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A Brief Review of Solving Biomass Ash Deposition with Aluminum-Silicate Based Additives and Future Perspective of Kaolin

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Biomass as an abundant "green" renewable and CO_2 neutral energy source have captured the entire world attention as a result of worsening energy crisis and environmental problems. Combustion of biomass have huge potentials of producing heat and power in a sustainable way. However, biomass fuels possess alkali metals i.e potassium (K) content which react with other ash forming elements i.e chlorine (Cl) to form alkali containing species i.e potassium chloride (KCl) which results in ash related operational problems (slagging and fouling). Kaolin; an aluminum-silicate based additive is regarded as the best additive at handling and capturing the problematic alkali containing species during biomass combustion with its ability to convert alkali containing species to high melting point potassium aluminum silicates (Kalsilite, Leucite). Therefore, this paper presents an overview of the mechanism of ash deposition, highlight key findings of aluminosilicate-based additives applications from previous studies and ends with kaolin future perspective.

1. Biomass ash related issues

Biomass fuels are solid organic materials that can be burn and use as fuel source. Biomass fuels can be obtained thermochemically through combustion of biomass in boilers or gasifiers. Base on source, biomass are classified into four major categories namely: woody, agricultural, wastes and excrements (Niu et al., 2016). Several thermochemical conversion methods have been employed in conversion of biomass to useful form (energy), however, biomass combustion stand out as the prevailing conversion technology for the production of heat and power (Demirbas et al., 2009) because of the quality of its end product. Biomass are of different significant benefits which include social, economic and energy security (Yongtie et al., 2017), but despite all, the conversion process suffers greatly from ash related issues i.e. slagging and fouling, agglomeration and corrosion (Figure 1). The presence of chlorine (Cl) and alkali metals (potassium [K] and sodium [Na]) in biomass result in quick formation of stubborn and awkward deposits on fired surface; especially alkali induced slagging on the superheater or boilers (Guo et al., 2020; Miccio et al., 2019; Niu et al., 2014), which impede the transfer of heat and also reduces boiler efficiency (Guo et al., 2020). According to (Wang et al., 2012; Yongtie et al., 2017), slagging and fouling reduces efficiency of biomass combustion system, causes unexpected boiler repair cost and also hinder further usage of biomass materials as fuel.

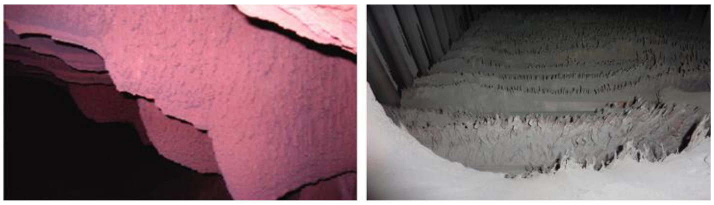

Figure 1: Ash related issue in biomass fired boiler. Adapted from (Niu et al., 2016)

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Generally, K are found in biomass which during combustion volatilize and lead to the formation of intransigent surface deposits, agglomeration and corrosion (Deng et al., 2019; Miccio et al., 2019; Niu et al., 2016). The more alkali metals and chlorides a particular biomass fuel contain, the less its ash melting point and the higher the tendency for it to slag. K has been identified as the root cause of all forms of disaster associated with the combustion of biomass. Soluble K which is present either in salt as ionic form or as direct organically bound ions is released as K(g), potassium hydroxide [KOH(g)], potassium chloride [KCl(g)], and other forms of K-species during combustion making it readily available for further reaction with other compounds of the flue gas during combustion (Niu et al., 2016). According to (Wang et al., 2012), the primary constituents of sub-micrometer particulate matter present in produced flue gas are KCl and potassium sulphate [K_2SO_4] which has melting temperature of 770 °C and 850 °C respectively. A system consisting of both KCl and K_2SO_4 salts could melt at a very low temperature of 550 °C and below (Lindberg et al., 2013).
A reliable solution to alleviate ash related problems during biomass combustion is by the use of additives. Additives are environmentally friendly, easy to apply and attracts no additional upkeep or maintenance cost for the combustion process (Wang et al., 2012). They are referred to as group of minerals that alters ash chemistry, transform problematic species to safe form and improve the ash melting temperature in thermal processes (Wang et al., 2013). Additives are generally classified into aluminum-silicate (Al-Si) based additives, sulphur (S) based additives, phosphorus (P) based additives and calcium (Ca) based additives. Of all the types, Al-Si based additives are the best at capturing K present in biomass during biomass combustion. Al-Si based additives are kaolin (Hardy et al., 2013; Wang et al., 2014a), bentonite (Hardy et al., 2013), zeolite (Wang et al., 2014a), bituminous/ lignite coal ash (Hardy et al., 2013; Wang et al., 2017), and spent bleaching earth (SBE) (Madhiyanon et al., 2020). Among the Al-Si based additives, kaolin is outstanding and mostly sort after due to its availability and ability to handle and also tackle biomass combustion issues better (Madhiyanon et al., 2020). (Batir et al., 2019; Wang et al., 2013) emphasized that kaolin increases the ash melting temperature of biomass and also regard it as the most effective additive. The main constituent of kaolin is kaolinite [$Al_2Si_2O_5(OH)_4$] which transform to meta-kaolinite when heated to a temperature of 450 °C (Batir et al., 2019). Meta-kaolinite reacts with K-species and form crystalline products such as kalsilite ($KAlSiO_4$) and leucite ($KAlSi_2O_6$) which are characterized with high melting temperature of 1600 °C and 1500 °C respectively (Konsomboon et al., 2011; Wang et al., 2012). The use of Al-Si based additives have been identified as the most appropriate additive to eliminate operational problems encountered during biomass combustion (Wang et al., 2012). The current review provides an understanding on the ash deposition mechanism and the application of Al-Si based additives. The future perspective of kaolin usage was also reflected on.

2. Mechanism of biomass ash deposition

Both theoretical and experimental studies have been carried out on ash deposition of biomass. Slag deposits on boiler or furnace wall is as a result of fine ash particles of K and Cl content. Cl fosters the release of K in biomass thereby resulting in the formation of troublesome KCl, which then condense on boiler heating surface (Zhu et al., 2014). Ash deposition issues depend largely on the presence of risky elements such as Na, K, Cl and protective elements such as Si and Al (Xiong et al., 2008). In biomass fired furnace, K and Cl combine to form KCl which then condense on heating surfaces. Partial KCl can either be sulfated or aluminosilicated. When sulfated, slagging is being promoted while when aluminosilicated, slagging is being inhibited (Zhu et al., 2014). Co-firing, leaching and the addition of additives can change the components of fuel and affect combustion in thermal processes. During cofiring, leaching or addition of additives, an increase in the ratio of (K+Cl)/(Si+Al) in the fuel will lead to an increase in KCl concentration which therefore result in slag aggravation. A decrease in the ratio of (K+Cl)/(Si+Al) denotes the capture of K in K-species by Si and Al, which interpret to less slagging experience during combustion (Zhu et al., 2014). Generally, the deposition of ash on heating surface have four main mechanisms namely: inertial impaction, condensation of vaporized inorganic compounds, thermophoresis and lastly, chemical reactions according to Shao et al. (2012); Zhu et al. (2014) which are illustrated in Figure 2. Inertial impaction tends to dominate at the wind side, which is not possible at the lee side of a superheater tube or boiler where elements are transported principally by condensation and by diffusion and chemical reactions partly. The main cause of the formation of ash deposit on heat surface in boiler is the condensation of volatile inorganic species. At the early deposition stage, very small sub-micron ash particles are conveyed to cool surface by the local gas temperature regardless of inertial impaction. This process is known as thermophoresis (Shao et al., 2012). During combustion, chemical reactions such as chlorination, oxidation and sulphation takes place between solid and gaseous compounds, and the deposit layer (Veijonen et al., 2003). For example, silica react with readily volatized alkali metal i.e potassium and low melting point compounds which slag and foul at regular biomass boiler temperature (800-900 °C) are formed (Shao et al., 2012; Veijonen et al., 2003). The produced alkali silicates or calcium chlorides tend to deposit on the reactor wall of the boiler, thereby causing fouling or corrosion at low fusion temperature (Shao et al., 2012).

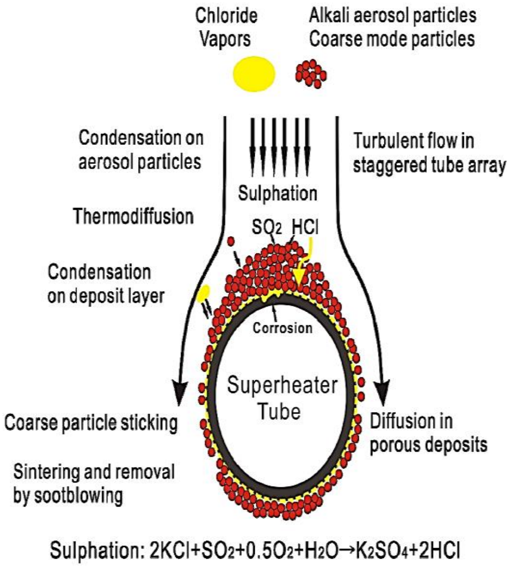

Figure 2: Schematic diagram of mechanism of ash formation and deposition on the surface of boiler. Adapted from (Veijonen et al., 2003)

Table 1: Aluminosilicate-based additives capturing potassium (K) during biomass combustion

Biomass	Additives	Remark	Reference
Danish wheat straw Milled wood pellets	Kaolin Coal fly ash	With fuel–K/ additive -Al molar ratio of 1, the deposition propensity of wheat straw combustion significantly reduced. (K+Cl)/(Si+Al)	Wang et al. (2022)
Wheat straw Corn stalk	Kaolinite	Kaolinite addition held back the release of potassium due to Kalsilite formation.	Li et al. (2020)
Thai rice straw and rice husk	Kaolin	(1) K-Al- silicates formation. (2) Reduced the formation of deposit and prevented the heat transfer from deteriorating.	Madhiyanon et al. (2020)
Olive cake White wood	Coal fly ash Kaolin powder	(1) Kaolin addition to high K and high Cl biomass (OCA) made ash composition viable for combustion. (2) Ash fusion test showed both additives increase flow temperatures.	Roberts et al. (2019)
Olive residue	Kaolin	(1) K retention in ash increased up to 4% Kaolin content forming mainly Kalsilite crystals. (2) Kaolin captured KCl(g) and KOH(g) and form potassium aluminum-silicates which also resulted in increased HCl(g) and SO_2(g) concentration in the gas phase.	Batir et al. (2019)
Softwood Wheat straw Olive residue	Aluminosilicate-based additive	The percentage of K retained at elevated temperature during biomass combustion of wood, wheat straw and olive pellets after additive addition were 70-100%, 60-80% and 70-100% respectively.	Clery et al. (2018)
Water slurry	Kaolin Coal fly ash	(1) Under suspension fired conditions (1100 - 1450℃), kaolin and coal fly ash effectively captured gaseous KCl. (2) Increase in mass ratio of KCl to Al-Si additives in reactant resulted to decrease in conversion of KCl to K-Aluminosilicate.	Arendt et al. (2016)
Wood pellets (2 Types)	Aluminosilicate-based additives (2 Types)	(1) The additives significantly changed both the composition and morphology of the wood pellet samples. (2) The feeding of fuel and additive at the same time facilitated the capture of gaseous K-species immediately they were released.	Paneru et al. (2016)

3. Aluminum-silicate based additives

Table 1 shows various instances where aluminosilicate-based additives have been used to abate ash deposition by capturing K in previous studies. The main product between Al-Si based additives and KCl is potassium aluminum-silicates as shown in equation (1). Kalsilite and leucite are the main product from reaction between kaolin and KCl. Kalsilite and leucite have melting temperature of 1600 °C and 1500 °C respectively (Steenari et al., 2009; Wang et al., 2012). Complex potassium aluminum-silicates such as Microcline ($KAlSi_3O_8$) are also a possibility from the reaction between kaolin and KCl (Wang et al., 2012).

$$Al_2O_3.xSiO_2 + 2KCl + H_2O \rightarrow K_2O.Al_2O_3.xSiO_2 + 2HCl \quad (1)$$

4. Future perspective of kaolin

Kaolin; the most sort after Al-Si based additives due to its availability and its ability to capture K to form high melting potassium aluminosilicates has other wide range of uses, making it essential to many manufacturing industries such as paper, ceramic, rubber and paint industry (Kaolin Market Size, Share & Growth | Industry Report [2027]). In paper industry, kaolin is used as coating and filling agent as it offers better paper opacity, printability and brightness of paper. In ceramic and sanitary industry, kaolin is used in the manufacturing of ceramic-based products and sanitary wares such as tableware, ceramic tiles and household utensils due to its beneficial properties such as strength, grit and fixed color. In rubber manufacturing, kaolin is used as filler to improve the mechanical strength and abrasion resistance of rubber. In paint and coatings, kaolin is used in infrastructural coatings to enhance durability, provide scratch resistance and gloss. The multipurpose nature of kaolin has led to its increasing demand from different end-use sectors which has resulted in its market competitiveness and also global price hike. Figure 4 shows the price and the linear forecast of kaolin in the United States (U.S) which is the largest producer of kaolin.

The biomass conversion industry can therefore not rely on the use of kaolin as an additive as the price keeps increasing. With increasing industrialization to cater for the needs of rising population and the establishment of more biomass conversion industry in line with United Nation affordable and clean energy goal, kaolin demand will definitely increase the more. This will result in further increase in the price in the near future which will be difficult for biomass conversion industries to cope with. The biomass conversion industry therefore needs to turn to the use of sewage sludge which is readily available and a cheaper alternative in combating the ash deposition issues. According to (Aho & Ferrer, 2005; Opobiyi et al., 2019; Wang et al., 2011), sewage sludge can be classified as an Al-Si based additive. Sewage sludge is a proven means as it has been used in combating ash deposition in different biomass (Wang et al., 2012). Alum sludge in particular among sewage sludges is highly dominated with aluminium and silicon content and can perform effectively as kaolin. It's all year-round availability makes it a better and reliable kaolin replacement for the conversion industry. Therefore, favorable government policies to encourage conversion industries in embracing the use of sewage sludge as kaolin replacement should be put in place to avoid the danger that lie ahead.

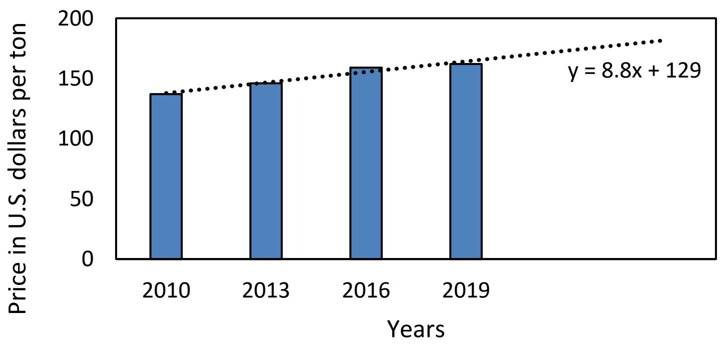

Figure 4: Price and linear forecast of kaolin in the U.S.

5. Conclusions

The biomass conversion process faces ash deposition as a major concern during the thermochemical conversion of biomass which impede the transfer of heat and also reduce boiler efficiency. K-species (KCl, K_2SO_4) formed as a result of the presence of K in biomass are problematic species challenging the efficiency of biomass conversion process.

The application of Al-Si based additives especially kaolin to capture K and form high melting point potassium aluminosilicates was embraced as solution due to kaolin availability, however, the price of kaolin keeps increasing and this threatens the continuous usage of kaolin by biomass conversion industry. Sewage sludge i.e. alum sludge is a cheap, readily available and proven alternative in combating ash deposition in biomass conversion. Therefore, the use of sewage sludge should be embraced by biomass conversion industries so as to avoid the danger that lies ahead with the increasing cost of kaolin.

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