energies

Review

Ash Deposition in Biomass Combustion or Co-Firing for Power/Heat Generation

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Abstract: This paper presents a concise overview of ash deposition in combustion or co-firing of biomass (woody biomass, agricultural residues, peat, *etc.*) with other fuels for power/heat generation. In this article, the following five research aspects on biomass combustion ash deposition are reviewed and discussed: influence of biomass fuel characteristics, deposit-related challenges, ash deposition monitoring and analysis of ash deposits, mechanisms and chemistry of fly ash deposition, and key technologies for reducing ash deposition and corrosion in biomass-involved combustion.

Keywords: ash deposition; biomass; combustion; co-firing

1. Introduction

The use of green energy sources, e.g., biomass (forestry residues, agricultural residues, peat, *etc.*) substituting for fossil fuels has attracted increased attention because of the necessity to reduce the environmental impacts of traditional electricity and heat generation from fossil fuels, as well as the depletion of these resources and the soaring prices of fossil fuels. However, large-scale utilization of biomass for power/heat generation is facing some technical challenges, not only the availability and affordability of biomass feedstocks, but the ash deposition/corrosion issues in biomass-fueled boilers.

Biomass fuels usually contain high levels of alkali/alkaline metals, in particular potassium, and high chlorine content, as well as low sulphur concentrations, which make the deposition of corrosive ash in biomass-fired boilers a more severe issue than that in traditional coal-fired boilers [1–3]. In the past decades, extensive studies have been conducted on the influence of biomass fuel characteristics on fly ash deposition and the deposit-related challenges in biomass-fired boilers, technology development for ash deposition monitoring and analysis, understanding of mechanisms and chemistry of fly ash deposition, and technology development for reducing fly ash deposition and corrosion in biomass-involved combustion processes. This paper aims to present an overview on the abovementioned aspects of ash-related research and technology development.

2. Influence of Biomass Fuel Characteristics on Ash Deposition during Combustion

Understanding the fuel characteristics is necessary in studies on ash deposition as the fuel characteristics would affect fly ash deposition behaviors during combustion and play an important role in optimizing combustor/boiler design for enhanced combustion efficiency and less operation problems, especially when biomass is used [4–6].

Table 1. Typical characteristics of solid fuels [7–12].

Characteristics	Coal	Peat	Wood	Bark	Forest residues (coniferous tree with needles)	Willow	Straw	Reed canary grass (spring harvested)
Moisture content, wt%	6–10	40–55	5–60	45–65	50–60	50–60	17–25	15–20
C, % (d.b.) [1]	50–87	52–56	48–52	48–52	48–52	47–51	45–47	45.5–46.1
H, % (d.b.)	3.5–5	5–6.5	6.2–6.4	5.7–6.8	6–6.2	5.8–6.7	5.4–6.0	5.7–5.8
N, % (d.b.)	0.8–1.5	0.8–3	0.1–0.5	0.3–0.8	0.3–0.5	0.2–0.8	0.4–0.6	0.65–1.04
O, % (d.b.)	2.8–11.3	30–40	38–42	24.3–40.2	40–44	40–46	40–46	44
S, % (d.b.)	0.5–3.1	<0.05–0.3	<0.05	<0.05	<0.05	0.02–0.10	0.05–0.20	0.08–0.13
Cl, % (d.b.)	<0.1	0.02–0.06	0.01–0.03	0.01–0.05	0.01–0.04	0.01–0.05	0.14–1.05	0.09
K, % (d.b.)	0.003	0.8–5.8	0.02–0.05	0.1–0.4	0.1–0.4	0.2–0.5	0.69–1.30	0.3–0.5
Ca, % (d.b.)	4–12	0.05–0.1	0.1–1.5	0.02–0.08	0.2–0.9	0.2–0.7	0.1–0.6	9

[1] on a dry basis.

The fuel characteristics of biomass are very different from those common fossil fuels, including moisture content, ash content, calorific value, and alkali/alkaline earth metal content, *etc.* [3,13,14]. As shown in Table 1, compared to coal, biomass fuels usually have much higher potassium (K) concentration and moisture content, as well as a lower sulfur component. In herbaceous plants such as straw and energy crops, significantly high chlorine (Cl) concentrations are very common. The distinct features of biomass fuels do not only influence combustion [2], but also significantly change ash behaviors. Firstly, the elements (e.g., K, Cl) in high concentration in biomass are mainly in the form of water soluble inorganic salts, and principally as the corresponding oxides, nitrates, and chloride, *etc.* (Table 2), which could be easily volatilized during the combustion, leading to high mobility for alkali

materials and, hence, high fouling tendency. Theis *et al.* [15] compared the ash deposition behaviors of three sorts of feedstock—straw, peat and bark with different chemical compositions. They found that straw presented higher fouling propensity than peat and bark, because of the large amounts of water soluble compounds found in the straw. The highly active alkali/alkaline metals (e.g., K, Na, Ca) and Cl contents may easily form vapor phase chloride compounds/ions, and then, deposit and form a sticky layer on the heat exchanger or heat transfer surfaces because of the low (<800 °C) melting points of these chloride compounds (e.g., 770 °C for KCl) [11,16]. Subsequently, more inorganic particles in fly ash will have a high tendency of adhering to the particles in the existing layer, resulting into the ash layer growth [17]. Moreover, some biomass fuels contain substantial amounts of silica, e.g., the silica content in rice straw is typically 10 wt% of dry biomass weight [18]. Silicates associated with alkaline/alkaline metals could melt or sinter at 800–900 °C, which can take place in either the solid phase or more commonly the vapor phase, via fly ash during combustion processes [19]. The produced alkali silicates and mixed alkali and/or calcium chlorides/sulfates tend to deposit on reactor walls or heat exchangers surfaces, causing fouling/corrosion even at a low fusion temperature (<700 °C) [20]. Additionally, the existence of heavy metals such as Pb, Zn and Cd [21,22] in some solid fuels (recycled tires) may also influence the ash melting behaviour as well as fouling and corrosion processes on furnace walls and in the combustor via reaction with Cl to form gaseous compounds during the combustion process, and eventually, form aerosols and agglomerate or condense on fly ash particles upon cooling down of the flue gas [23,24].

Table 2. Water soluble inorganic materials in high plants [25–28].

Element	Compound	Formula	Share of the element
Na	Sodium nitrate, chloride	$NaNO_3$, $NaCl$	>90%
K	Potassium nitrate, chloride	KNO_3, KCl	>90%
Ca	Calcium nitrate, chloride, phosphate	$Ca(NO_3)_2$, $CaCl_2$, $Ca_3(PO_4)_2$	20%–60%
Mg	Magnesium nitrate, chloride, phosphate	$Mg(NO_3)_2$, $MgCl_2$, $Ca_3(PO_4)_2$	60%–90%
Si	Silicon hydroxide	$Si(OH)_4$	<5%
S	Sulphate ion	SO_4^{2-}	>90%
P	Phosphate ion	PO_4^{3-}	>80%
Cl	Chloride ion	Cl^-	>90%

Although the aforementioned high moisture content in biomass fuels may not greatly influence combustion (e.g., emissions and combustion efficiency) [29], it could affect ash deposition during combustion. Shao *et al.* [30,31] conducted the first investigation of the effects of moisture content (<5 wt% and 30–35 wt%) in the feed on ash deposition during combustions of individual fuels (woody biomass/peat/coal) and some fuel blends. In their observations, the as-received/air-dried feedstock that contains around 30% to 35% moisture performed better than the oven-dried feedstock in retarding ash deposition and chlorine deposition. Additionally, burning biomass fuels or biomass-coal mixtures containing a low sulfur content is beneficial for significant reduction of SO_x/SO_2 emissions [32], but it may negatively impact on the ash deposition behaviors, in particular Cl deposition [16,33,34]. It has been commonly accepted that the occurrence of S could alleviate the corrosion problems associated with chlorides deposits via the following sulphation mechanism [35]:

$$2KCl + SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow K_2SO_4 + 2HCl \ \Delta H^0 = -646.5 kJ/mol \tag{1}$$

$$2KCl + SO_2 + O_2 \rightarrow K_2SO_4 + Cl_2 \tag{2}$$

In other words, combustion of low-S-containing biomass fuels could increase Cl deposition and the corrosion related to Cl deposits.

## 3. Challenges with Ash Deposition in a Biomass-Fired or Co-Fired Combustor

As discussed in the last section, ash behaviors during combustion are closely related with the characteristics of biomass fuel (e.g., high K, Cl and moisture content, low S content, *etc.*), which usually lead to greater ash-related challenges for almost all combustors/boilers when firing or co-firing biomass materials, particularly for boilers fueled with some herbaceous materials like straw and wheat straw [2,36–39]. Some major negative impacts of the increased ash deposition by biomass combustion/co-firing on the efficiency and operation of a combustion system can be summarized as follows:

(1) Decrease in the combustor utilization efficiency. The increased ash deposition as well as the changed properties of the ash deposits containing low-melting compounds such as K, Na, S and Ca would form a kind of coating on the bottom ash particles, which is partly in a liquid form, and begin to bind the particles together like glue [40], leading to agglomeration of the ash particles in the combustor. Bed agglomeration would eventually cause de-fluidization for a fluidized bed combustor, which would hence result in greatly reduced combustor utilization efficiency. Moreover, deposition of fused or partially fused ash deposits on the heat exchanger surfaces will retard the boiler heat transfer, leading to a decline in the combustor thermal efficiency, and its capacity too.

(2) Damage to the combustor equipment. Ash deposits may grow to the extent that the flue gas flow through the boiler may be restricted, often by bridging across the steam tubes and tube bundles. This could cause mechanical damage of the combustor components and boiler equipment, and more importantly, the ash deposits are associated with corrosion at high temperatures. Even for large pulverized fuel furnaces, the ash deposition on burner component and divergent surfaces could result in interference with the burner light-up and operation. Again, the accumulation and subsequent shedding of large ash deposits on the upper furnace and the steam tubes surfaces could restrict gas flow and thus damage the components of the combustion system.

(3) Maintenance problems. Severe deposits, on steam tubes, in hoppers and on grates (for grate boilers) would require premature shut-down for maintenance. Unplanned outages for off-load cleaning are required for removing the ash deposits. For example, severe slagging occurring in a full-scale boiler (Amager Power Statoion Unit 2 in Denmark) caused the system shut-down undesirably after only weeks of operation burning straw pellets [41]. Moreover, the build-up of accumulations of ash deposits on heat transfer surfaces also leads to increased combustor exit gas temperatures, reducing the boiler efficiency.

4. Ash Deposition Monitoring and Analysis of Ash Deposits

The mostly commonly applied technique for ash-related research involves using air-cooled steel probes as the simulation of superheater tubes or heat exchangers, and collecting the ash deposits during biomass co-firing/combustion to monitor ash deposition rate as well as to collect fly ash deposit for analysis. K-type thermocouples are usually embedded into the outside of a deposition probe wall to monitor the probe's surface temperatures. The surface temperatures of deposition probe can thus be monitored or controlled to some extent via adjusting the flow rate of cooling air depending on flue gas temperature and the probe properties (*i.e.*, size, metal conductivity). In most of deposit-related studies, the surface temperature of ash deposition probes was controlled at the steam-tube metal temperature in boilers, typically at 430–600 °C [10,12,30,31,42–45]. On the other hand, ash deposit sampling was performed at the superheater zone in a small boiler furnace or multiple locations in a large scale unit using the air-cooled deposition probes. Generally, after an operation period during the biomass co-firing/combustion test, the sampling probe(s) was/were carefully removed from the combustion system. Ash deposits were then brushed off from the probe surfaces to be weighed and analyzed. An example of the air-cooled ash deposition probe developed by the authors [19,20] is illustrated in Figure 1. In some lab-scale experiments, on-line weight measurements have been achieved by connecting a balance to the probe [33]. Moreover, some researchers employed some detachable rings [45] or coupons [46] on the probe surface to collect deposits instead of a permanent metal surface. Deposit samples collected from these single-used rings/coupons could then be sent for laboratory analyses, which minimized the contamination during brushing off the ash deposits.

Figure 1. Air-cooled ash deposition probe.
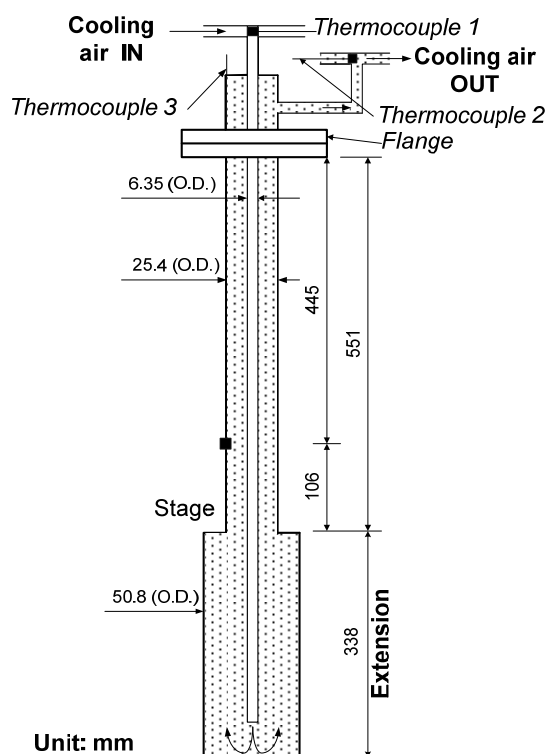
After collection, the ash deposits obtained from biomass co-firing/combustion are usually characterized by a variety of laboratory techniques, including inductively coupled plasma-atomic emission spectrometry (ICP-AES), X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX), and ion chromatography (IC). ICP-AES, XRF and SEM-EDX were applied to analyze the major elements present in the fuel ash and deposits, including Si, Al, Fe, Ca, Mg, Ti, Na, K, P, Cl and S [37,45–49], as well as Pb and Zn for some fuels such as recycled tires [21,22]. Most of these elements would contribute to ash deposition and agglomeration/clickers formation, especially for grate and fluidized bed combustion applications. The elemental concentrations determined by ICP-AES can be used to calculate the molar ratios of K/Si and K/Cl, *etc.*—useful parameters for interpretation of fuel ash/deposit chemistry. The ash elemental compositions are also commonly reported as oxides, in their highest oxidation states, which reflect the principal inorganic compositions. Furthermore, SEM is a particularly powerful analytical technique for the examination of the microstructure of ashes and deposits [50–52]. XRD is commonly used for the identification of the major crystalline phases in deposits [47,53,54]. Because of high chlorine contents in most of biomass, IC has been developed as a practical method to determine chlorine and sulphur concentration in the deposits [15,48].

With the abovementioned techniques, researchers have been focusing their efforts on: (1) the mechanisms of ash deposition, slagging/fouling, and high temperature corrosion; and (2) the technologies for tackling the ash-related issues for biomass co-firing/combustion, which are discussed separately in the following sections.

5. Mechanisms and Chemistry of Ash Deposition

Research efforts have been put into attempting to understand the mechanisms involved in the formation [15,44,48,55,56], slagging/fouling [52] and corrosion [35] of the ash deposits during biomass combustion or co-firing. During combustion processes, ash is formed from the fuel-bound inorganic materials through a combination of complex chemical and physical processes. After undergoing different physical processes including fragmentation, shedding, and coalescence during char burnout, the extraneous inorganic materials may be converted into volatile compounds (such as KCl or KOH) or non-volatile ash compounds that remain inside and on the surface of the char depending on the temperature and chemical composition of the particles. Depending on the density and size of the residual ash particles, the combustion technology, operating conditions and the flue gas velocity, a fraction of the non-volatile ash compounds will also be entrained with the flue gas and form the coarse part of fly ash with a large particle size (typically greater than 5 μm, as shown in Figure 2a). In grate furnace combustion, the coarse fly ash can be up to 850 μm depending on the biomass fuel properties and the configuration of the combustor, while the rest remains inside the combustor and form bottom ash [57].

Similarly, the inherent inorganic species may undergo several transformations including chemical and physical reactions during combustion/co-firing. Very small primary particles (about 5–10 nm) are formed by vaporization of the volatile species and subsequent nucleation in the boundary layer first, then they grow by coagulation, agglomeration and condensation in the flue gas. These particles are the basic fine fly ashes with a particle size of <1 μm as shown in Figure 2.

Figure 2. SEM-EDX images of coarse fly ash (**a**) and aerosol particles (**b**) from wood combustion in a grate furnace [57].
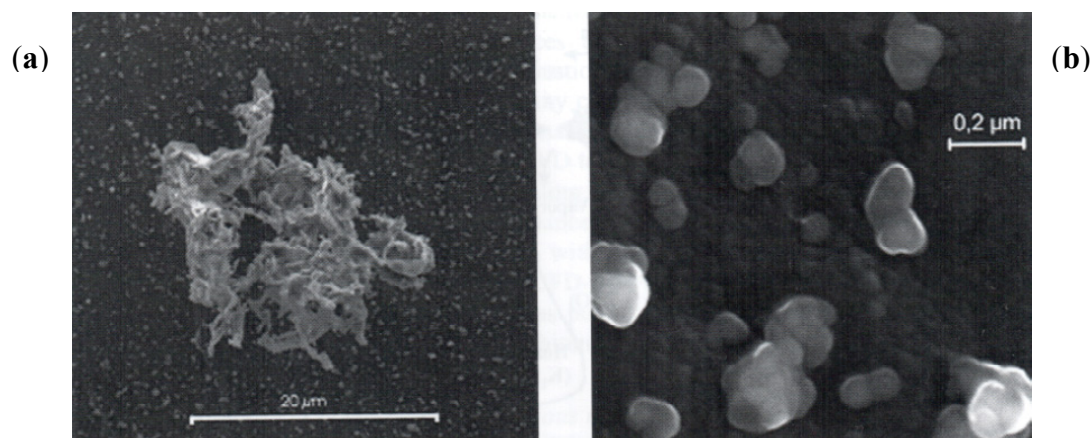
When the flue gas at high temperature containing many coarse and fine particles contacts the relatively cool heat transfer surface, coarse ash particles (typically greater than 10 μm, Stokes number is greater than 1) would cause inertial impaction, a dominant process responsible for the high temperature slag formation. Then, heterogeneous condensation between the pre-existing ash particles and the vapors of volatilized compounds in the flue gas will occur on the heat transfer surfaces. If the concentration of inorganic vapors in the flue gas and the cooling rate in the heat exchanger are both high, a local supersaturation of salts, e.g., Na_2SO_4, K_2SO_4, or KCl, could occur and cause formation of new particles by nucleation [11,57]. With the example of potassium, the major and most mobile/volatile alkali in the biomass fuels during combustion, vaporized K may be present mainly as gaseous KCl or KOH in the flue gas at a high temperature >800 °C, as shown in Figure 3. As the gas temperature decreases and given the presence of SO_2 in the flue gas, the chloride and hydroxide may be converted to sulphate by homogenous gas-phase reactions (a highly exothermic reaction, thus thermodynamically favorable at lower temperatures), as shown in Equation (1). K_2SO_4 has a very low vapor pressure and becomes highly supersaturated as soon as it is formed, forming high numbers of new primary particles by homogenous nucleation. However, according to gas phase kinetic considerations, the equilibrium conversion to K_2SO_4 may not always be possible, *i.e.*, only a part of the K in vapour phase is converted to K_2SO_4 [58]. The remaining part of the gaseous potassium may present as KCl or K_2CO_3. As time proceeds in the flue gas, solid KCl or K_2CO_3 on the particles may also undergo heterogeneous reactions with SO_2 (g) and form solid K_2SO_4.

Generally there are four main mechanisms for ash deposition on heat transfer surfaces, *i.e.*, inertial impaction, condensation of vaporized inorganic compounds, thermophoresis and chemical reactions, as illustrated in Figure 4. Inertial impaction tends to dominate at the wind side [34], whereas it cannot dominate on the lee side of a superheater tube where elements are transported mainly by condensation and partly by diffusion and chemical reactions [17,59]. The condensation of volatile inorganic species is the principle mechanism for the formation of convective pass fouling, e.g., on the heat transfer surfaces in a co-fired boiler, in particular when biomass fuels contain high levels of volatile species. In addition to condensation of vaporized inorganic compounds and inertial impaction, at the initial stage of the deposition when the local temperature gradients are at a maximum, very small, sub-micron ash

particles could be transported to cooled surface driven by the local gas temperature gradients regardless inertial impaction.

Figure 3. Equilibrium concentrations in gas phase for the major potassium containing species present in biomass fuel under typical biomass combustion conditions [11].
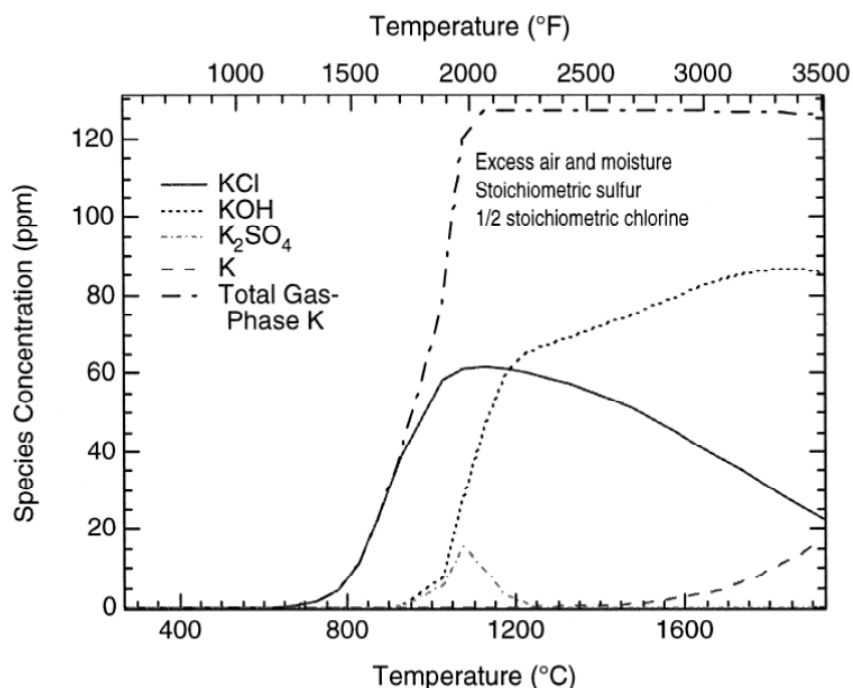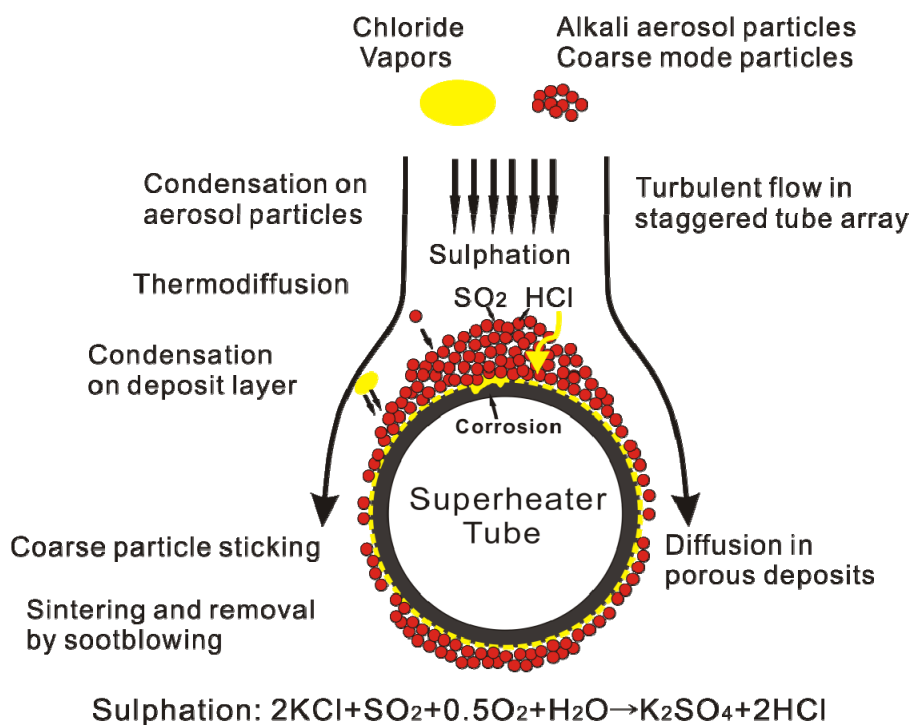

Figure 4. Schematic of mechanisms of ash formation and deposition on a superheater tube surface [7].

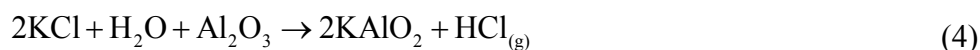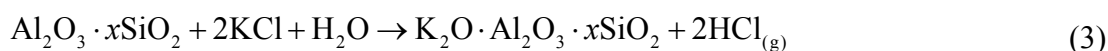Sulphation: $2KCl + SO_2 + 0.5O_2 + H_2O \rightarrow K_2SO_4 + 2HCl$

This process is called thermophoresis. Such chemical reactions as oxidation, sulphation and chlorination processes would occur within the deposit layer and between gaseous and solid compounds under the combustion conditions [7,15,37,45]. For example, silica in combination with alkali and alkaline earth metals, especially with the readily volatilized forms of potassium present in biomass, can lead to the formation of low melting point compounds which readily slag and foul at normal biomass boiler temperatures (800–900 °C) [7,11]. The produced alkali silicates and/or mixed alkali and/or calcium chlorides/sulfates tend to deposit on the reactor wall or the heat-exchanger surface causing fouling/corrosion at a low fusion temperature (typically <700 °C) [19].
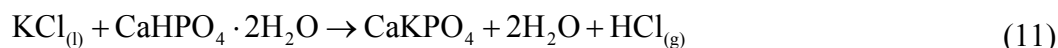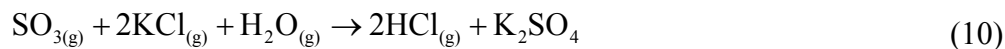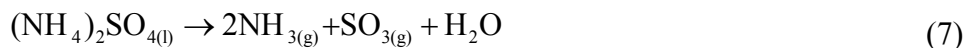
6. Technologies for Reducing Ash Deposition and Corrosion

As discussed before, firing or co-firing high-alkali (K/Na) herbaceous biomass fuels such as switchgrass and wheat straw would lead to severe problems of slagging and fouling on boiler surfaces, and the chlorine compounds in volatile ash would result in corrosion of heat transfer surfaces inside the boiler. Various technologies for reducing ash deposition as well as corrosion have been studied. These include: (1) addition of so-called combustion additives such as sulphur or SO_2 and Al_2O_3/SiO_2 [10,20,41,60–76]; (2) co-firing bio-fuels with low fouling-tendency fuels [8,55,77–81]; (3) pretreatment of the feedstock to reduce the alkali metals [82,83], and (4) modification of the boiler (e.g., modification of the re-heater and super-heater in order to allow for larger spacing, more soot-blowing and a decrease in the live steam temperature to less than 500 °C, *etc.*) [60]. The first two ash-deposition tackling technologies as mentioned above (which are the most widely studied) are reviewed and discussed in the following sections.

6.1. Addition of Combustion Additives

Use of additives to tackle the ash-related issues is mainly based on the idea of converting the vaporized inorganic species to less volatile forms, thus enhancing the melting temperature of ash residues via chemical reactions and physical interactions (*i.e.*, absorption/dilution) [41,62,67,68] and reducing the formation of fine particles or water-soluble alkalis [84–86]. So far, dozens of different additives have been tested and used to increase the melting points of the alkali compounds (e.g., KCl, K_2O, $KSiO_3$, *etc.*) in biomass combustion/co-combustion. Among these, the four major classes are: Al-Si-based, S-based, Ca-based, and P-rich substances [73]. Some key reactions are listed in Equations (1–12) that could take place between the additives and the alkali-containing species, mainly K-species from biomass fuels [35,73].

$$Al_2O_3 \cdot xSiO_2 + 2KCl + H_2O \rightarrow K_2O \cdot Al_2O_3 \cdot xSiO_2 + 2HCl_{(g)} \tag{3}$$

$$2KCl + H_2O + Al_2O_3 \rightarrow 2KAlO_2 + HCl_{(g)} \tag{4}$$

$$2KCl + SiO_2 + H_2O \rightarrow K_2O \cdot SiO_2 + 2HCl_{(g)} \tag{5}$$

$$SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow SO_{3(g)} \tag{6}$$

$$(NH_4)_2SO_{4(l)} \rightarrow 2NH_{3(g)} + SO_{3(g)} + H_2O \tag{7}$$

$$Fe_2(SO_4)_{3(l)} \rightarrow 3SO_{3(g)} + Fe_2O_3 \tag{8}$$

$$Al_2(SO_4)_{3(l)} \rightarrow 3SO_{3(g)} + Al_2O_3 \tag{9}$$

$$SO_{3(g)} + 2KCl_{(g)} + H_2O_{(g)} \rightarrow 2HCl_{(g)} + K_2SO_4 \tag{10}$$

$$KCl_{(l)} + CaHPO_4 \cdot 2H_2O \rightarrow CaKPO_4 + 2H_2O + HCl_{(g)} \tag{11}$$

$$K_2O \cdot SiO_2 + 2CaCO_3 \rightarrow 2CaO \cdot K_2O \cdot SiO_2 + 2CO_2 \tag{12}$$

For better effectiveness of the additive, it is generally required that the additive have a smaller pariticle size and more surface area to facilitate the physical adsorption and chemical reactions. Al-Si-type additives are mostly the first choice in the literatures [61,62,67–69,72] due to their strong ability for converting vapor/liquid-phase KCl and $KSiO_3$ to potassium aluminum silicates (e.g., $KAlSiO_4$, $KAlSi_2O_6$, $KAlSi_3O_8$, *etc.*) with high melting-points (>1100 °C) by the reactions indicated in Equation (3).

Moreover, an excess of S in the flue gas could facilitate the sulphation [Equations (1) and (2)] of alkali chlorides and make the ash less sticky, as well as increase the melting point of the deposits, thus preventing the slagging/fouling of the heat transfer surface [37,45]. Therefore, the sulphur-to-chlorine atomic ratio (S/Cl) in the feedstock was adopted as a useful indicator for the deposition and corrosion propensity of chlorine-containing ash, and it was suggested that if the S/Cl ratio of fuel is less than two, there is a high risk of superheater corrosion in combustion [37,45]. If the S/Cl ratio is at least four, the fuel blend could be regarded as non-corrosive [7,66], while Theis *et al.* [15] recently reported the deposition could not be reduced unless the S/Cl ratio reached at or above 6.7 due to the presence of Ca compounds that could capture sulfur and thus restrained the sulphation. Moreover, Ferrer *et al.* [34] suggested that the molar ratio of S (in flue gas)-to-Cl (in the fuel) molar ratio (S_{fg}/Cl) would be a better indicator of Cl deposition than the S/Cl molar ratio in the fuel when limestone is added to reduce SO_2 emissions. Theoretically, a minimum value of 0.5 of S_{fg}/Cl would be required to complete the sulphation of all alkali chlorides, but the least S_{fg}/Cl could be reduced with the amounts of available aluminosilicates in fuel-ash. Furthermore, Kassman *et al.* [74–76] applied ammonium sulphate as a combustion additive in full-scale biomass combustion. They found that gaseous SO_3 decomposed from $(NH_4)_2SO_4$ during combustion was more efficient than gaseous SO_2 to react with KCl, even at a low S/Cl molar ratio (~1.0).

Additionally, Ca-based additives such as lime and limestone are likely effective via dilution of the ash or adsoption of alkali salts on their porous surfaces when they are calcinated rather than chemically reacted with alkali metals or alkali containing compounds. The calcination process usually occurs at a high temperature and prolonged time [34,68]. However, calcium additives containing CaO, $CaCO_3$ and $Ca(OH)_2$ are more active in biomass combustion, in particluar for P&K-rich biomass fuels, to help convert vapor K species into high-melting-point potassium silicates/phosphates [63,65,69–71]. Correspondingly, when biomass fuels containing high contents of K, Si and Ca, P-based additives could be used to reduce ash sintering and bed agglomeration [64,65].

6.2. Co-Firing Biomass with Low Fouling-Tendency Fuels

Although addition of combustion additives would solve ash-related problems to some extent during biomass combustion/co-firing, selection of the most optimal additive to achieve the best efficiency while keeping a low extra cost and avoiding materials handling risks and possible environmental issues is still challenging. Co-firing biomass with low fouling-tendency fuels would be an effectively alternative measure for preventing ash deposition by utilizing fuels of either low ash-content or abundant ash-deposition-retarding compounds [55,61]. For instance, co-combustion of straw with coal was proved to be an effective way to avoid the sintering problems associated with the problematic straw combustion. As kaolinite and other aluminosilicates are abundantly present in most coals [87], it is likely that an alkali absorption mechanism is active during the co-combustion. Moreover, some biofuels such as sewage sludge contain different aluminum silicates, silica and alumina, which could increase biomass ashes sintering temperatures and reduce their fouling deposition in various studies [77–80].

Because of the potential in reduction of ash-related issues as discussed above and reduction of emissions of greenhouse gases and other toxic gases such as SO_x and maybe NO_x [8,16,81,88–90], biomass co-combustion (co-firing) technology has found broad applications in the energy production field, particularly in the USA, many EU countries (Finland, Denmark, Germany, Austria, Spain, and Sweden, The Netherlands, Poland) and a number of other countries [91]. To date, more than 150 coal-fired power plants (mainly 50–700 MW_e) around the World have adopted or tested co-firing of coals with woody biomass or waste materials [92]. Biomass co-firing systems can also be used for agricultural applications such as electricity and steam generation in the sugar cane industry [32], and in utility-scale (e.g., 150 MW) electricity generation [93]. Owing to the capability to meet diversified needs, biomass-based power generating systems are so far the only non-hydro renewable source of electricity that can be used for base-load electricity generation.

Co-firing has been successfully demonstrated in almost all types of coal boiler, including pulverized fuel combustor (PFC), fixed bed and fluidized beds combustors, as well as grate boilers [94]. For example, a very large-scale biomass co-firing plant, the Alholmens Kraft Combined Heat and Power plant in Pietarsaari (Finland)**,** has been in operation since 2001. This plant employs a circulating fluidized bed (CFB) boiler with an electricity output of 240 MW_e [7]. Although fluidized bed combustors, bubbling fluidized beds (BFBs) and circulating fluidized beds (CFBs) are advantageous in terms of their fuel flexibility, being able to handle different types of fuels, solid, semi-solid, or liquid fuels, PFC is the most common technology used for co-firing biomass with coal. This is because less equipment modification is required for co-firing biomass and coal in an existing large PFC plant. There has been rapid progress worldwide over the past decade in development of the biomass co-firing technology for pulverized coal-fired boiler plants, particularly in Europe, North America and Australia [91]. According to the report by Baxter and Koppejan [95], worldwide approximately 41.5% of 135 coal-fired power plants that have experience co-firing biomass use PFC boilers. However, biomass co-firing in PFCs has encountered both technical and non-technical problems. For example, the co-firing ratio of biomass in most PFC boilers is no more than 10%–15% on a thermal input basis due to the issues of increased ash deposition or accelerated corrosion rates for the boiler components. On the other hand, for grate boilers that have been traditionally used for solid fuel combustion on a

relatively small-to-medium scale (15 kW up to 150 MW), co-firing of recycled fuels, packaging derived fuels, refuse derived fuels, recovered fuels and plastics with wood fuels or other by-products of forest industry was successfully demonstrated [56]. Co-firing of recycled fuels in small power plants is relatively less challenging as the steam temperature is usually lower than 400 °C and there is no risk of high-temperature corrosion. Nevertheless, special attention must be paid to flue gas cleaning. For biomass firing on grate boilers, the following key issues need to be addressed: homogeneity of the feedstock (particle size), proper sizing of the combustion chamber and efficient mixing of the feedstock with the combustion air.

In a recent study by the authors [20], the ash deposition behaviors of co-combustion of three-fuel blends of white pine pellets (WPP), peat pellets (PP) and crushed lignite (CL) coal were studied on a pilot-scale bubbling fluidized bed combustor operated at 40% excess air ratio. Reference tests with individual fuel (pine, peat or lignite) and two-fuel blends of lignite and pine or peat were also performed and discussed in this study. As a very interesting finding from this work, co-combustion of three-fuel blend at 50% lignite-25% peat-25% pine resulted in a higher ash deposition rate than co-combustion of two-fuel blend of either 50% lignite-50% peat or 50% lignite-50% pine. In contrast, co-combustion of three-fuel blend at 20% lignite-40% peat-40% pine resulted in the lowest deposition rate and the least deposition tendency among all the combustion tests with various mixed fuels or individual fuels, as shown in Figure 5. The greatly decreased ash deposition tendency of co-firing three-fuel blend of 20% lignite-40% peat-40% pine might be accounted for by the formation of more minerals containing CaO, MgO, Al_2O_3 and SiO_2 with high ash melting points and high crystallinity. The chemical compositions of deposits obtained from the co-combustions of three-fuel blends were found to be enriched with the elements of Si and Al and depleted in the elements of P, S and K.

Although co-firing technologies have been well developed and relatively widely applied in industries worldwide, co-firing processes are not yet completely understood. Due to the inferior properties of biomass (e.g., higher moisture contents, low bulk densities, *etc.*), direct co-firing processes are normally limited to low co-firing ratios. The major technical challenges associated with the biomass co-firing technology are summarized as follows:

(1) More research is needed to better understand and find cost-effective measures to tackle the ash-related issues in combustion and co-firing biomass due to the strong dependency of these issues on the properties of selected fuels, configuration of co-firing system, and the operation conditions;

(2) Biomass materials are generally moist and strongly hydrophilic as well as non-friable, which poses difficulties in fuel preparation, storage, and delivery;

(3) Depending on the quality of the biomass feedstock, co-firing might result in reduced thermal efficiency and increased NO_x emission;

(4) Economic utilization of the fly ash from co-firing biomass and coal shall be explored. It herewith shall be noted that the fly ashes from biomass co-firing processes are currently unacceptable for cement manufacture as biomass fly ashes do not conform to the ASTM standards.

Figure 5. Comparison of relative ash deposition rates RD_A obtained from the combustions of 100% lignite and three-fuel blends FB1 (25% WPP + 25% PP + 50% CL) and FB2 (40% WPP + 40% PP + 20% CL), in comparison with those from combustion of 50% WPP + 50% CL, 50% PP + 50% CL, 80% WPP + 20% CL, 80% PP + 20% CL as well as 100% WPP, and 100% PP (modified from [20]).
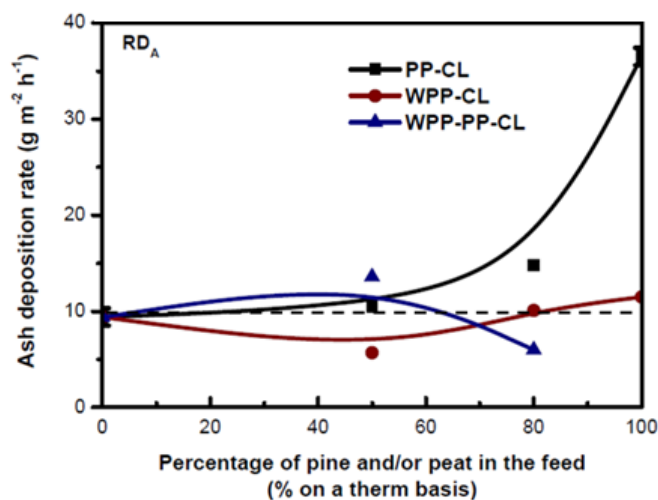
7. Conclusions

Water soluble potassium along with the Cl in biomass fuels are the most problematic elements during biomass combustion/co-firing in a combustor/boiler, which could result in issues of severe ash deposition/fouling/slagging and high-temperature corrosion. With air-cooled ash deposition probes, the ash deposition in the combustion/co-combustion can be monitored and analyzed, which helps understanding of the mechanisms and chemistry of ash deposition/corrosion. Addition of combustion additives and co-firing high-risk biomass with low fouling-tendency fuel(s) are effective measures to tackle the ash deposition issues for biomass combustion/co-firing. However, selecting an optimal combustion additive is very difficult and it is hard to achieve the maximum performance without greatly increasing the operating costs, introducing some side-issues related to material handling/emissions. Co-firing high-risk biomass with low fouling-tendency fuel(s) seems to be a more cost-effective measure for reduction of ash deposition.

Despite many researches contributing to the ash-related studies for biomass thermo-utilization that have covered different types of boilers and a large number of biomass species, the fates and detailed reactions of the alkali elements during the combustion processes are yet to be elucidated. Some questions remain unanswered: e.g., do the reactions occur before the fly ash contacting with the heater exchange surface, or on the surface? What are the practical and cost-effective means to retard these reactions? Answers to these questions would be very helpful to address the ash-related problems in biomass combustion/co-firing for heat/power generation.

Acknowledgements

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