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## **Fuel Processing Technology**

journal homepage: www.elsevier.com/locate/fuproc

## Investigations on biomass slagging in utility boiler: Criterion numbers and slagging growth mechanisms



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#### ARTICLE INFO

Article history: Received 24 May 2014 Received in revised form 25 July 2014 Accepted 26 July 2014 Available online 1 September 2014

Kevwords: Biomass Slagging Ash KC1  $K_3Na(SO_4)_2$ 

### ABSTRACT

To solve the intractable slagging problem in biomass utility boilers, the effects of Si, Al, K, Cl, S, and initial slagging layer on slagging were performed by comparing the distinct slagging characteristics of two cotton stalks. The criterion numbers of slagging, namely, Cl ratio  $(Cl + K_2O + Na_2O)/(SiO_2 + Al_2O_3)$  and S ratio  $(S_{volatile} + K_2O)$ + Na<sub>2</sub>O)/(SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>), were proposed quantitatively. When Cl ratio and S ratio are higher than 2.4 and 1.9, respectively, the biomass is easy to slag; by contrast, the slagging is low when Cl ratio and S ratio are lower than 1.0 and 0.5, respectively. The slagging growth mechanisms were further improved by coupling the alternating layer structure of the whole slagging, which was formed by the re-enrichment of fine particles that primarily contained high concentrations of K, Na, Cl, and S in the form of KCl and  $K_3Na(SO_4)_2$  and by the re-capture of coarse large particles that primarily contained higher Si, Al and so on.  $K_3Na(SO_4)_2$ , originated from the interaction between sulfates, promotes the growth of the slagging. Nonetheless, the influence of K<sub>3</sub>Na(SO<sub>4</sub>)<sub>2</sub> on slagging is minimal in comparison with KCl. The disruption or inhibition of initial slagging layer significantly weakens slagging.

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#### 1. Introduction

Biomass power generation capacity has taken up 70% of all generated renewable fuel power in Western countries, and the biomass power installed capacity has reached 10 GW in USA [1]. In China, the biomass power installed capacity will reach 30 GW that will account for 3% of the total installed capacity in 2020 [2]. Unfortunately, high concentrations of Cl and alkali metals (K and Na) in biomass result in grave slagging in both circulating fluidized bed and grate furnaces [1,3,4]. Slagging not only reduces heat transfer and boiler efficiency, but also damages super-heaters, thereby leading to an unscheduled shutdown.

Generally, KCl is the most stable gas phase alkali-containing substance throughout the entire combustion process, and it is also the dominant substance that influences biomass slagging together with  $K_2SO_4$  [5]. C.J. Yu [1] and Y.Q. Niu [4] suggested that  $K_2Ca(SO_4)_2$  and  $K_3Na(SO_4)_2$  also have a significant role in slagging. In addition, some researchers argued that K<sub>2</sub>SO<sub>4</sub> is the dominant substance that nucleates first when gas temperature is lowered [6]; KCl then condenses on the nucleon of K<sub>2</sub>SO<sub>4</sub> at lower temperature [7]. The contradictions in the presented studies are primarily caused by the different biomass species, planting environments, combustion atmospheres, and temperatures

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[8-12]. Therefore, the extensive research on slagging remedies including co-firing [13,14], additives [9,15], and chemical pretreatment [16.17] are all targeted in certain condition.

Researchers have recently focused on criterion numbers or evaluation indexes to solve slagging problems fundamentally and to provide useful guideline for the selection of co-firing fuels, additives, and biomass fired in the utility boiler. K.O. Davidsson [18] estimated biomass slagging through the alkali index  $(AI = kg(K_2O + Na_2O)/GI)$  that is used for the evaluation of the coal slagging; slagging is probable when AI is in the range 0.17 to 0.34 kg $\cdot$ GJ<sup>-1</sup>, whereas slagging is almost certain to occur when AI is greater than 0.34 kg $\cdot$ GJ<sup>-1</sup>. H. Oleschko [19], M. Diaz-Ramirez [20], and D. Vamvuka [21] proposed (Na + K + 2 Mg + 2Ca)/S, (K + Na)/(Ca + Mg), and S/Cl as evaluation indexes, respectively. In addition, B.M. Jenkins [22] and X.M. Jiang [23] used base-to-acid ratio of coal ( $R_{b/a} = (Fe_2O_3 + CaO + MgO + K_2O +$  $Na_2O$ /(SiO<sub>2</sub> + TiO + Al<sub>2</sub>O<sub>3</sub>)) to estimate biomass slagging. However, Y.J. Ye [24] and Y.P. Hu [25] emphasized that the evaluation indexes of coal cannot reliably predict the slagging behavior of biomass and proposed a new biomass slagging evaluation index (MgO +  $Al_2O_3$  +  $Fe_2O_3$ /(CaO +  $P_2O_5$ ). When this index is below 0.7, then ST (soften temperature) < 1000 °C; when it is above 1.7, ST > 1200 °C. Although many evaluation indexes have been tried, few originated from the utility boiler or were verified by industry practice. Moreover, the influences of Si, Al, K, Cl, and S were not accounted simultaneously.

Biomass slagging is closely related to the concentrations of protective (Si, Al, and S), risky (Cl, Na, and K), and especially volatile (Cl, S, K

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and Na) elements in bio-fuels [26,27]. High concentrations of Cl, K, and Na promote the formation of the fine particles of alkali chlorides that cause serious slagging [27–29]; on the contrary, high concentrations of Si and Al can trap alkali substances through alumina-silicify and further weaken the slagging. Although the consensus mentioned above has been extensively reported, a universal criterion number that incorporates the influences of Si, Al, K, Cl, and S and can guide the selection of co-firing fuels, additives, and biomass effectively is yet to be formulated.

Otherwise, the alternating layered structure [1,4] presented in the slagging of biomass utility boiler requires the further development on the slagging mechanisms of biomass. Presently, the alkali metal slagging in biomass fired furnace consists of two steps (Fig. 1): the first step is the formation of the initial slagging layer; and the second step is the deposition of ash particles on the initial slagging layer. During combustion, the alkali metals released into the flue gas in the forms of KOH<sub>(aerosol)</sub>, KCl<sub>(aerosol)</sub>, K<sub>2</sub>SO<sub>4(aerosol)</sub>, NaCl<sub>(aerosol)</sub>, and Na<sub>2</sub>SO<sub>4(aerosol)</sub> undergo complex chemical reactions and transformations [30]. Partial alkali metal aerosols further grow and form submicrometer ash particle through a series of mechanisms such as nucleation, adsorption, condensation, and chemical reaction upon the decrease of flue gas temperature; these aerosols then condense on heating surfaces and form sticky initial slagging layer through thermophoresis and turbulent diffusion, and this initial slagging layer adhesively bonds the subsequent fly ash into the heating surfaces [29,31]. Partial alkali metal aerosols condense on the surface of the fly ash and form a sticky layer or generate lowmelting substances by further reacting with SiO<sub>2</sub>(R1 and R2) [10] and Fe<sub>2</sub>O<sub>3</sub>(R3) [31] in the fly ash. Moreover, partial alkali metal aerosols can form low temperature eutectic substances by co-existing with other substances, such as  $Na_2SO_4 + NiSO_4$  that are molten in the temperature range of 671 to 884 °C [31]. The coarse fly ashes with and without a sticky layer deposit on the surface of the sticky initial slagging layer through inertial impaction [4,5]. In addition, partial fly ashes form the molten slagging caused by the high ambient temperature in furnace and the remaining fly ashes discharge along with the flue gas.

$$2\mathsf{MCl} + n\mathsf{SiO}_2 + \mathsf{H}_2\mathsf{O} \rightarrow \mathsf{M}_2\mathsf{O} \cdot n\mathsf{SiO}_2 + 2\mathsf{HCl} \tag{1}$$

$$M_2SO_4 + nSiO_2 \rightarrow M_2O \cdot nSiO_2 + SO_3$$
(2)

where *n* represents 1, 2 and 4; M represents K and Na.

$$3Na_2SO_4 + 3SO_3 + Fe_2O_3 \rightarrow 2Na_3Fe(SO_4)_3$$
(3)

Although many studies concerning slagging incentives, remedies, and criterion index have been published, these studies principally focused on the initial slagging layer and were conducted in a laboratory. Moreover, inevitable differences are present when these studies are compared with the real situation in utility boilers. Furthermore, minimal research has been done on the comprehensive comparison of the effects of Si, Al, K, Cl, S, and initial slagging layer on the slagging of biomass fired in utility boilers. Although some published studies focused on the effects of Si, Al, K, Cl, and S on slagging, the quantitative criterion number consisting of the influences of Si, Al, K, Cl, and S is yet to be formulated; and the slagging mechanisms respecting of the formation of the alternating layered structure still need to be improved.

The main objectives of the present work consist of four aspects: 1) reveal the effects of Si, Al, K, Cl and S on slagging through comparing the distinct slagging characteristics of two cotton stalks (planted in the northwest (Fuel 1) and southeast (Fuel 2) of China respectively) burned in existing biomass-fired furnaces (12 and 30 MW) and disclose the formation mechanisms of the alternating layered structure; 2) to reveal the effect of the initial slagging layer on slagging; 3) to explore and propose the criterion numbers consisting of the influences of Si, Al, K, Cl, and S and 4) to develop the comprehensive and in-depth biomass slagging growth mechanisms based on the above research and related references.

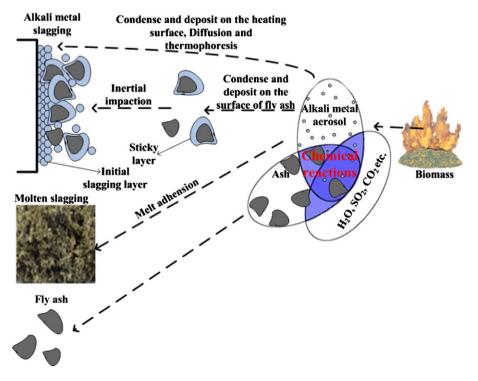


Fig. 1. The fate of biomass ash in furnace.

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