SHORT REPORT

Experimental study on the effect of fly ash on the combustion characteristics of rice husk in a one-dimensional furnace

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Biomass, as a substitute of conventional fossil fuels, can greatly alleviate the energy crisis. However, alkali metals and alkaline earth metals rich in biomass will cause problems such as ash deposition and slagging combustion, which seriously affect the continuous and stable operation of boilers and other equipment. In this study, combustion experiments using biomass rice husks as fuel and fly ash as additive on the 30 KW one-dimensional furnace was carried out to analyze the influence of mixed proportions of fly ash on alkali metal migration and occurrence, ash deposition, and slagging in biomass rice husk combustion. The ash collected during rice husk combustion was observed macroscopically, analyzed by electron microscope, scanning electron microscope, and X-ray diffraction. The results showed that, when rice husk and fly ash were burned at the ratio of 2:1 and 1.5:1, the ash deposit had obvious stratification, the structure became loose, the particle size of the slag body became significantly smaller, and the degree of adhesion decreased. High melting point potassium- aluminum-silicon (K-Al-Si) composite salts were generated in the ash deposit. In the high temperature area, Al_2O_3 in the fly ash could form high melting point aluminosilicate with alkali metals and SiO_2, which played the role in solidification of alkali metals. However, the K content in the probe ash deposit in the low temperature area was also reduced. It was concluded that the mixture of biomass rice husk with fly ash reduced ash deposition and slagging in rice husk combustion, and inhibited corrosion to the boiler.

Keywords: one-dimensional furnace; fly ash; rice husk combustion; scanning electron microscope; X-ray diffraction.

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Introduction

Biomass is a renewable and clean energy. The amount of biomass energy generated by vegetation through photosynthesis every year is almost 5-8 times of the annual energy consumption on the earth [1]. Under the current global energy crisis, biomass energy has been included in the new energy development plan of various countries. There is a large content of alkaline ash forming substances in biomass fuel such as potassium (K), sodium (Na), and mineral elements such as silicon (Si), chlorine (Cl), sulfur (S) [2], which will undergo a series of physical and chemical reactions, generate low melting point compounds or eutectic, and deposit on the surface of boiler heat exchanger to form ash [3]. Ash deposition will increase thermal resistance and reduce efficiency of the boiler [4], and even worse, it may lead to shut down the boiler and cause great economic losses [5]. In the worst case, severe ash deposition may cause serious accidents and affect the operation of the boiler during combustion [6]. In addition, alkali metals and chlorine elements in the ash will also cause corrosion on the surface of the heat exchanger at high temperature. Ash deposition and corrosion are hindering the development of biomass combustion technology [7].

At present, solutions to ash deposition and slagging biomass combustion mainly include mixed combustion, adding additives, pre-treatment of fuel such as water washing, pickling, *etc*., improvement of heating surface materials, and adjustment of boiler operating parameters such as temperature, excess air coefficient, *etc*. [8]. Among them, adding additives is a common method in industry. Some elements in the additives firstly react with alkali metal elements in biomass to form high melting point compounds to alleviate or solve ash deposition and slagging caused by alkali metal elements [9]. Different active components of additives are divided into phosphorus rich additives, aluminosilicate additives, sulfur-based additives, calcium-based additives, and composite additives [10].

Fly ash is a kind of aluminosilicate additive with rich reserves and low price [11]. It is a solid industrial waste [12]. According to the statistics, the reserves of fly ash in China exceeds 3 billion tons, which ensures the continuous supply of fly ash to biomass-fired power plants. Fly ash is rich in SiO_2 (23.1 - 62.4% by mass) and Al_2O_3 (17.8 - 30% by mass), as well as a small amount of CaO, MgO, TiO_2, *etc*. Al_2O_3 and CaO have been proved to be effective in mitigating ash deposition, slagging, and corrosion during biomass combustion [10, 13]. Clery, *et al*. studied the effect of aluminosilicate additive of fly ash on potassium in biomass combustion, which was directly related to the ratio of K / Cl and K / (Si + Al) [14]. High Cl and low (Si + Al) helped to release KCl or KOH into the gas phase, while high (Si + Al) helped to retain K in the ash. The results showed that aluminosilicate additive could retain a high proportion of potassium in ash. Corona, *et al*. found that the addition of fly ash to waste firewood could minimize ash deposition and slagging in firewood combustion and reduced the operating cost of the power plant while reducing CO_2 emissions [15]. Wang, *et al*. analyzed the capture capacity of fly ash to alkali metal K and found that the addition of fly ash significantly inhibited the formation of aerosols, and the adsorption effect of fly ash on KOH and K_2CO_3 was better than that of KCl and K_2SO_4 [16]. In addition, fly ash with high Si content and low melting point could capture KCl more effectively. In this study, the combustion experiment with biomass rice husk as fuel and fly ash as additive was carried out on the one-dimensional furnace experimental platform. The objectives of this study were to investigate the influence mechanism of mixed proportions of fly ash on alkali metal migration, occurrence, ash deposition, and slagging in combustion; to propose effective methods to prevent ash deposition and slagging; to reduce the contamination and corrosion of heating surfaces of boilers and other equipment. The results of this study would provide technical reference for large-scale utilization of biomass combustion for power generation.

Materials and methods

30 KW one-dimensional combustion furnace

The 30 KW one-dimensional combustion furnace used in this study is manufactured by Shanghai Energy Key Technology Co., Ltd. (Shanghai, China). It is composed of furnace body, burner, powder feeder, air intake system, flue gas system, and control system. The one-dimensional furnace body structure is divided into four sections including ignition chamber (top section), combustion chambers (second and third sections), and burnout chamber (forth section). Each section is connected by flanges. Eight temperature sensors and four pressure measuring points are evenly distributed on the furnace. The system diagram of one-dimensional furnace test bench was shown in Figure 1.

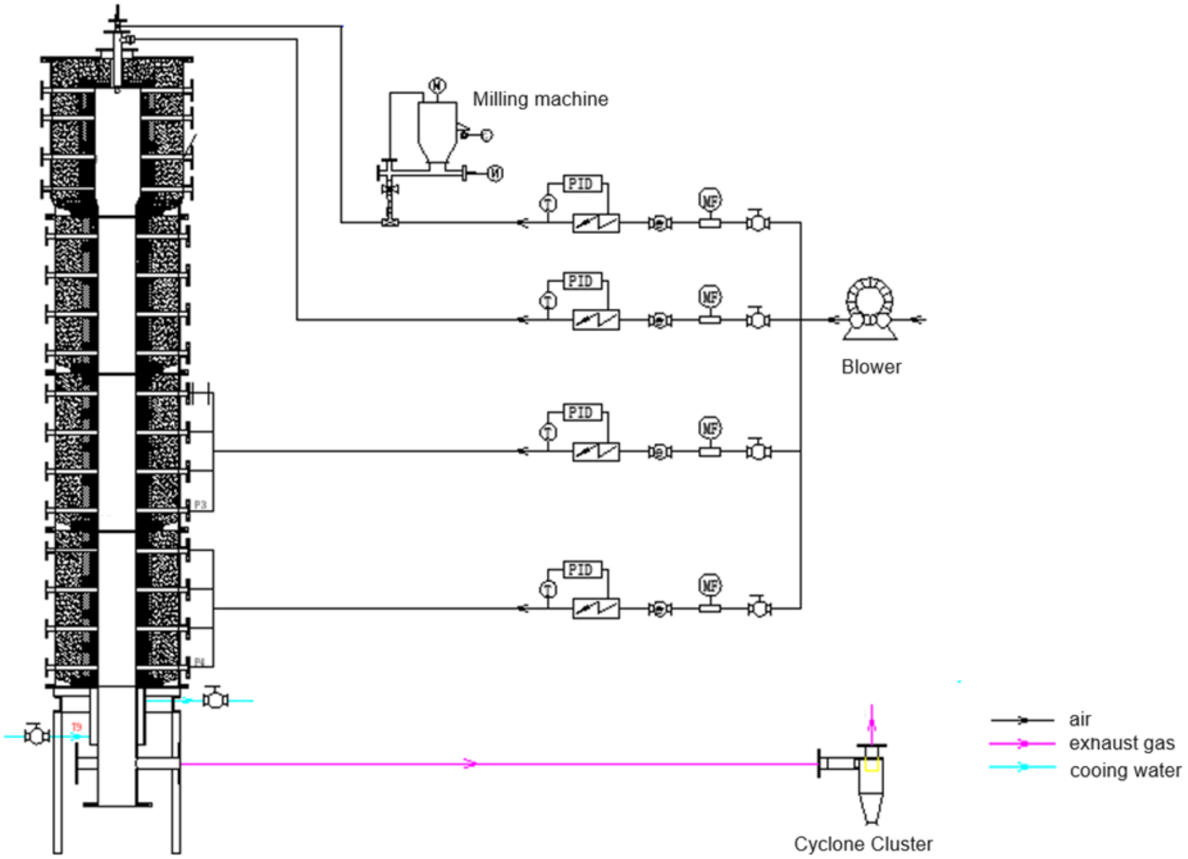


Figure 1. System diagram of one-dimensional furnace test bench.

Biomass fuel was sent into the furnace at a speed of 4.65 kg/h through the conveyor. The primary and secondary airs were heated to 200°C and 350°C, respectively, through the electric heater. Under this condition, the temperature of the combustion flame zone could reach 1,000 – 1,200°C. Along the axis of the furnace, four probe sampling holes were set down from the burner. The direction of probe insertion was perpendicular to the flue gas direction. When the temperature in the furnace raised and the temperature on the probe surface was higher than the melting point of the ash slag, the slagging attached to the probe surface began to melt. The ash particles in the flue gas fell on the probe surface under the action of air flow and gravity, and sticked to the upper layer of the molten slagging, and eventually being taken out for analysis.

The analysis of biomass fuel characteristics

The rice husks used in the experiment were obtained from Lianyungang, Jiangsu Province, China. The coal ash additive was the product of lignite combustion in Benxi coal-fired power plant (Benxi, Liaoning, China). The combustion of biomass was roughly divided into three stages as water release, volatilization analysis, and fixed carbon oxidation. The combustion characteristics of biomass rice husk were obtained by industrial analysis and element analysis. The industrial analysis of biomass refers to the general terms for the determination of four items including moisture (M), ash (A), volatile (V), and fixed carbon (FC) of fuel. The industrial analysis standard was determined by the Industrial Analysis Method for Solid Biomass Fuels (GB/T212-2008). As the analysis reference, the sample air-drying (ad) basis was determined by the fuel sample with external moisture removed

Table 1. Proximate analysis and ultimate analysis of biomass samples.

Industrial Analysis (%)				Elemental analysis (%)				
M_{ad}	A_{ad}	FC_{ad}	V_{ad}	C	H	O	N	S
8.48	16.62	14.92	59.98	35.34	5.37	41.59	0.95	0.13

Note: air-drying basis moisture (M_{ad}), ash (A_{ad}), volatile (V_{ad}), and fixed carbon (FC_{ad}).

by natural drying method, which included moisture (M_{ad}), ash (A_{ad}), volatile (V_{ad}), and fixed carbon (FC_{ad}) of the sample. The element analysis was to determine the element composition in biomass. The content of C, H, O, N, and S in biomass was determined by using Vario EL cube analyzer (Elementar, Langenselbold, Hesse, Germany) with the analysis accuracy of 0.1%.

Experiment design and analysis of ash after combustion

Three stages including sample pretreatment, one-dimensional furnace combustion, ash and slag detection and analysis were examined in this study. The fly ash and rice husk powder were fully mixed and sent into the furnace for combustion through the feeder. After combustion, the ash samples were collected for morphology analysis, particle size, and void analysis, and crystal phase analysis to explore the influence of adding different proportions of fly ash on the ash deposition after rice husk combustion, the optimal proportion of fly ash, temperature, and the morphology of ash deposition, and then, the mechanism of fly ash to mitigate the ash deposition generated by material combustion.

Macroscopically comparing the color, pore size, and density of ash and slag, and microscopically analyzing the particle size and phase composition of biomass were performed to find out the occurrence rule of alkali metals. The macro morphology of the ash deposited samples was studied by using Aniti 3R-MSTVUSB82D optical electron microscope (3R Eddytek, Beijing, China). The impact of fly ash on the loose degree of ash deposited after biomass combustion and the size of air gap were then analyzed. The ordered and proportional surface images of the dusty sample were converted into video signals by using ZEISS EVO 18 scanning electron microscope (Zeiss, Oberkochen, Germany) with the point-by-point imaging method for the observation of the different features on the sample surface. The composition of the ash samples was analyzed by using Bruker D8 ADVANCE x-ray diffractometer (XRD) (Bruker, Billerica, MA, USA). The diffraction pattern was smoothed by MDI Jade 5.0 software package (Materials Data, Inc, Livermore, California, USA). After peak searching and matching, the ash sample composition was qualitatively obtained. Shimadzu XRF-1800 x-ray fluorescence (XRF) spectrometer (Shimadzu, Nakagyō-ku, Kyoto, Japan) was employed to determine the type of fly ash elements.

Results and discussion

Sample analysis

The analysis results of biomass rice husk were shown in Table 1. The volatile matter contained in rice husk accounted for 59.98%, making rice husk fuel easier to ignite comparing to fossil fuels like coal. However, the fixed carbon content of rice husk was lower than 15%, indicating that a low combustion heat value. In the element analysis of biomass, the contents of C and O were high, while the contents of N and S were low, indicating that the nitrogen and sulfide produced during rice husk combustion were low, which was conducive to cutting the emissions of NOx and SOx in industrial application and protecting the ecological environment. The morphology of fly ash was shown in figure 2. The fly ash was spherical ash particle. Some parts of the sphere surface were smooth while the other parts showed convex binders. The distribution of particles was irregular and relatively dispersed. Some spheres were agglomerated or existed as

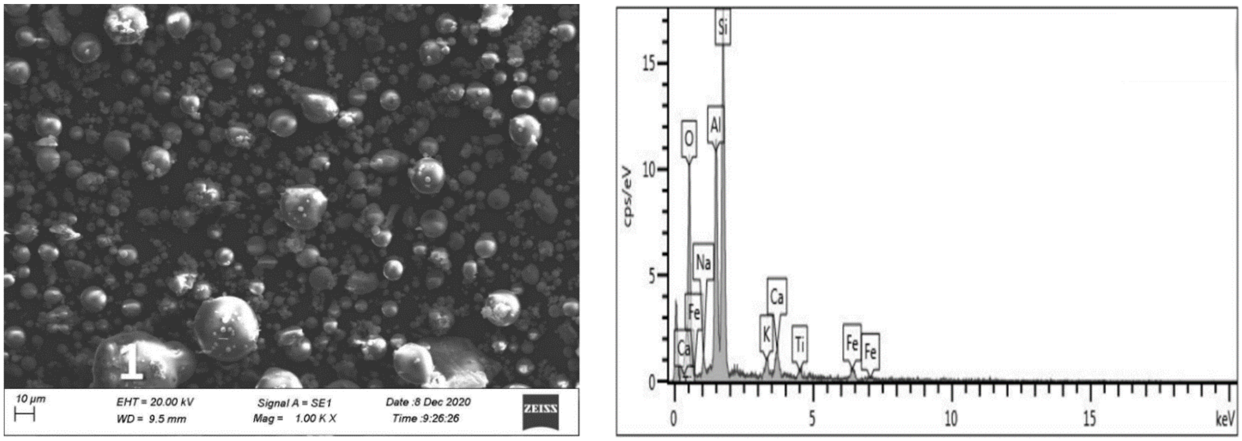


Figure 2. SEM image of Fly Ash. Point 1 (left image): the analysis point for components.

Table 2. XRF analysis of fly ash additives.

SiO_2	Al_2O_3	CaO	Fe_2O_3	Na_2O	MgO	K_2O	P_2O_5	SO_3
64.58%	19.41%	6.43%	4.71%	0.16%	0.72%	1.96%	0.64%	0.39%

monomers. The fly ash particles contained a large amount of Al, Si, O, and a small amount of Fe, Ca, K. (Figure 2, point 1).

The compositional proportion of main elements in the fly ash was obtained by using XRF (Table 2). The majority of fly ash components were SiO_2 and Al_2O_3 with the contents of 64.58% and 19.41%, respectively. Because SiO_2 and Al_2O_3 will react with alkali metals in biomass to generate K-Al-Si composite salts, the melting point of aluminosilicate is usually high. Therefore, the fly ash as an additive makes the ash after combustion difficult to agglomerate.

Macro morphology analysis of ash deposits

The ash sample after burning the rice husk alone showed that the sample was black, hard and brittle, and had adhesion to the probe surface. The sample demonstrated obvious sintering phenomenon and was hard to clean with a brush (Figure 3A). However, the ash deposited sample after burning rice husk and fly ash at a mixing ratio of 1.5:1 showed that, after adding fly ash, the surface of the sample was uneven with obvious stratification. The amount of slag formation was significantly reduced and loose. It had less hardness and easily being separated from the surface of the probe, which indicated that adding a certain amount of fly ash additive could effectively alleviate the ash deposit and slag formation during rice husk combustion (Figure 3B).

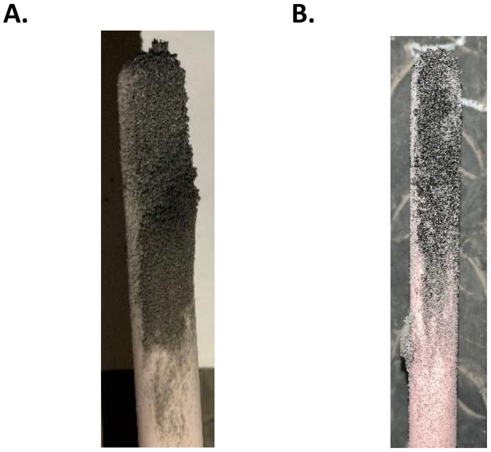


Figure 3. The macro morphology of ash samples collected by deposition probes under different working conditions after rice husk and fly ash were stably burned for 30 minutes in a one-dimensional furnace at 850°C. **A.** ash sample after burning rice husk alone. **B.** ash sample after burning rice husk and fly ash in a ratio of 1.5:1.

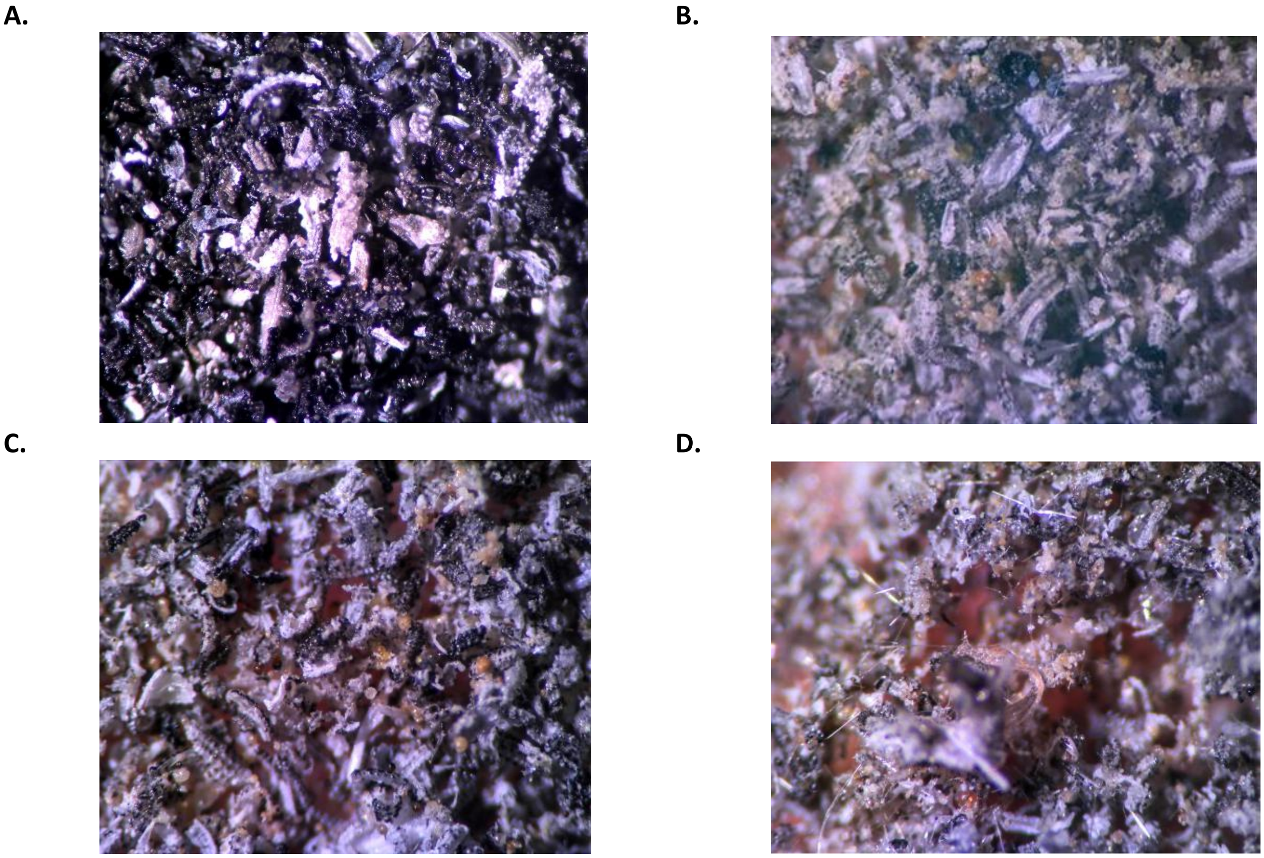


Figure 4. The structure of after burning ash sample under electron microscope (130×). **A.** rice husk alone. **B.** rice husk and fly ash (1:1). **C.** rice husk and fly ash (2:1). **D.** rice husk and fly ash (1.5:1).

Microstructure analysis of ash deposits

The structure of the ash sample after mixed combustion of rice husk and fly ash was observed under electron microscope (130×) (Figure 4). The structure of the ash sample after burning rice husk demonstrated a large number of boned black particles. The pores were very small, and the structure was dense. The slagging phenomenon was caused by the adhesion of unburned fixed carbon (Figure 4A). When the mixing ratio of rice husk and fly ash was 1:1, the fly ash particles were embedded between the slag bodies, and the pores between the slag bodies were increased (Figure 4B). The structure of the ash sample at the mixing ratio of 2:1 was shown in Figure 4C. A three-dimensional framework was formed between the slag bodies. The slag became brittle, and the bonding degree was decreased after adding fly ash when the ash sample was moved by using tweezers. When the addition ratio of fly ash was 1.5:1, the particle size of the slag body became significantly small with loose structure (Figure 4D). Through the comparison of fly ash addition in different proportions, it was concluded that the ratio of 1.5:1 could better alleviate the slagging caused by rice husk combustion.

SEM analysis of ash deposits

The SEM images of ash samples after mixed combustion of rice husk and fly ash in different proportions were shown in Figure 5. When the mixing ratio of rice husk powder and fly ash was 1:1, many spherical ash particles were observed. Some of these spherical ash particles were silica crystals produced in the combustion, while some particles did not participate in the reaction. A spherical particle with uneven surface was shown in labeled area 1 (Figure 5A). According to the energy dispersive x-ray (EDX) composition

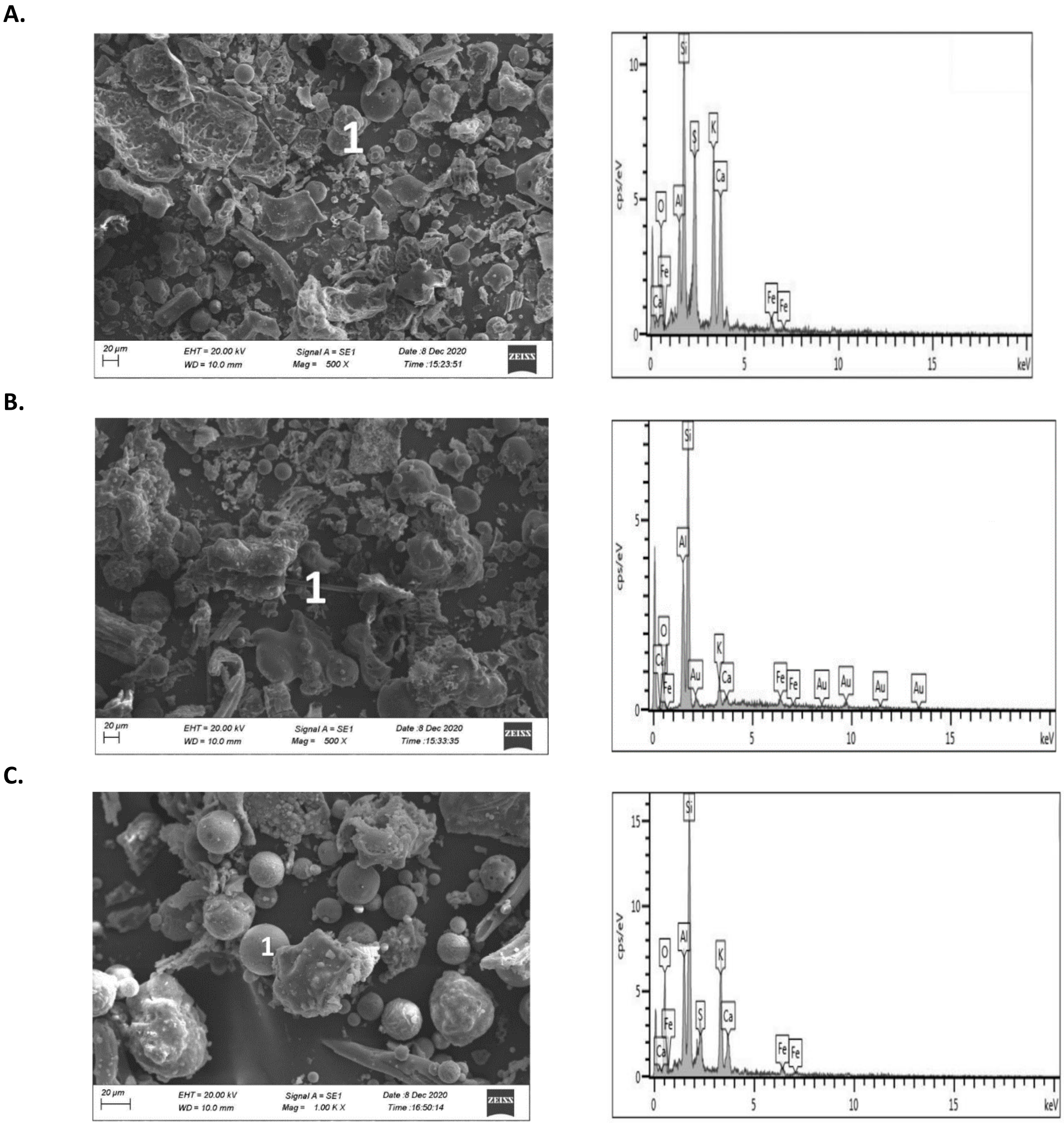


Figure 5. SEM images of ash sample after mixed combustion of rice husk and fly ash in different proportions (**A:** 1:1, **B:** 2:1, **C:** 1.5:1).

analysis, the contents of Si, K, Al, Ca, and S were very high, while the content of Fe was low. Comparing to the labeled area 1, the content of K element in the fly ash sphere was low. It could be concluded that the sphere was a K-Al-Si and K-Ca-Si composite salt produced in the reaction of rice husk powder and fly ash [15]. Meanwhile, silicate with low melting point might be formed. There were more ash particles in the molten state at 1:1 mixture comparing to the original rice husk combustion, and the ash particles in the flue gas were adsorbed on the surface, which aggravated the slagging corrosion of rice husk powder combustion. Figure 5B demonstrated the ash formed by 2:1 mixture of rice husk powder and fly ash. A great difference in the spherical ash particles was observed. In general, the number of spherical ash particles was decreased significantly, and the number of irregular massive and fragmented ash particles was increased. The labeled area 1 showed a strip crystal. From the element composition of EDX, the contents of Si, Al, and K were very high, followed by O and Ca. The results confirmed that the compounds in the labeled area 1 were mainly K-Al-Si composite salts. The result of 1.5:1 mixture ratio was shown in Figure 5C. Some sphere ash particles were embedded between the massive slag bodies, while some existed in the form of spheres. There were still holes on the surface. The distance between slag bodies was large, which reflected the effect of fly ash in increasing porosity. By comparing the SEM images of three groups at different mixing ratios, the materials produced in the reaction of fly ash and rice husk powder were mainly K-Al-Si and K-Ca-Si composite salts with high melting points, which were mainly spherical and filamentous ash particles. When mixture was at 1:1, the low melting point silicate was generated, which increased the slagging of rice husk powder combustion, while mixing ratios of 2:1 and 1.5:1 alleviated slagging corrosion to some extents.

XRD phase analysis of ash deposits

The ash samples collected under different working conditions were analyzed. The X-ray wavelength was 0.15405 nm with the scanning rate of 4°/min and the scanning range of $10° \leq 2\theta \leq 90°$. Figure 6 demonstrated the XRD patterns of the ash samples after the rice husk was burned alone. In the XRD spectrum, the SiO_2 peak intensity was large, and there were also widely distributed Ca_2SiO_4, CaO, and K_2SO_4 observed. These crystal compounds were the main causes for the ash deposition and slagging of rice husk combustion. It was concluded that Si-rich rice husk was oxidized to SiO_2 and reacted with alkaline earth metals to form Ca_2SiO_4. The formation of CaO was due to the oxidation of Ca in rice husk. The content of K in rice husk was low. During heating, K was mainly released into the gas phase in the form of KOH, then reacted with SO_2, O_2, and H_2O to produce K_2SO_4. Three working conditions were tested for the comparative studies of the influence of fly ash on the ash deposition and slagging of rice husk combustion.

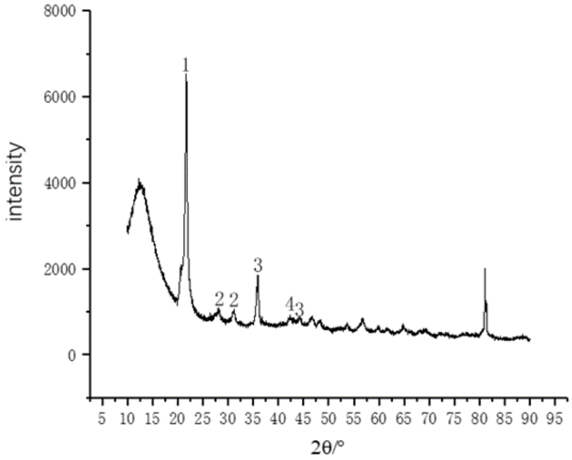
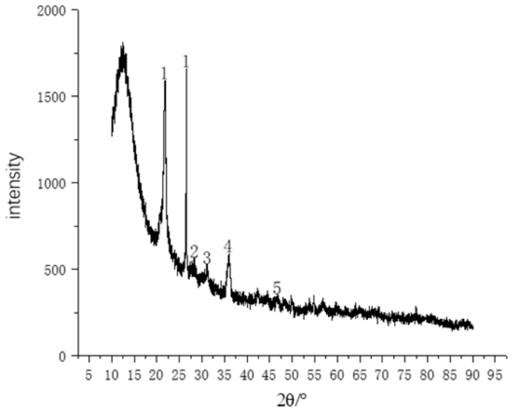


Figure 6. XRD patterns of ash samples after rice husk combustion alone (**1:** SiO_2. **2:** Ca_2SiO_4. **3:** CaO. **4:** K_2SO_4).

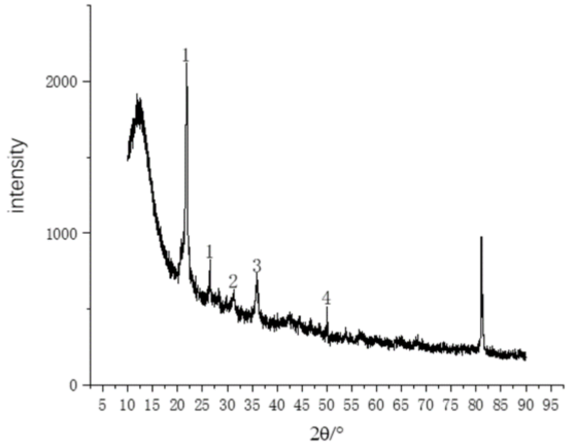
Figure 7 showed the XRD patterns of ash samples after burning rice husk and fly ash in 1:1, 2:1, and 1.5:1 ratio, respectively. After adding fly ash in the burning, $KAlSiO_6$, $MgAl_2Si_3O_{10}$, and other compounds were generated in the ash sample, which were typical composite salts of high melting points, indicating that fly ash could fix alkali metals and alkaline earth metals in the bottom ash, and generate compounds of high melting point. In addition, the addition of fly ash made the ash forming a refractory compound $MgAl_2O_4$ with high melting point, which could reduce the viscosity between ash particles, effectively alleviate melting and agglomeration, and reduce ash deposition and slagging.

A.



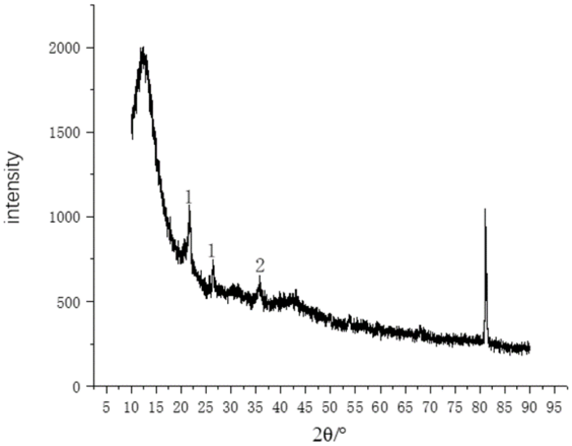
1: SiO_2. **2:** $KAlSiO_6$. **3:** K_2SO_4. **4:** KCl. **5:** $MgAl_2O_4$.

B.



1: SiO_2. **2:** K_2O. **3:** $KAlSiO_6$. **4:** Ca_2SiO_4.

C.



1: SiO_2. **2:** $MgAl_2Si_3O_{10}$.

Figure 7. XRD patterns of ash samples after burning rice husk and fly ash in 1:1 (A), 2:1 (B), and 1.5:1 (C) ratios.

Conclusion

During one-dimensional rice husk combustion, mixing a certain proportion of fly ash made the ash deposit obviously stratified, the particle size of the slag body obviously small, and the structure loose. When the rice husk and fly ash ratio was 2:1 or 1.5:1, both the amount of slag and the degree of adhesion decreased. In the high temperature zone, Al_2O_3 in the fly ash could form aluminosilicate of high melting point with alkali metal and SiO_2, which played a role in solidifying alkali metals, while the K content in the ash of the low temperature zone also decreased. Si, Al, Ca, and other elements in the fly ash reacted with the alkali metal in the rice husk to form K-Al-Si and other composite salts of high melting point, which fixed the K element in the bottom ash, and eased the ash deposition and slagging in the biomass combustion.

Acknowledgments

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