

# BED MATERIAL AGGLOMERATION IN PFB BIOMASS GASIFICATION

Nader Padban, Samuel Kiuru & Anders L. Hallgren  
Dept. of Chem. Eng. II, P.O.B. 124 Chemical Center  
University of Lund, S-221 00 Lund, Sweden

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## 1. Introduction

Small amounts of alkali compounds can drastically change the behavior of bed materials in fluidized bed gasification systems. Alkali-induced agglomeration and defluidization of the bed may cause severe operational problems and can be detrimental to the overall process. Enhanced tendency for agglomerations in the bed has been found in systems utilizing biomass or so called alternative solid fuels as feed-stock. The fuel alkali may add to the accumulation of alkali compounds in the bed. Adhesion tendencies between the particles seem to increase due to sticky layers of alkali condensations on the particle surfaces. In the present study an endeavor was made to establish a method for investigating suitable bed materials and the effect from biomass ash on the bed behavior in PFB biomass gasification. In this approach first results show that the composition of the particles in the bed, the temperature, and the mobility of the particles are of primary importance.

Agglomeration of bed material and problems caused by ash sintering in fluidized bed combustion/gasification processes has been reported frequently in the literature. According to Prabir et al [1] agglomeration of bed material can under certain conditions occur even at the temperatures below the ash fusion temperature and gas velocity higher than minimum fluidization velocity. Squire [2] and Siegill [3] describe the defluidization phenomena as a direct consequence of stickiness of bed material. This could be caused by changed properties of bed material at a certain temperature or due to liquid deposition on the surface of the particles.

Ash agglomeration in a fluidized-bed coal gasifier may be influenced by the high surface tension of mineral matter. Capillary forces may draw mineral matter from the interior of a hot carbon particle in order to be accumulated as ash on the particle surface [2].

Gerald P. Huffman et al [4] investigated the high-temperature behavior of coal ash in reducing and oxidizing atmospheres. The results from that study suggest that significant partial melting of the ashes occurs at temperatures as low as 200-400 °C below the initial deformation temperature defined by ASTM ash cone fusion test. According to their experiments ash melting is accelerated by reducing conditions. In a reducing atmosphere the ash melting will mainly be controlled by the iron-rich corner of the FeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> phase diagram.

B.K.Dutta et al [5] propose that the softening temperature of a coal ash is lower in mild reducing atmosphere than in oxidizing or strongly reducing atmosphere. The decreased ash fusion temperature is caused by the fluxing effect of different iron oxides. Depending on the temperature, the state of these oxides will change and consequently even their fluxing effect. In an oxidizing atmosphere iron will be present as Fe<sub>2</sub>O<sub>3</sub> and in mild reducing atmosphere as FeO, while in a strong reducing environment it tends to exist in metallic form. Ferrous oxide has the maximum fluxing effect on coal ash. Additionally, Dutta et al report that in the case of excess iron and in oxidizing atmosphere, the effect of alkali in decreasing the ash softening temperature may be very low or even insignificant.

R.G. Rizeq and F. Shadman [6] describe two different mechanisms for alkali-induced agglomeration of solid particles in coal combustors and gasifiers. In the case of low alkali concentration agglomeration is a result of formation of low-melting glassy phases on the

particle surfaces. In alkali rich conditions alkali salts will form a molten layer on the surface of particles which result in adhesion of particles. Their experiments even show that the minimum agglomeration temperature of some minerals can be decreased several hundred degrees depending on the alkali content.

In connection to the effect of alkaline compounds on ash sintering and deposit forming in peat gasification, Moilanen [7] show that there is a clear correlation between chemical composition and sintering strength of peat ashes at 800°C. According to those investigations the sintering strength of peat ashes rises by increased B/A (bas/acid) ratio in these ashes.

Up to now most research efforts considering ashes and bed materials have been concentrated to coal combustion and gasification processes. Since the bed material in these processes often differs from those used in biomass gasification there is a need for further investigations in this area. In gasification and combustion of biomass, where external bed material is used, not only the problems caused by ash melting and sintering but also problems created by reactions between bed material and ashes must be considered.

Previous work at the department of Chem. Eng. II [8] have shown that the agglomeration and cake forming phenomena in bed material in presence of alkaline compounds depend on both temperature and the kind of alkali present. The stable alkali compounds such as chlorides do not react with bed materials consisting of Al and Si at temperatures below 800°C, while unstable compounds such as alkali nitrates cause agglomeration of bed materials at the temperatures as low as 550°C. Therefore the knowledge about the composition of different alkali and other fluxing materials in ashes is necessary for prediction of ash effects on bed material.

In the present work ash content and chemical composition of ashes for two different biomass has been investigated. The effect of temperature on the chemical composition of these ashes has been studied. Different mixtures of ash/bed material have been treated thermally to study the agglomeration or cake forming phenomena in the bed material.

## 2. Experimental

### 2.1 The Sample preparation

To study the temperature effect on ash chemical composition two different biomasses was preliminary ashed at 550°C. The ashing procedure has taken place in presence of air and at atmospheric pressure. The produced ashes were subsequently heated at 650°C and 900°C in 1 hour. The chemical composition of the ashes obtained from the temperature treatment was determined by **atomic absorption Spectrophotometry (AAs)** and **ion chromatography (IC)**.

Mixtures of ashes (obtained in 550°C) and bed material (consisting 99.5% of SiO<sub>2</sub>) were used in investigating the agglomeration and cake forming phenomena caused by alkali in the bed material. The bed material/ash quotes for the samples were 0, 0.25, 1 and 4. In the preparation of mixtures the required bed material amount was placed as a layer on the weighted ash sample.

Samples were treated thermally in an oven to 900°C. The residence time at 900°C was one hour for all samples. **Scanning Electron Microscopy (SEM)** was then used for analyses.

### 2.2 Analysis procedures

Analysis for solid samples in the form of ashes, ceramics, glasses, minerals and etc. can be made in several different ways:

- i. X-ray fluorescence spectroscopy (XRF) is the most simple and accurate method without need for any cumbersome digestion procedure of the sample.
- ii. methods that require melting + digestion in order to transfer the solid sample into a solution before the real analysis can start. Such method may be ICP and AAS with flame and preferably with graphite furnace and IC.

For analyses, AAS with air-C<sub>2</sub>H<sub>2</sub> and N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame and IC were available. All elements Al, Si, Ca, Fe, Mg, Mn, K, Na, S and P can be analyzed by AAS with a graphite furnace. Since the last mentioned instrumentation was not available AAS with flame was used for all the mentioned elements except for S and P which were analyzed by isocratic IC. For phosphor a new analytical method for IC had to be developed and because sulfur cannot be analyzed on AAS, the next best way was to analyze both S and P by existing IC equipment. S and P separated in the IC column system as SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> ions. In the determining of S and P a small volume, typically 1 to 2 ml, filtered through 0.22 micron membrane filter, was introduced with a syringe or with a sample changer into a 50 µL loop. The anions of interest, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>, were separated and measured using a isocratic system comprised of a guard column, separator column, suppressor column and conductivity detector.

For the AAS analysis, 40-70 mg fine-grounded ash sample was mixed with 1:12 parts lithium methaborate dihydrate, LiBO<sub>2</sub>·2H<sub>2</sub>O in a graphite or platina crucible. The mixtures were then molted at 900°C in CO<sub>2</sub> atmosphere. The melt was dissolved in dilute nitric acid under stirring (10-15 hour). After appropriate dilutions the obtained solutions were analyzed by AAS for measuring the amount of Si, Al, Ca, K, Na, Fe, Mg and Mn in samples.

In the Scanning Electron Microscopy (SEM) studies the investigated areas were different for pure ashes and ash-bed material mixtures. In order to achieve a more general conception of the ash surfaces, in the case of pure ash the studied area was relatively large, however, for the characterization of different particles in mixtures point analyses (studied area~ 9µ<sup>2</sup>) were performed.

### 3. Results and discussions

Heating pure ashes results in a decrease in volume and the ash particles tend stick together. However the adhesion is not strong and can easily be destroyed by finger touch.

Agglomeration of bed material particles was observed in all ash-bed material mixtures, independently on ash/bed material quote. The size of the agglomerate for EB,biomass was much smaller than for those related to Salix. Generally the agglomerate size increases by increasing ash/bed material quote.

The AAS/IC (bulk) analysis of ashes from different-temperatures shows no significant temperature-related variations in chemical composition in ash of any sort. This could indicate that the ashes, already in the lowest ashing temperature, have reached a chemical equilibrium in solid /or condensed phase.

Comparison between the results from AA/IC and SEM shows considerable differences in chemical composition for both ashes. Generally Si, Al and K content determined by SEM analysis is much lower than those determined by AA/IC. Although

SEM analysis shows the chemical composition of the outer surfaces of particles (max. penetration =  $3\mu$ ), the explanation can be that most of these elements are in the inner part of the ash particles. According to this assumption the outer shell will consist of oxides, sulfates, carbonates and phosphates of Ca, Mg, Mn and K.

The stronger agglomeration tendency for Salix mixtures may depend on the higher potassium content in these samples.

Table III shows some results of SEM point analysis studies for particles in the mixtures. The particles containing high silicon represent bed material grain from the agglomerates. These results indicate that the composition of the particle surface can vary drastically from one point to another in the same sample. Applied SEM analysis method has not shown to be satisfactory for larger surface examinations.

#### 4. Conclusions

The ashes from biomasses are not homogeneous materials, and their chemical composition differ from one particle to another. Higher alkali content in ash surfaces contribute to a stronger agglomeration tendency in ash- bed material mixtures. The agglomerates consist of bed material particles surrounded by small particles rich in Ca and with varying concentration in K, P, S and another elements. Preliminary results indicate that agglomeration may be related to a wide range of low melting compounds consisting of this elements and Si. Studies of phase diagrams [9] show that since only the compounds containing alkali can have melting points lower than  $900^{\circ}\text{C}$ , we can not exclude the importance of alkali in agglomeration phenomena.

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**Table I. Composition of ashes in different temperatures ; analyzed by AAS/IC**

Content, %		Si	Al	Ca	K	Na	Mg	Mn	Fe	S	P
EB,biomass	550°C	11.7	1.8	24.9	9.1	0.9	6.4	2.3	0.8	1.1	1.2
	650°C	12.6	1.9	25.1	9.9	1.3	7.0	2.6	0.9	1.1	1.6
	900°C	12.0	1.9	29.4	9.4	1.5	7.4	2.9	1.0	1.5	1.6
Salix	550°C	2.6	0.8	30.1	11.0	0.7	4.6	0.3	0.5	1.4	2.2
	650°C	1.6	0.9	29.5	12.1	1.0	4.3	0.3	0.7	1.6	2.5
	900°C	2.4	0.9	33.6	12.6	0.8	5.3	0.4	0.7	1.8	3.1

**Table II. Ash composition for Salix and EB,biomass ; SEM studies**

Content%	Si	Al	Ca	K	Mg	Mn	S	P
EB,biomass ash	3.02	0.78	37.33	3.58	4.56	9.97	2.23	4.27
	4.21	1.07	39.23	3.23	3.59	7.06	2.93	3.41
Salix ash	0.354	0.065	43.92	6.81	3.5	0.56	0.52	9.45
	0.68	0.089	43.82	6.01	2.78	0.73	2.66	7.69

**Table III. Chemical composition of some particles in agglomerates ; SEM studies**

Content%	Si	Ca	K	S	P
EB,biomass;ash/BM=0.25	24.64	18.48	2.04	1.08	2.48
EB,biomass;ash/BM=0.25	5.19	39.6	0.19	2.28	4.04
EB,biomass;ash/BM=1	2.87	52.53	2.58	2.58	1.48
EB,biomass;ash/BM=4	8.4	33.64	1.04	1.4	4.26
EB,biomass;ash/BM=4	34.38	10.75	0.41	0.68	1.83
Salix,ash/BM=0.25	34.36	6.25	13.51	0.17	0.0
Salix,ash/BM=0.25	5.33	38.19	1.64	4.18	7.17
Salix,ash/BM=0.25	1.17	40.30	0.24	3.94	10.97
Salix,ash/BM=1	41.92	3.09	0.27	0.27	1.72
Salix,ash/BM=1	2.78	42.23	1.4	0.54	11.89
Salix ,ash/BM=4	0.39	24.68	23.36	1.51	11.77
Salix ,ash/BM=4	0.42	57.2	0.89	0.57	5.7



SEM-photo of quartz sand particle embedded in alkali (50X).