 3 °C. The gases O₂, CO₂, CO, SO₂, NO and NO₂ are continuously monitored, using conventional instruments.

Figure 3 Detailed illustration of the modified bed section

The previous construction work, the controlling possibilities, as well as the analytical details of the reactor have been reported elsewhere [Nordin et al. 1995].

Normal combustion tests

To initially determine the tendencies for bed agglomeration, several attempts were made to combust the two biomass fuels in the pilot FBC, using normal operating conditions. Totally three repeated experiments were performed for each fuel alone. A bed temperature of 850 °C and an oxygen concentration of 6 %_{dry} were used. Samples of the resulting bed agglomerates were analysed with SEM EDS.

To verify the previous findings of the possibilities to control bed agglomeration and defluidization by co-combustion with coal, four ten hour extended test runs were performed. Mixtures of 50%_{wt} coal and 50%_{wt} of either of the two biomass fuels were combusted under the same operating conditions as for the biomass fuels alone. Samples of the final bed materials were analysed with SEM EDS.

Controlled agglomeration tests

The most important individual parameter for bed agglomeration is the actual process temperature. However, the particle temperature in FBC is an unknown variable and

may exceed the bed temperature by 20-600 °C, the largest difference being found for the smallest particles and highest particulate phase oxygen concentrations [c.f. Yates 1983, Roscoe 1980, Halder and Basu 1991]. To avoid this uncertainty in the surface temperature of burning particles in FBC, controlled bed agglomeration tests were performed in the pilot FBC without actual combustion. Each bed experiment was started by loading the bed with ash (6%wt). Initial experimental runs showed that less than 1.5% ash is sufficient for agglomeration and defluidization to occur. In the present work, the loading temperature was chosen to be 600 °C for the biomass fuels and 750 °C for the coal blends. In addition, one experimental run was performed using 750 °C also for the olive fuel. Subsequent to this "ashing procedure" the fuel feeding was stopped and the bed temperature was externally raised by 3 °C per minute. The onset of bed agglomeration is indicated by measuring differential pressures and temperatures of the bed as well as by video filming of the process. The detection of initial bed particle cohesion by considering all bed related variables simultaneously is performed by on-line multivariate statistical process control (MSPC), i.e. on-line principal component analysis (PCA).

Throughout the experimental runs, samples of bed material were collected by an air cooled suction probe, equipped with a cyclone separator. These samples, as well as the produced agglomerated beds, were analysed by ICP, SEM EDS and X-ray diffraction analysis. The samples for SEM EDS were mounted in epoxy, cut by a diamond saw, polished and the resulting cross-sections were carefully examined. Prior to the X-ray analysis, the samples were sieved, to reduce the quartz content (increase ash reflections), and then ground.

Laboratory compression strength method

The agglomeration temperatures obtained in the pilot FBC were compared with the results from a laboratory method based on compression strength measurements of ash pellets, previously described by Skrifvars et al. [1992] and Skrifvars [1994]. The fuels were ashed at 550 °C and well homogenised samples of ash were crushed and screened. A narrow, controlled particle size fraction then was pressed to a pellet with a diameter of 10 mm and a height of 10 mm. These pellets were heat treated in a laboratory furnace under controlled conditions (gas atmosphere, different temperatures). After the heat treatment, the pellet samples were crushed in a standard crushing device. The compression strength was taken as a measure of the degree of sintering and the transition temperature as a measure of predicting the bed agglomeration temperature.

CHEMICAL EQUILIBRIUM CALCULATIONS

Agglomeration of ash and bed particles in a fluidized bed will take place if a liquid phase is present to form a bond between particles. Thus, the temperature at which a liquid phase would first form, i.e. the solidus temperature, and the effect on the solidus temperature of changing the ash composition, is of importance. Further, the smaller the difference between the solidus and liquidus temperatures, the greater the increase in the amount of liquid present for a small temperature rise. Therefore, the melt content of the ash, assuming chemical equilibrium, was determined as a function of

temperature for the fuels and fuel mixtures used. The equilibrium calculations were performed using the computer program CHEMSAGE 3.0 and stoichiometric data were taken mainly from the Scientific Group Thermodata Europe (SGTE). Only stoichiometric condensed species were considered in these first calculations. Phase diagrams were then consulted for a rough estimate of the melting behaviour of the major ash constituents.

In a second set of calculations non-ideal solution models were also included. In addition to 110 stoichiometric species from SGTE, ten solid solutions and two liquid solutions (melts) were considered. Of the two liquid phases assumed, one comprises alkali salts, and the other oxides and silicates. As described previously by Nordin et al. [1994b] this is not fully correct but probably an applicable approach, considering the limited data on liquid models available at present. The two phases rarely co-exist, as the liquid salt solution dominates at lower temperatures and the liquid silicate solution at higher temperatures.

RESULTS AND DISCUSSION

Normal combustion tests

The repeated experiments of normal combustion (850 °C, 6% O₂) of the two biomass fuels alone, all resulted in severe bed agglomeration within less than 30 minutes of operation. The progress of initial agglomeration to total defluidization was found to be very rapid. The time from the first signs of any disturbance of the bed (as indicated by MSPC) to total defluidization was estimated to only a few minutes. In a full scale process this would probably quickly lead to severe defluidization and catastrophic shut-down of the plant.

The results from SEM EDS analysis of the agglomerated beds of both fuels showed a clear association of the elements Si, K, Al and Ca, indicating a potassium rich silicate layer, fusing the quartz particles together (Fig. 4). However, it should be mentioned that due to the agglomeration, loss of fluidization and heat transfer the final fusing temperature of the agglomerates are not known.

Figure 4 Typical elemental composition of a bed agglomerate (Lucerne) after severe defluidization

The experiments also confirmed that the surface temperature of a burning particle is significantly higher than the bed temperature. When the process was rapidly quenched after initial agglomeration, silicate aggregates with the same appearance as the original fuel pellets were found in the bed material, indicating that the agglomeration starts at the surface of the fuel particles due to the higher temperature there.

When co-combusted with coal, both biomass fuels could be successfully processed during more than ten hours (one working day) of normal combustion (850 °C, 6% O₂). No tendency for agglomeration was discovered and, in addition, high sulphur retentions (> 80%) were obtained throughout the tests.

Controlled agglomeration tests of the biomass fuels

The principles of a typical controlled pilot FBC agglomeration test for the Lucerne fuel, as well as the corresponding X-ray maps of some of the periodically removed samples, are shown in Fig. 5. Examination of the maps shows continuous build up of a salt matrix (Ca, K, S, P, CO₃ and some Cl) in the bed. By the external increase of the bed temperature, the critical agglomeration temperature was determined to be 680 °C. At this and higher temperatures, the salt ash matrix will partly melt and "glue" the bed material together. Agglomeration and defluidization in FBC of Lucerne under normal operating conditions would therefore probably be initiated by formation of a liquid (sticky) potassium-rich salt cohering the quartz particles.

Results from the controlled agglomeration tests of the olive fuel are presented in Fig. 6. For this fuel, a continuous enrichment of mainly K and Ca (and Si) on the quartz surfaces was detected. A partial melt of a K-rich silicate phase, already covering the bed particles, is therefore the most likely active "glue" for this fuel. The initial agglomeration temperature was determined to 940 °C. This temperature is in good agreement with the solidus temperatures of the corresponding area in the SiO₂-CaO-K₂O-phase diagram.

The results from repeated experiments with different ash to bed material ratios for the Lucerne fuel are presented in Fig. 7. Different ratios did not seem to influence the actual agglomeration temperature significantly. The spread in some of the data can be explained by the state of the experimental set-up during these first series of tests in our work. However, the process controlling possibilities were significantly improved during the course of the work and the six recent reproducibility tests, utilising constant operating conditions, indicated that repeated agglomeration temperatures within ±10 °C can now be obtained.

Figure 5 Bed temperatures and differential pressures of a typical controlled agglomeration run for the Lucerne fuel, as well as SEM EDS elemental maps of some of the collected samples

Figure 6 Bed temperatures and differential pressures of a typical controlled agglomeration run for the olive fuel, as well as SEM EDX elemental maps of some of the collected samples.

Figure 7 FBC agglomeration temperature as a function of ash to bed material ratio (Lucerne)

Controlled agglomeration tests of the fuel blends

The controlled agglomeration tests of the Lucerne/coal blend resulted in an agglomeration temperature of 950 °C, whereas the olive/coal blend did not agglomerate at any of the studied temperatures (< 1050 °C).

Laboratory compression strength method

The results from the laboratory compression strength method for the two biomass ashes are shown in Fig. 8. Sintering temperatures of about 650 and 900 °C were obtained for Lucerne and olive flesh, respectively and different ash to bed ratios did not influence the actual sintering temperature. A higher ash fraction in the bed results in a stronger agglomeration but does not significantly influence the sintering temperature. All these results are in good agreement with the results obtained from the pilot FBC.

Figure 8 Compressive strength of heat treated ash pellets from Lucerne (closed symbols) and olive flesh (open symbols)

Chemical equilibrium calculations

The general results from the chemical equilibrium calculations verified the results obtained by SEM EDS analysis. The Lucerne fuel will predominantly form salts with low melting temperatures whereas the Olive fuel rather forms silicates with somewhat higher melting temperatures. Although a complete non-ideal data-set was not available for consideration in the calculations, the general results, as well as the trends obtained agree well with the experimental results obtained.

DISCUSSION

The results from the controlled agglomeration tests with the Lucerne fuel, where a molten salt matrix was identified as the "glue" in the agglomerate, seem to be inconsistent with corresponding results obtained during actual combustion, where a silicate "glue" was found. This is probably an effect of the actual agglomeration temperature and the following explanation is proposed. In a normal process with actual combustion, the salt matrix will melt and agglomerate. When these oversized agglomerates of particles exceed a critical dimension, the degree of mixing is reduced and higher temperatures will be reached locally, resulting in further agglomeration and finally complete bed defluidization. If not controlled, this self accelerated process will finally lead to very high temperatures, increased relative stability of silicate melt and thereby severe viscous sintering. Such transformations from salts to silicates at the interface between the quarts and the salt were identified using SEM EDX and high resolution line mapping over some of the agglomerates. A sufficiently high surface temperature of the fuel particles would also result in a silicate melt and viscous sintering.

The conclusion from the equilibrium calculations was that the salt and silicate liquid solutions rarely co-exists as salts are more stable at "low" temperatures whereas silicates dominate at "higher" temperatures. The transformation temperature is further highly influenced by the fuel compositions, or more correctly the amounts of available ash forming elements of the fuels. The dominant fraction of inorganic constituents of biomass fuels are organic or ionic bound and will be released in a highly reactive form during the combustion of the fuel [Nordin, 1993 and Baxter 1993]. The potential for chemical equilibrium calculations for prediction of the formation of inorganic ash products is therefore higher for biomass fuels than for coal. At the relatively low temperatures found in FBC, the organically bound ash forming elements are more likely to undergo major transformations than the mineral inclusions in the coal. It was therefore difficult to judge which elements should be regarded as available and which should be regarded as inert in the equilibrium calculations of the fuel blends.

The experimental results indicated that the explanation for prevention of agglomeration by co-combustion could be that the in-bed ash composition is altered towards higher melting temperatures. By the introduction of additional sulfur from the coal, somewhat higher melting temperatures (within the salt system) could be expected. However, supplementary combustion experiments with the biomass fuels and addition of SO₂ to the primary air rejected this hypothesis. A more likely explanation could be that the fluxing elements from the biomass fuel are chemically and/or physically adsorbed on the large total surface of the coal ash particles (clay minerals). This was

also confirmed by adding corresponding amounts of kaolinite to the biomass fuels. Hereby, no agglomeration was experienced.

CONCLUSIONS

- The two biomass fuels studied, Lucerne and Olive flesh, will rapidly form agglomerates and cause severe defluidization when combusted in a fluidized bed. The chemical explanation is a coating of the bed material by sticky molten or partly molten ash layer, consisting of salts in the case of Lucerne and silicates in the case of the Olive fuel.
- Different ash to quartz ratios did not influence the actual agglomeration temperature significantly, but rather the physical effects of the agglomeration process. This is also in agreement with the compression strength method; a higher ash fraction in the bed results in a stronger agglomeration but does not influence the sintering temperature.
- When co-combusted with coal, agglomeration can be effectively prevented. The in-bed ash compositions in both cases are altered towards higher melting temperatures and the reason may be that the coal ash will act as a physical and/or chemical adsorbent for the "fluxing" elements in the biomass ashes. Other measures to reduce the agglomeration tendencies therefore also includes using coal minerals (e.g. kaolinite) as additives.
- A relatively good agreement was obtained between chemical equilibrium results, results from the compression strength method and actual bed agglomeration results from the pilot FBC. However, future validation work, involving improved non-ideal solution models and several different biomass fuels, will give more accurate and quantitative results.

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REFERENCES

- Baxter, L. L. (1993). "Ash deposition during biomass and coal combustion: a mechanistic approach." *Biomass and Bioenergy* 4, 2, 85-102
- Bitowft, B. K. and Bjerle, I. (1986). "A generic study of the sintering aspects of biomass in a fluid-bed gasifier." *Energy from Biomass and Waste XI*, 511-529
- Dawson, M. R. and Brown, R. C. (1992). "Bed material cohesion and loss of fluidization during fluidized bed combustion of midwestern coal." *FUEL*, 71, 585-592

- Gulyurtlu, I., Reforco, A. and Cabrita, I. (1991). "Fluidised bed combustion of corkwaste." *Fluidized Bed Combustion ASME*, 1421-1424
- Halder, P. K. and Basu, P. (1991). "The temperature of burning carbon particles in a fast fluidized bed of fine particles." *Chem. Eng. Comm.* **104**, 245-255
- Nordin, A. (1993). "On the chemistry of combustion and gasification of biomass fuels, peat and waste - environmental aspects." Thesis, Dept. of Inorganic Chemistry, Umeå University
- Nordin, A. (1994). "Chemical elemental characteristics of biomass fuels." *Biomass and Bioenergy*, **6**(5), 339-347.
- Nordin, A. (1995). "Optimization of sulfur retention in ash when cocombusting high sulfur fuels and biomass fuels in a small pilot scale fluidized bed." *FUEL*, **74**, 615-622.
- Nordin, A., Marklund, S., Wikström, E. (1995). "Construction of a pilot-scale fluidized bed combustor for combustion chemistry applications." Submitted for publication.
- Höglund, K., Wikström, A., Hägerstedt, L-E., Medin, K., Hagström, U., Nordin, A. (1995). "Illustration of slagging and fouling problems during combustion of biomass fuels", Poster presentation at the Int. Conf. on Application of Advanced Technology to Ash-related Problems in Boilers, Waterville Valley, July 16-21.
- Roscoe, J. C., Witowski, A.R. and Harrison, D. (1980). *Trans. I. Chem. Engrs.*, **58**, 69.
- Salour, D., Jenkins, B. M., Vafaei, M. and Kayhanian, M. (1993). "Control of in-bed agglomeration by fuel blending in a pilot scale straw and wood fueled AFBC." *Biomass and Bioenergy*, **4**, (2), 117-133
- Skrifvars, B-J., Hupa, M. and Hiltunen, M. (1992). "Sintering of ash during fluidized bed combustion." *I&EC Research*, **31**, 1026-1030
- Skrifvars, B-J. (1994). "Sintering tendency of different fuel ashes in combustion and gasification conditions." Thesis, Dept. of Chemical Engineering, Åbo Akademi University.
- Skrifvars, B-J. and Hupa, M. (1995) "Characterization of biomass ashes." Proc. of the Int. Conf. on Application of Advanced Technology to Ash-related Problems in Boilers, Waterville Valley, July 16-21.
- Viktorén, A. (1991). "Combustion of salix in a CFB-boiler." Report no. 416, Thermal Engineering Research Foundation, Stockholm, 36 p.
- Yates, J. G. (1983). *Fundamentals of fluidized-bed chemical processes*. Butterworths, London