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A review: Fly ash and deposit formation in PF fired biomass boilers

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In recent years suspension fired boilers have been increasingly used for biomass based heat and power production in several countries. This has included co-firing of coal and straw, up to 100% firing of wood or straw and the use of additives to remedy problems with biomass firing. In parallel to the commercialization of the suspension biomass firing technology a range of research studies have improved our understanding of the formation of fly ash and the impact on deposit formation and corrosion in such boilers. In this paper a review of the present knowledge with respect to ash and deposit formation in biomass suspension fired boilers is provided. Furthermore the influence of co-firing and use of additives on ash chemistry, deposit properties and boiler operation is discussed.

Keywords: Biomass, suspension firing, deposits, ash

1. Introduction

While fluid bed and grate fired boilers initially was the choice of technology used for power production from both wood and herbaceous biomass, in recent years suspension fired boilers have often been used for biomass based power production. Suspension fired boilers are often called pulverized fuel boilers (PF boilers). PF boilers deliver often the most competitive biomass based electricity with respect to power generation efficiency, capital investment cost and generations costs [1]. A key issue when the pulverized fuel boiler technology uses biomass as fuel instead of the traditionally use of coal is the large change in ash composition and ash properties. Biomass ash contains relatively high contents of alkali metals typically together with elements as Ca, Si, S and Cl. This review therefore deals with the transformation of biomass ash species in PF boilers as well as the implications of the biomass ash on boiler operation.

The use of PF firing technology for biomass is typically implemented in the following ways [1]:

- Co-firing of a small amount of biomass (up to 10% on energy basis) together with coal. Using the relatively low amount means that the ash properties are dominated by the coal ash.
- Co-firing of large amounts of biomass and coal (10 to 50% biomass on an energy basis).
- 100% biomass firing in new or modified PF boilers.

In this review we will mainly deal with PF systems using more than 10% input (on energy basis) of biomass. Since the year 2000 biomass firing power plant PF boilers using both 100% biomass and co-firing of biomass and coal have increasingly been in operation in countries as Great Britain, Denmark, Netherlands, Belgium and Canada [1]. The fuel ash properties have a large influence on boiler operation and the following areas are strongly influenced when a boiler is changed from operation on coal to biomass:

- Slagging and fouling properties are significantly changed and further discussion of this issue is provided in section 4.
- Corrosion test of superheater metals exposed to biomass ashes have been conducted in several studies [2-4]. An in depth review on biomass induced corrosion is not a part of this paper. It has been observed that a high deposit KCl content leads to high corrosion rates, while if the Cl is only present as gaseous HCl less severe corrosion appear.
- Flue gas cleaning systems on large PF power plants often includes an SCR unit to remove NOx. It has been shown that the vanadium based catalytic units often used in SCR systems are de-activated by salts as KCl and K_2SO_4 [5].

- Residual product utilization of fly ash has been diverse including distributed at fields or in forests and in the case of co-firing the fly ash can in some cases be utilized for cement or concrete production [6].

To the authors knowledge a review looking specifically into the biomass ash behavior in PF boilers have not previously been published. Some broader reviews is available as the IEA bioenergy report by W. R. Livingston et Al. [1] and the doctoral thesis by F. Frandsen [2]. In this review we will discuss the influence of biomass ash on PF boiler operation and the fundamentals of biomass ash processes that may influence boiler operation. Sections dealing with ash formation, co-firing, ash deposit formation and use of additives are included in this review.

2. Fly ash formation

In table 1 is shown a comparison of the ash forming elemental composition of a bituminous coal and typical Danish wood and straw. Wood ashes are often dominated by Ca and K, while herbaceous fuels often have high contents of Si and K. The content of Si, Al, S and Fe are lower in biomass than in coal while the Cl content is higher. Wood pellets are the most used biomass type for PF firing in some cases wheat and barley straw have been used [7].

Tab. 1. Comparison of the lower heating value, ash content and concentrations of ash forming elements in bituminous coal [6], straw and wood [8].

Fuel		Coal	straw	Wood
LHV	Mg/kg (dry and ash free)	31.5	18.6	19.5
Ash	Wt.% dry	15	4.5	1.0
S	Wt.% dry	0.6	0.15	0.05
Cl	Wt.% dry	0.01	0.4	0.02
K	Wt.% dry	0.08	1.0	0.1
Na	Wt.% dry	0.02	0.05	0.015
P	Wt.% dry	0.11	0.08	0.02
Si	Wt.% dry	3.4	0.8	0.1
Ca	Wt.% dry	0.93	0.4	0.2
Al	Wt.% dry	2.68	0.005	0.015
Mg	Wt.% dry	0.16	0.07	0.04
Fe	Wt.% dry	0.42	0.01	0.015

The fly ash elemental composition of PF boilers is in most cases quite similar to the fuel ash composition [7, 9]. Typical conditions in suspension fired boiler chambers are local temperatures up to 1600°C and mean furnace chamber gas residence times from 2 to 5 seconds. Studies have been conducted in entrained flow reactors [10-12] to investigate the formation and properties of biomass ash generated at suspension firing conditions. The result regarding fly ash formation of the entrained flow studies are summarized in Figure 1 and commented below.

The inorganic matter in biomass can be ionically bound (K, Cl), organically bound (Si, Ca, K, S), appear as minerals included in the fuel structure (Ca, Si) or appear as excluded minerals, which is often a minor part of the fuel and can be in the form of clay or quartz particles.

Ash properties after most combustion have taken place (temperature above 1000°C and before the flue gas is cooled in the convective pass) are the following: Besides volatile elements as Cl and S that are completely released to gas phase also a large fraction of K, Na and P appear in the gas phase [13]. This leads to a range of ash forming species appear in the gas phase in boiler chamber; including HCl, SO_2/SO_3, KOH, KCl, K_2SO_4, KPO_3. A high fraction of potassium is in most cases released to the gas phase during the combustion process. However in relatively Si rich fuels (high Si/K ratio and low Ca/Si ratio) a reduced gas phase release was obtained [10].

In most cases the fly ash after cooling contains particles of three distinct size classes. A submicron aerosol fraction rich in K, S, P and Cl, an intermediate fraction with ash particles of 20 to 100 μm rich in Ca, K and Si (in case of straw highest Si content and in case of wood highest Ca content) and in some cases a fraction of larger particles greater than 200 μm. The larger particles mainly appeared if residence times of less than 1 second were used and contained significant carbon content, showing only partial conversion. The 20 to 100 μm (intermediate size) particles appear in most cases as spherical particles but also with some irregular particles [13].

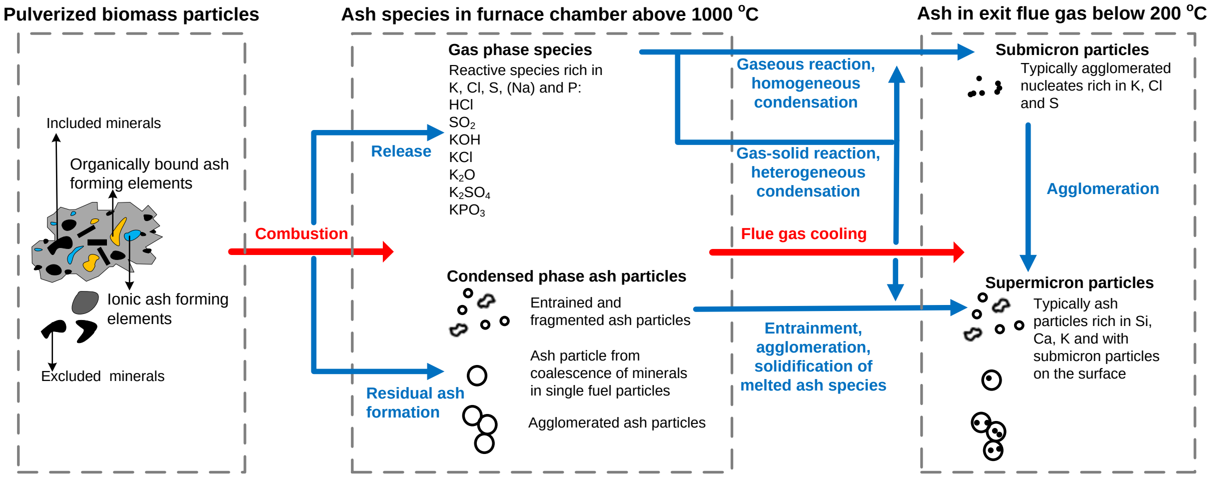

Fig. 1. The transformation of ash forming elements during suspension firing of biomass. From reference [10].

A reasonable mechanistic understanding of the ash forming process is available today, but there are areas where more knowledge is wanted. This includes verified predictions of the residual ash size distribution and melting faction of single ash particles, as well as a detailed mechanism for determining the alkali distribution in different gas species.

3. Co-firing

Co-firing of wood and oil [14], coal and wood [15] as well as coal and straw [16, 17] have been performed in PF power plants. In this section the implication for the resulting ash from coal and biomass co-firing and the influence of this ash on boiler plants will be discussed. The speciation of the alkali metals have a large influence on the properties of the ash. By mixing of fuels the S and the ash species from coal can influence the speciation of the alkali metals. The different alkali species have different implications for boiler operation [6]:

- KCl: A fly ash with a high KCl content can induce problems with increased deposit formation, increased boiler coil corrosion, deactivate SCR catalysts and impede the utilization of fly ash for cement and concrete use.
- K_2SO_4: If potassium appear as sulphate less problems with boiler corrosion and ash utilization are observed. However deactivation of SCR catalysts will still take place
- K-silicates: The deactivation of SCR catalyst will not take place, but alkali silicates do have low melting temperatures so severe deposit formation may still take place.
- K-aluminum-silicates: The melting temperature of those minerals is higher than of potassium silicates and a less troublesome deposit is formed.

In all cases where the dominant species are others than KCl most chlorine will be emitted from the boiler as HCl in the flue gas.

The alumina silicates from coal can react with biomass alkali as KCl (or as K_2SO_4 or KOH) according to the global reaction 1 [6]. KCl can also be sulfated according to reaction 2. Both experiments and equilibrium calculations shows that if a coal and straw mixture is used as fuel with high molar ratios of S/K, Si/K and Al/K then nearly a complete conversion of KCl can be obtained at high temperatures (1000°C and above). In most cases both sulphation and formation of potassium alumina silicates takes place. However in cases with high temperatures and an abundant amount of Si and Al then mainly alumina silicates are formed. Some EQ calculations have indicated [17] that Lusite ($K_2O \bullet Al_2O3 \bullet 4SiO_2$) is the most stable product if Al and Si is abundant. This indicates that a molar ratio of Si/K in the fuel above 2 is optimal.

$$KCl(g) + Al_2O_3\bullet2SiO_2(c) + H_2O(g) \rightarrow K_2O\bullet Al_2O_3\bullet2SiO_2(c) + 2HCl(g) \quad (1)$$
$$2KCl(g) + H_2O(g) + SO_2(g) + 1/2O_2(g) \rightarrow K_2SO_4(g \text{ or } c) + 2HCl(g) \quad (2)$$

Full scale boiler studies [16, 17] and laboratory studies [6, 18] investigating the deposit and fly ash properties of biomass co-firing have been conducted. Based on those studies the following could be concluded regarding the influence of co-firing of biomass and coal on the fly ash product:

- Capture of potassium and release of HCl can be achieved by sulphation and reaction with Al and Si in coal ash. If a bituminous coal with an ash rich in Si and Al is used for co-firing then up to 20 wt% of straw can be co-fired with formation of only very small amounts of KCl in the ash.
- Lignite ash does not have a large capability to bind alkali in Si-Al species. This is because lignite has a high content of calcium and magnesium that react with alumina and silica so they are not available for reaction with KCl.
- The deposit formation rate were only increased for a low ash coal (5 wt %) while co firing with a high ash coal (15.5 wt %) led to unchanged deposit formation rates.
- Sulfur and aluminasilicates competes to react with alkali metals. At high temperatures the aluminisilicates are more stable than the sulfates [12].

4. Deposit chemistry, deposit formation and deposit shedding

In many cases the most severe deposit formation is seen at the position in the boiler system where the flue gas inters the first superheaters. Here is both the metal surface temperature and the flue gas temperature high. The deposit formation mechanism important for biomass fuels have been described in several papers [2,19,20]. The mechanisms involved include: Direct condensation of gaseous ash species, ash particle deposition by initial impaction, thermophoreses driven impaction and furthermore the strength buildup of the deposit, which can be influenced by sintering and chemical reactions. Modeling studies [21] indicates that the bulk deposit mass uptake in most cases is dominated by impaction. At high flue gas temperatures (>900°C) direct condensation of KCl and K_2SO_4 on heat transfer surfaces are the dominant mechanism for forming the initial inner layer of deposit. At low flue gas temperatures themophoresis can be the dominant deposit formation mechanism.

Biomass and especially straw do compared to bituminous coal in some cases leads to larger deposit formation rates and deposits that are more difficult to remove. There are several reasons for this relatively high formation rate of troublesome deposits of biomass fuels:

- Relatively high partial vapor pressures of salts as KOH, KCl and K_2SO_4 leads to direct condensation of the salts on heat transfer surfaces [21].
- Low melting temperature of salts as KCl (770°C), K_2CO_3 (891°C) and K_2SO_4 (1069°C) cause the particles to stick to surfaces with a high probability when they impact on surfaces.
- Also the low melting temperatures of alkali silicates cause that the ash particles to have a high sticking propensity. Typical initial deformation temperatures (initial melting of a laboratory ash) have appeared for straw at 780 to 900°C and for wood at 1150 to 1200°C [7].
- Sintering and strength build up appears to start at lower temperatures for biomass than for coal ashes [7].

A series of probe measurements in PF boilers applying wood and straw have been conducted [7, 9, 22-25] to investigate deposit formation, deposit shedding and chemistry of deposits and fly ash. The measurements have revealed the main characteristics of the deposit chemistry [15, 26] and how it is influenced by the used biomass type, flue gas temperature and probe surface temperature. Some examples of the conditions influence on deposit chemistry are summarized below:

- Wood PF combustion in a 800 MWth PF boiler plant using a probe temperature of 550°C and flue gas temperature of approximately 800°C [15]: The deposit contains mainly K_2SO_4, KCl and KOH/K_2CO_3 and smaller amounts of Si and Ca rich particles on both the upstream and downstream side of the probe. Larger particles rich in Si are not seen indicating that inertial impaction is not important for this deposit build up.
- Wood combustion, probe approximately temperature 550 – 600 °C and flue gas temperature of approximately 1300°C [15]: The downstream side was dominated by K_2SO_4, and

KOH/K_2CO_3, and some K-Ca-Si rich particles. On the upstream side K-Ca-Si and K-Si rich particles dominated the deposit with some inner most K_2SO_4.

- Straw combustion with a probe temperature of 500°C and a flue gas temperature of approximately 870°C [7, 23]: The deposit bulk composition is dominated by Si, K and Ca. The inner most layers have some Cl while the outer layers are nearly depleted of Chlorine [23].

It has been observed that for both wood and straw firing that the Cl content decrease with an increased flue gas temperature. Comparison of the fuel ash to deposit compositions have shown some variations, however it is observed that at low flue gas temperatures (bellow 800°C) the deposits has relatively high contents of K, Cl and S and relatively low contents of Ca and Si [7, 9].

The deposit formation rates were measured with the probes in such a way that a natural shedding event was excluded. This is called the DDF rate (Deferential Deposit Formation rate), and it was determined as the slope of the mass increase between natural shedding events. In Figure 2 is shown an example of some of the measurements on deposit formation rate as a function of flue gas temperature. There is observed a large increase in straw deposit formation rate at flue gas temperatures above 800°C for straw, while in the case of wood moderate deposit formation rates is observed even at temperatures above 1200°C.

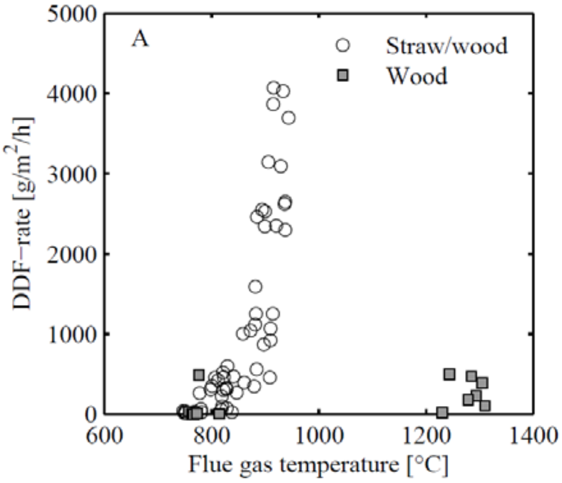

Fig. 3. DDF formation rates obtained by probe measurements in suspension fired biomass boilers.[7, 15, 24, 25].

Both natural shedding and soot blower induced shedding were investigated by the probe measurements. Natural shedding happened mainly as de-bonding and is a stochastic process [7, 25]. A soot-blower with variable PIP pressure was mounted along the deposit probe and the needed PIP to remove a given deposit could be measured. It was shown that both increased residence time since last soot-blowing, and increased surface temperature leads to deposits that are more difficult to remove.

The deposit formation in biomass PF boilers are influenced by many different conditions such as boiler and convective section design, installation of soot blowing equipment, used fuel type and the use of additives. Even a reasonable mechanistic understanding of biomass deposit formation is presently available especially the sintering and removability of deposits are sometimes difficult to predict.

5. Use of additives

As already discussed in the section regarding co-firing, the speciation of the biomass alkali greatly influences the operation of boiler plants, such that the appearance of KCl gives rise to issues regarding deposit formation, corrosion and deactivation of SCR catalysts, while if the potassium appears in alumina silicates that have relatively high melting temperatures then it is relatively manageable. In biomass boilers additives can be used to decrease the biomass ash negative influences on boiler operation. As shown in Table 2 many different additives have been tested in both laboratory and boiler studies. An additive can work in two ways by a reaction with alkali metals such as KCl and KOH and binding of the alkali in more benign species, or simply by dilution such that the critical alkali species are present in a lower concentration in the fly ash [34]. Furthermore for an additive to be applicable on boilers it shall be cheap, not harm the boiler and flue gas cleaning systems, and also residual product utilization shall be considered.

Tab. 2. The most used types of additives studied as additives used for biomass firing.

Type of additive	Species used	References
Sulfur based	SO_2, elemental sulfur, $(NH_4)_2SO_4$, Fe2(SO4)$_3$, $Al_2(SO_4)_3$	27, 28, 29
Al-Si based	Kaolin (Si,Al), Coal ash, Diatomite (Si), Quartz (Si), Bentonite (Si, AL, Mg),Bauxite (Al), Emathelite (Si,Al), Alumina (Al), SBE (spent bleaching earth)	15, 13, 30, 31, 32, 33
Ca or Mg based	$CaCO_3$, Dolomite	26
P or P-Ca based	$Ca(H_2PO_4)_2$ or $CaHPO_4$, H_3PO_4, $(NH_4)_2HPO_4$	23, 34, 35

The capability of kaolinite to react with alkali metals was demonstrated by Gale and Wendt [30], which showed that sodium acetate at a temperature of 1280°C very efficiently can be scavenged by 2 μm sized kaolin particles. The reaction of potassium species with kaolin result in high melting products as kalsilite ($KAlSiO_4$) or leucite ($KAlSi_2O6$) [34]. Kaolin and SBE (spent bleaching earth) a Si rich waste product have been tested by entrained flow reactor studies where the generated fly ash and deposits from a small deposit probe were investigated [13]. The entrained flow reactor studies showed that both by use of kaolin and SBE the Cl content in the fly ash and deposit was reduced, SO_2 emission increased, and the fraction of water soluble alkali species in the fly ash was reduced.

A study using deposit probes were conducted at the 880 MWth wood fired Avedøre unit 2 boiler to investigate the influence of applying coal fly ash from pulverized coal firing as an additive [15]. The addition of coal ash increased the deposit formation rate, but a similar increase in shedding rate was observed so the thickness of the deposit was approximately similar. There was injected a coal ash amount corresponding to approximately 4 times the amount of wood ash. The wood firing fly ash (without coal ash injection) included K_2SO_4, KCl, KOH and K_2CO_3 that all was not present in the fly ash when coal ash were injected, confirming that the alkali metals was bound in k-aluminosilicates or k-silicates. The use of coal ash together with wood is presently done at several power plant boilers [1] and because wood typically only contains 1 wt% ash the amount of coal ash needed is manageable.

For sulfur based additives the main effect is to convert alkali chlorides to alkali sulfates which are less harmful with respect to deposit formation and corrosion [9,27,29]. To the authors knowledge sulfur additives is presently not applied on power plant PF boilers.

Generally biomass PF combustion has not been based on straw with additives. Because of the high alkali content of straw large amount of additives would be needed making it an expensive approach. Coal fly ash injection with wood is applied on several boilers [1] and works well. With respect to fundamental knowledge a better detailed understanding of the coal ash alkali species reactions could lead to an improved optimization of wood boilers using coal ash.

Conclusion

The use of biomass on PF boilers have in recent years been shown to be an efficient and relatively mature technology where large amounts of wood is applied to produce reasonably CO_2 neutral heat and power. The last 20 years a lot of laboratory and power plant boiler studies on biomass ash behavior at suspension combustion conditions have been conducted, and those studies is reviewed in this article with respect to fly ash formation, biomass co-firing with coal, deposit formation and use of additives. While a lot of important knowledge is obtained there are still areas where further studies could be of great value:

- Development of SCR catalyst that is not de-activated by alkali salts
- Further understanding of alkali corrosion that can lead to increased superheater temperature use in biomass fired plants
- Improved understanding of the formation of residual ash particles (the non-volatile part of the biomass ash) with respect to size distribution and material properties as melting fraction, viscosity and visco-elastic properties.

- Improved mechanism to determine the distribution of alkali in different gas phase species.
- Improved capability of accurate predictions of reactions between alkali species and minerals to make it possible to optimize co-firing and the use of additives.
- Better data on ash deposit strength and development of quantitative data on ash shedding.

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