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Entrained Flow Reactor Test of Potassium Capture by Kaolin

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Abstract –In the present study a method to simulate the reaction between gaseous KCl and kaolin at suspension fired condition was developed using a pilot-scale entrained flow reactor (EFR). Kaolin was injected into the EFR for primary test of this method. By adding kaolin, KCl can effectively be captured, forming water-insoluble K-aluminosilicate. The amount of K captured by 1 g kaolin rose when increasing the molar ratio of K/Si in the reactant. Changing of reaction temperature from 1100 °C to 1300 °C did not influence the extent of reaction, which is different from the results observed in previous fixed-bed reactor. The method using the EFR developed in this study will be applied for further systematic investigation of different additives.

1. Introduction

Using biomass on suspension-fired boilers leads to relatively high concentrations of vapor phase K-species such as KCl, K₂SO₄ and KOH which tend to condense on heat transfer surfaces, leading to increased deposition and corrosion [1-4]. Upon flue gas cooling the K-species condense as aerosols that may lead to deactivation of SCR (Selective Catalytic Reduction) catalysts [5]. A possible solution to abate those problems is injection of additives into boilers to react with gaseous K-species forming less corrosive species with higher melting points. Kaolin [4, 6], coal fly ash [6, 7], aluminum and ferric sulfate [8] have previously been shown to react with volatile K-species, and thereby remedy the problems induced by K-rich ash species. The reaction between gaseous K-species and solid additives is affected by local temperature, gas composition, additive particle size, additive composition and reaction time [4, 6]. Detailed knowledge on the reaction of solid additives with volatile K-species at suspension firing conditions is still limited.

Most previous studies on K capture by different additives have been conducted in thermal gravimetric analyzer or fixed bed reactors [4, 6], where reaction conditions are noticeably different from that in suspension-fired boilers. In suspension-fired boilers, additives disperse in high-temperature flue gas and the maximum temperature is as high as 1300 - 1700°C. The objective of the present work is to develop a method using an entrained flow reactor (EFR) to simulate the K capturing reaction by different additives at suspension-fired condition. The impact of reaction temperature and molar ratio of K/Si in reactant was investigated by preliminary tests. The developed method will be used for further systematic study on different additives. Recommendations for optimal use of additives in biomass fired boilers will be provided.

2. Experiment

All experiments were conducted in an entrained flow reactor (EFR) which can simulate the combustion process in suspension-fired boilers. The EFR consists of a gas supply system, a sample feeding system, a gas preheater, a 2-meter long vertical reactor which is electrically heated by 7 heating elements, a bottom chamber and a particle and flue gas extraction system. A schematic drawing of the EFR is shown in Figure 1, and more detailed information about the setup can be found elsewhere [9].

Instead of feeding KCl (s) directly into the reactor [10], KCl and pulverized kaolin ($d_{50} = 6.3 \mu\text{m}$) were mixed with water, in order to make a homogeneous slurry, and the slurry was subsequently fed into the reactor by a peristaltic pump. The slurry was also added with 5 wt % ethanol which burned in the reactor forming CO_2 . In this way, the feeding rate of slurry can indirectly be monitored by measuring the CO_2 concentration in the off-gas. Slurry fed into the reactor was atomized at the outlet of the water-cooled feeding probe by 30 Nl/min feeding air. The atomized slurry droplets ($d < 40 \mu\text{m}$) as well as KCl were mixed with preheated main air (60 Nl/min) and subsequently evaporated. After reactions in the reactor, the solid particles and aerosols were caught by a cyclone and a metal filter respectively. The cyclone had a cut size of about $2 \mu\text{m}$ and the filter can collect particles above $0.1 \mu\text{m}$.

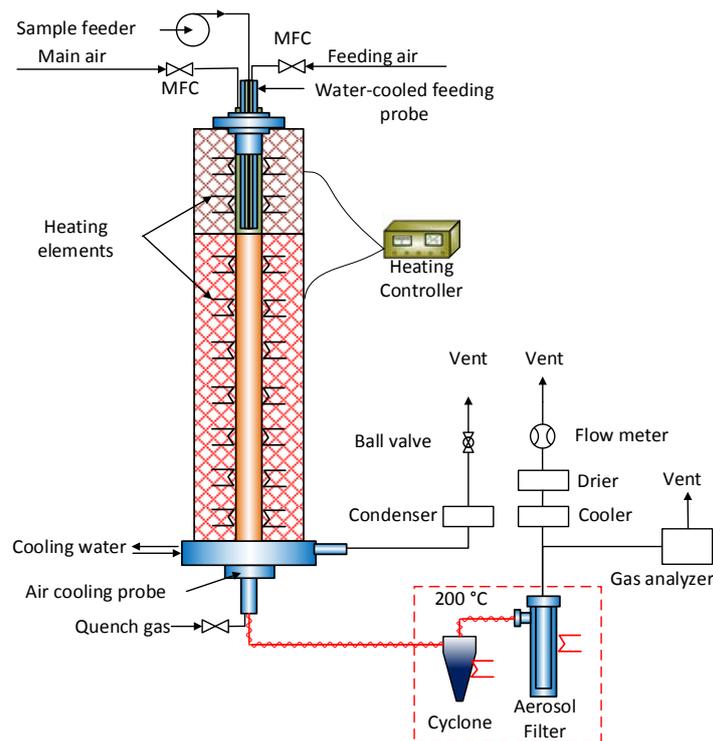


Figure 1. Schematic drawing of the entrained flow reactor.

The solid samples collected from cyclone and filter were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis to get the sample elemental composition. Concentration of water-soluble K, total K and total Cl in products were obtained. The extent of reaction between kaolin and KCl under different conditions (Table 1) was evaluated by the amount of formed water-insoluble potassium.

Table 1. Experimental matrix and conditions.

Run no.	Temp./°C	Gaseous KCl concentration /ppmv	K/Si molar ratio	K/(Al + Si) molar ratio	Gas residence time /s
1#	1300	1021	0.82	0.44	0.78
2#	1100	1019	0.82	0.22	0.89
3#	1300	500	0.41	0.66	0.78
4#	1300	1551	1.23	0.66	0.78

3. Results and discussion

The concentration of water-soluble K, total K and total Cl in samples caught by cyclone and filter were analyzed by ICP-OES. The molar ratios of total Cl to water-soluble K in collected solid samples was calculated and they mostly fell into the range from 0.94 to 1.00 (Figure 2). Only for the 1300°C cyclone sample, the molar ratio is 1.05, slightly higher than 1. This is probably related to analysis uncertainties. The results indicated that more than 94% water-soluble K in reacted products was present in the form of KCl.

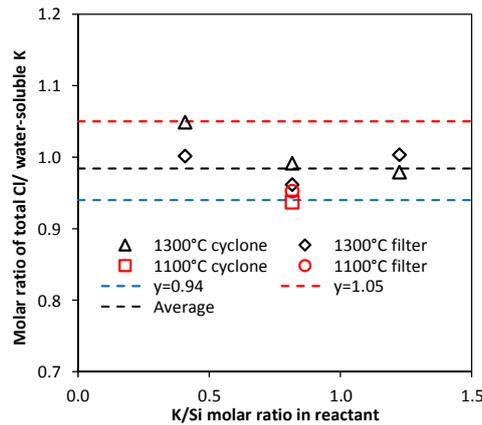
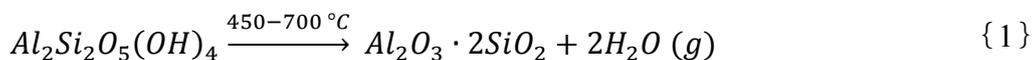
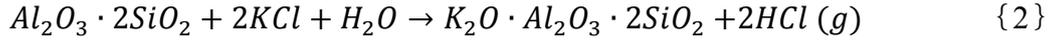


Figure 2. Molar ratio of total Cl to water-soluble K in reacted products.

Water-insoluble K detected in the reacted solid particles was formed by the high temperature reaction between kaolin and KCl. When kaolin is heated above 450 °C, dehydroxylation takes place and a kind of amorphous mixture of alumina and silica called metakaolin is formed (Reaction 1) [6, 11]. In the EFR metakaolin reacted with gaseous KCl and was transferred into water-insoluble K-aluminosilicate, and releasing HCl to gas phase (Reaction 2) [4]. In order to quantify the extent of KCl binding reaction, K-capturing capability by kaolin (C_K) is defined as the mass of K captured by 1 g dry kaolin during the reaction. According to Reactions 1-2, the maximum theoretical K-capturing capability (C_K) by kaolin is 0.30 g K/ 1g kaolin. Similarly, the Cl-reduction capability by kaolin (R_{Cl}) is defined as the mass of Cl reduced by 1 g dry kaolin during the reaction. The maximum theoretical Cl-reduction capability (R_{Cl}) is 0.28 g Cl/ 1g kaolin.





For the actual C_K under different conditions in this study, it is calculated based on the composition of reactant fed into the reactor and the molar ratio of water-insoluble K to total K ($X_{in,K}$) in reacted solid samples (Eq. 1). The Cl-reduction capability of kaolin (R_{Cl}) under different conditions can be calculated similarly.

$$C_K = \frac{m_{KCl} \frac{M_K}{M_K + M_{Cl}} X_{in,K}}{m_{kaolin}} \quad (1)$$

In Equation 1, m_{KCl} is the amount of KCl fed into EFR; m_{kaolin} is the amount of kaolin fed into EFR; M_K and M_{Cl} is the molar mass of K and Cl respectively.

The molar ratio of water-insoluble K to total K ($X_{in,K}$) in reacted solid samples is obtained by:

$$X_{in,K} = \frac{\frac{w_{in,K}}{M_K}}{\frac{w_{tl,K}}{M_K}} = \frac{w_{in,K}}{w_{tl,K}} \times 100\% \quad (2)$$

where $w_{in,K}$ (wt %) is the measured concentration of water-insoluble K, and $w_{tl,K}$ (wt %) is the concentration of total K in reacted solid samples.

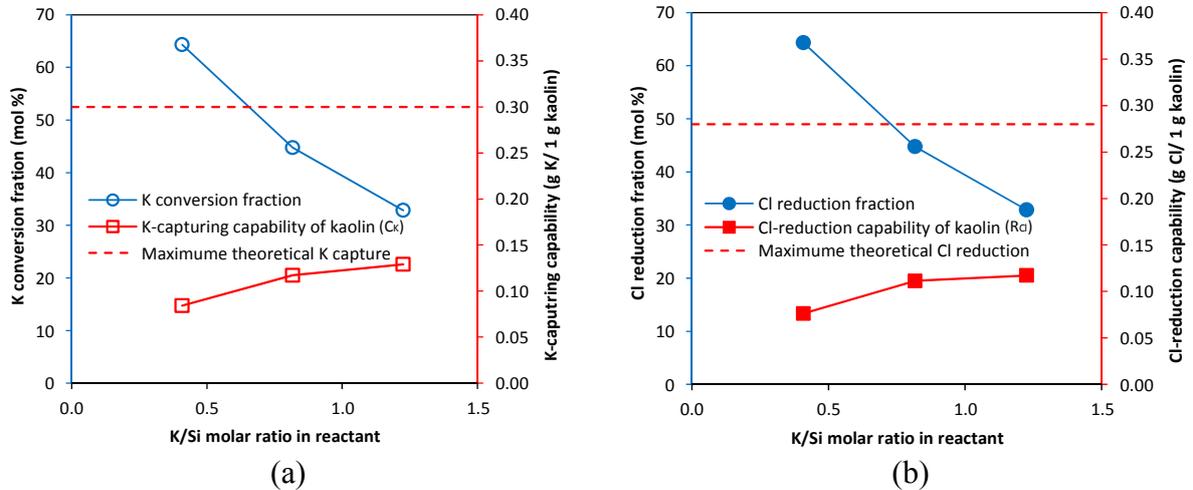


Figure 3. Effect of K/Si molar ratio in reactants on the K conversion fraction and K-capturing capability of kaolin (C_K) (a); Effect of K/Si molar ratio on the Cl reduction fraction and Cl-reduction capability of kaolin (R_{Cl}) (b).

To investigate the influence of molar ratio of K/Si and reaction temperature, experiment was carried out at different conditions as shown in Table 1. The influence of changing K/Si molar ratio in reactant on the conversion fraction of K and the K-capturing capability of kaolin (C_K) is illustrated in Figure 3. With the increase of K/Si molar ratio in reactants, the conversion fraction of K decreased from 64% to about 33%, simply because more KCl stayed unreacted, and was therefore present in the collected products. The K-capturing capability of kaolin (C_K) was in the range of 0.08 - 0.13 g K/ 1 g kaolin under the conditions investigated, which is obviously lower than the maximum theoretical K-capturing capability of 0.30 g K/ 1 g kaolin,

indicating that more than half of the metakaolin collected from the experiment stayed unreacted. Similar trends were observed for the reduction of Cl.

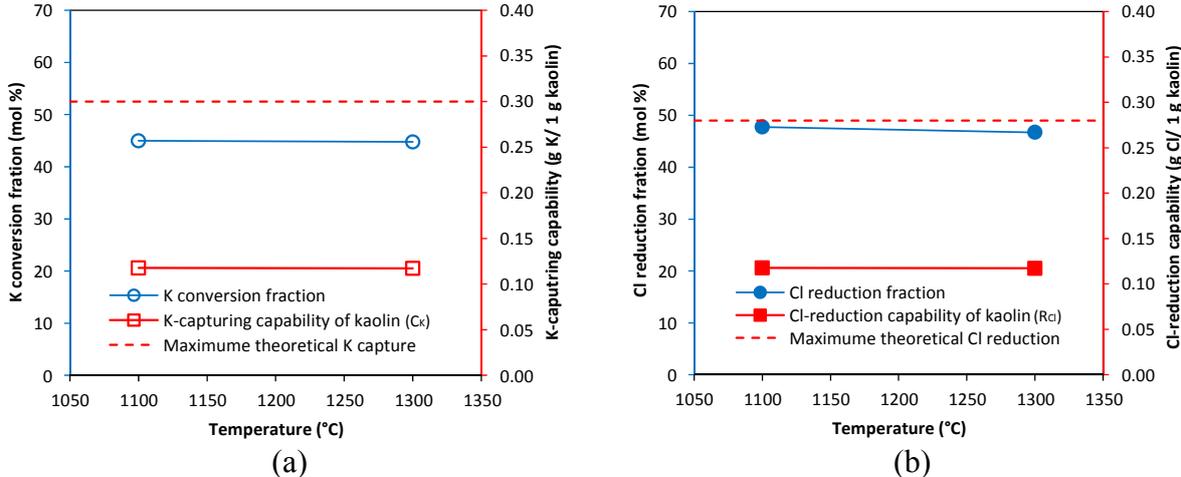


Figure 4. Effect of reaction temperature on the K conversion fraction and K-capturing capability of kaolin (C_K) (a); Effect of reaction temperature on the Cl reduction fraction and Cl-reduction capability of kaolin (R_{Cl}) (b).

The results of experiment conducted at 1100°C and 1300°C is shown in Figure 4. There is no obvious impact of changing temperature on the extent of reaction, which is significantly different from previous fixed-bed results[6], where less KCl was captured at 1300 °C than at 1100 °C due to the formation of less active mullite at higher temperature. One probable reason for the difference is that the residence time of additive in the reactor is too short for metakaolin to transfer into mullite in the entrained flow reactor[6].

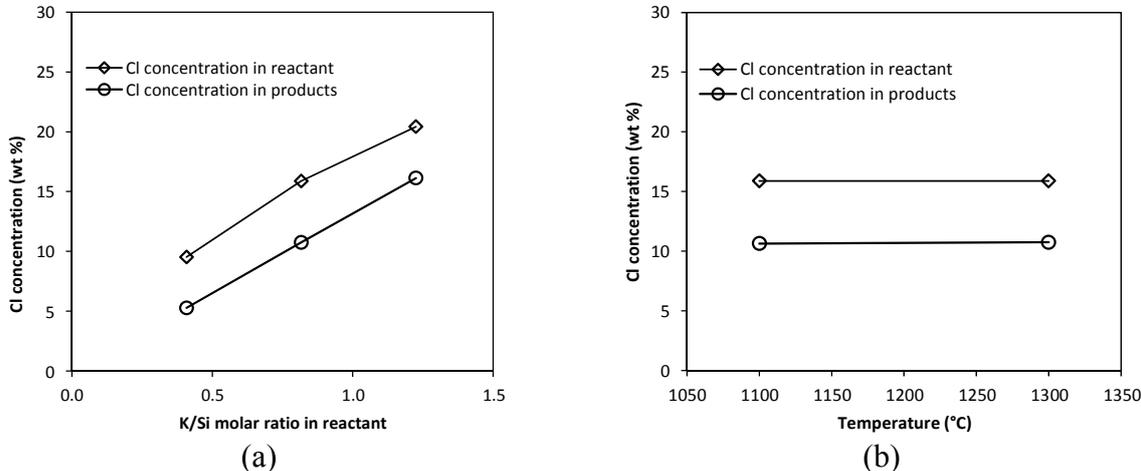


Figure 5. Cl concentration in reactants and in reacted products.

In biomass combustion, Cl is the most corrosive element, and the Cl concentration in ash deposit affects the corrosion rate of metal heat transfer surfaces. The Cl concentration in reactants and in reacted products are shown in Figure 5, and the Cl concentration decreased obviously in products comparing to that in corresponded reactants.

4. Conclusion

A method of simulating the reaction of capturing gaseous KCl by solid sorbents at suspension fired conditions was developed using an entrained flow reactor (EFR). Kaolin was employed

in the primary tests of this method. The results showed that addition of kaolin can effectively capture corrosive gaseous KCl. K-capturing capability by kaolin rose when increasing molar ratio of K/Si in reactant. The KCl capturing behavior of kaolin in entrained flow reactor was different comparing to that in fixed-bed reactor when changing reaction temperature, and one possible reason is the shorter residence time in the EFR. The develop method using the EFR in this study will be used for further systematic quantitative investigation of different solid additives.

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