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New insight to migration and influence of potassium element on combustion of coal/biomass char-slag interface



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ABSTRACT

Co-combustion of biomass and coal can both support heat requirement of a boiler and reduce carbon emission while the high contents of alkali metals (e.g. Na, K) in ash are key factors in the stable operation. In this study, the migration behavior and influence of K on the combustion of coal/biomass char particles on the slag surface were investigated with visualization experiments and surface analytical techniques. The results showed that the addition of K in the slag can accelerate the combustion process of coal char particles on the slag surface, which proved that K⁺ was not deactivated as ionic state in the slag. The promotion effect of potassium was mainly reflected in accelerating the combustion rate at the beginning stage, where the carbon conversion was below 0.2, compared to the resting stage. K was proved to migrate from the slag side to the interface of char particles and slag and aggregated with Al during the combustion process, while other elements were enriched on the slag surface outside the combustion zone. Results also showed that the combustion of biomass char particles (rice straw char) on the slag surface with less K was inhibited. However, K was found to aggregate on the interface of biomass char and slag throughout the combustion process with no diffusion. A migration mechanism was proposed that the combustion of char particles on the slag surface caused an increasing temperature and further depolymerization of aluminosilicates, with alumina replacing silicon to form aluminum tetrahedra while adsorbing K⁺ to the interface and promote the combustion.

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1. Introduction

With the energy transition extending worldwide, governments and institutions are implementing carbon reduction actions, including but not limited to carbon capture, utilization, and storage (CCUS) and replacement of combustion material, such as biomass and ammonia [1–3]. Co-combustion technology of coal and biomass is a key pathway to achieving carbon neutrality, which has been widely used to reduce coal consumption and carbon emissions [4,5] Nevertheless, due to some natural properties of biomass resources, such as low heating value and relatively high content of alkali metals (e.g. K and Na), some issues need to be solved when biomass is used in the co-combustion technology. Alkali metals will reduce the melting temperature of ashes and transfer ash to liquid slag on the heat transfer surface. Ash-related issues, such as fouling, slagging, sticky particle agglomeration, and

* Corresponding authors. E-mail addresses: zjshen@ecust.edu.cn (Z. Shen), hfliu@ecust.edu.cn (H. Liu). particulate matter aggregation, etc. directly increase the deposition possibility of ash particles and thermal resistance on the heat transfer surface [6,7].

Ash deposition is considered a serious concern in stationary power plants burning solid fuels [8], especially for biomass combustion [4]. Volatile fly ash (fine ash) and non-volatile burnt ash (coarse ash) after combustion of coal or biomass performed different properties [9]. Researchers found that the coarse ash mainly contained silicates and was melted at high temperatures, and further encapsulated carbonaceous particles to impede the combustion process [10]. Fly ash particles consisted of volatile alkali metal compounds and were easily carried by flue gas to reach the heat transfer surface, owing to the depolymerization of alkali metal elements on ash structure [11]. In a coal or biomass combustor, the flame temperature was commonly higher than the ash fusion temperature. Thus, at high temperatures (above ash fusion temperature), fly ash particles were melted to form a liquid surface on the furnace wall. Studies showed that the molten slag surface captured fly ash particles and formed high-temperature coalescing de-

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posits, resulting in a high alkali metal content on the melted surface or inside the slag [12–14]. Liu et al. [6] found that the high alkali coal ash or slag was subject to multiple controls of inertia, thermophoresis, and impact effects during combustion. The tendency of ash and slag depositions increased with the increasing bed temperature, and the melting or partial melting behaviors were caused by Na-Fe-Ca eutectic. Ni et al. [15] developed a submodel to predict the deposition of molten particles in the liquid slag discharge of a combustion chamber. The results showed that the deposition rate of large-size slag particles was higher than that of small-size particles, and the deposition rate increased with the increasing temperature. Alkali metals in the slag at high temperatures would react with silicates, iron, and magnesium oxides to form low-temperature eutectics [16]. Low melting point minerals were melted to the molten state, of which the liquid surface captured unreacted carbon particles, and this stage seriously hindered the further conversion of deposited particles [17,18]. In addition, the slag adhered to the wall increased the heat transfer resistance and reduced the overall heat transfer efficiency.

Ash particles deposited on the liquid slag layer also affected chemical and physical properties, including melting point, viscosity, and crystallization behaviors [19,20]. Wei et al. [12] found that S-bearing compounds in the ash decomposed and ashes containing Na, Ca, and Fe have different slagging mechanisms. Li et al. [6] found that the transformation of minerals, especially K-bearing minerals, and carbon composition were key factors for influencing the ash fouling and slagging behaviors, which in turn directly affects the particle surface viscosity within the slag phase. The formation of liquid slag on the heat transfer wall increased the deposition possibility of coal or biomass particles. The deposition of unburnt carbon particles would cover a layer on the liquid slag surface and further continue to burn [21]. At this condition, some minerals were proved to have a catalytic effect on the combustion of coal particles [22], which can significantly reduce the activation energy of combustion. On the contrary, the presence of residual carbon in the ash or slag promoted the crystallization behavior and increased the slag viscosity [23]. Therefore, a study of deposited unburnt particles and the interaction with slag components particularly for alkali and alkaline earth metals (AAEMs) is essential to improve the conversion of coal particles in the furnace and to gain insight into the coal to ash or slag behaviors.

AAEMs in coal or biomass resources were found to have synergistic effects on combustion and ash melting properties. [24,25]. Meanwhile, with the widespread use of biomass in combustion, the effect of the high content of alkali metals in biomass on cocombustion received attention [26]. Among these AAEMs, the migration and transformation of potassium element were more active while attentions were on particle combustion. Research showed that about 60 to 90% K was released as a K⁺ state during combustion above 1000 °C and was condensed in the fly ash surface of the boiler wall and formed a sticky deposit layer [27-29]. Jones et al. [30] concluded that potassium can maintain the coal char structure during combustion and thus accelerate the combustion process. Similar conclusions were reached in a study by Deng [31], K promoted a release of volatiles and carbon oxidation as a catalytic effect while obtaining the optimum loading concentration of K₂CO₃ at 5 wt.% for oxy-biomass combustion. While the catalytic ability of K was superior to other AAEMs, it was generally believed that the catalytic ability of K was deactivated at high temperatures, attributing to the formation of insoluble potassium silicaaluminates [32]. However, recent studies have found that the addition of K to the slag was beneficial for the interfacial gasification process of coal char particles. K was not deactivated in an ironic state in the coal slag. The reaction rate of coal char was significantly accelerated and a large number of pores appeared on the particle surface, confirming the promotion of K on the gasification [33]. However, the migration and influence of potassium on the combustion of coal char or biomass char particles on the molten slag surface are seldom in the literature.

In this study, the effects of K and its content in the liquid slag on the combustion characteristics of coal char and biomass char particles on the molten slag surface were investigated by using a high-temperature visual in-situ experimental technique. The carbon conversion of deposited coal char and biomass char particles were calculated and compared. The elemental distribution of AAEMs, especially K, on the char-slag interface was also analyzed. The migration patterns of AAEMs on the interface were determined for both coal char and biomass char combustion. Raman spectroscopy was used to determine the mineral phase that K reacted with other compounds. Meanwhile, with experimental and theoretical analyses, a mechanism of K element in the slag was proposed to reveal the specific combustion and element migration behavior.

2. Materials and methods

2.1. Materials

Samples used in this study were Shenfu bituminous coal char (SF char) and rice straw char (RS char), which were prepared from Shenfu bituminous coal (Shanxi, China) and rice straw (Zhejiang, China) through a pyrolysis experiment in a drop tube furnace at 1350°C under an argon atmosphere. During the pyrolysis process, the feeding rate of solid fuel was about 200 g/h and the flow rate of the carrier gas was set to 1.2 L/min. The particle size of the char sample was chosen as 100 \sim 150 μ m. The proximate analysis and ultimate analysis were tested and the results were given in Table 1. Element contents of the RS char sample were measured via an inductively coupled plasma-optical emission spectroscopy (ICP-OES, Thermo Fisher, America). Compared to SF char, RS char has higher volatile matter and lower carbon content. Meanwhile, the alkali metal content in SF coal char is lower than that of RS char, with potassium exhibiting the most significant difference.

During the co-combustion of coal and biomass, researchers have proved that K released as a K⁺ state during combustion above 1000 °C and was condensed in the fly ash surface of the boiler wall and formed a sticky deposit layer [28,29,34]. Co-combustion of biomass with coal can effectively reduce coal consumption and reduce CO₂ emissions, while ensuring the required calorific value. However, there are issues with increasing the mixing content of biomass. There are more alkali metals K and Na in biomass than in coal, causing issues such as fouling and slagging. Therefore, to keep the heat supply, the current biomass addition amount in the co-combustion process of biomass and coal is about $5{\sim}10\%$, which shows that the main composition of ash comes from the coal resource. Based on a comprehensive consideration of operating temperature, combustion efficiency, and corrosion damage, the co-combustion level is expected to be controlled below 20% afterward [3,35]. Hence, the main ash resource in the industry is form the coal combustion, particularly in the deposited ash on the furnace wall. Accordingly, this study used coal ash as the main deposition layer. Meanwhile, to evaluate the impact of potassium on combustion and mobility at the char-slag interface, we selected SF coal ash (0.55 wt.% K), as a blank control group for the slag without potassium.

To investigate the effect of potassium in the slag on the combustion of deposited char particles, K2CO3 powder (5.0 wt.%, 10.0 wt.%, and 15.0 wt.% of coal ash weight) was used to add in the SF coal ash sample. Then, the four ash samples were named 0% K-Slag, 5% K-Slag, 10% K-Slag, and 15% K-Slag, respectively, according to the added amount of K₂CO₃. Ash samples were pre-melted

Table 1

The proximate and ultimate analyses of samples used in this study.

Proximate ana	lysis (ad	, wt.%)			Ultimat	e analys	is (ad, w	t.%)	
Components	М	V	FC	А	С	Н	S	Ν	0
SF char	0.68	4.70	80.46	14.16	81.05	1.02	0.26	0.88	1.95
RS char	6.07	4.67	69.86	19.40	67.60	1.29	0.24	1.08	4.38
Element conte	ent of ch	ar sampl	es (wt.%)						
Element	К		Ca		Na		Al		Si
SF char	0.0	54	2.47	2	0.193		0.618		0.537
RS char	2.2	03	0.37	8	0.323		0.009		0.049

Table 2

Chemical compositions (wt.%) and the melting point of coal slag samples after pre-melting experiments.

SF Ash	Compon	ent content	(wt.%)							FT(°C)
	SiO ₂	CaO	Al_2O_3	Fe ₂ O ₃	K ₂ O	TiO ₂	MgO	Na ₂ O	SO ₃	
0%K-Slag	35.02	29.07	17.72	11.98	0.55	0.56	0.98	3.22	0.90	1173
5%K-Slag	33.77	28.04	17.09	11.55	4.09	0.54	0.95	3.11	0.87	1181
10%K-Slag	32.95	27.31	16.59	10.98	6.92	0.52	0.91	3.02	0.80	1214
15%K-Slag RS ash	31.91 64.92	26.49 5.85	16.15 1.37	10.92 1.11	9.38 16.95	0.51 0.03	0.89 4.45	2.93 2.68	0.82 2.64	1261 1280



Fig. 1. The schematic diagram of the visual experimental platform.

in a high-temperature furnace (Yifeng, China) at 1350 °C for 1 h to achieve uniform distribution of K⁺. The ash flow temperature (FT) of SF coal ash was 1173 °C measured by an ash melting point tester (5E-AF4000, China). The addition of potassium increased the FT as shown in Table 2. Thus, in this study, the experimental temperature was set to 1300 °C. During the pre-melting process, K₂CO₃ decomposed and part of K precipitated in the gas phase, resulting in the loss of K in ash samples, while the rest reacted to form potassium silica-aluminate complexes in the slag [36,37]. K content in the ash sample was determined by Advant'X IntellipowerTM 3600 X-ray fluorescence (XRF, Thermo Fisher Scientific, America) and the actual composition was shown in Table 2.

2.2. Experimental methods

In this study, an in-situ high-temperature hot stage coupled with a microscope was applied to investigate the combustion of deposited coal/biomass char particles on the molten slag face. The detailed information of the experimental platform is shown in Fig. 1. The platform consists of a TS1500 high-temperature stage (Linkam, U.K.), a DM4500P light-emitting diode microscope (Leica, Germany), a gas supply system, a recirculated cooling water system, and a computer. The char samples were spread on the ash layer on the sapphire slip (Al₂O₃, 99% purity) and then placed in

the ceramic crucible (7 mm in diameter, 3 mm in height). Before combustion, the ceramic crucible and samples in the chamber were first heated to 105 °C at the heating rate of 50 °C/min to preheat the apparatus and remove the moisture. Then, the temperature rose to 1300 °C at the heating rate of 100 °C/min in N₂ (300 mL/min) to melt the ash sample into liquid slag. The sample was held for 10 min at the temperature of 1300 °C to stabilize the particle temperature. Then, the air was injected into the chamber and reacted with char particles (300 ml/min). Meanwhile, the camera on the microscope was turned on to record the whole reaction process. After the combustion experiment, samples on the sapphire slip were analyzed for element distribution and structure. Each experiment was repeated 3 to 5 times to reduce the measuring error. In addition, Raman spectroscopy (ThermoFisher Scientific, America) was used to analyze the structure of the cooled sample under different experimental conditions.

ImageJ software was used to measure the variation of particle cross-sectional area during the interfacial combustion process. In this study, from the results in Table 1, the ash contents of coal char and biomass char were 9.80 wt.% and 12.21 wt.%, and the ash was melted into the liquid slag during the combustion on the slag surface. Thus, the char particle can be assumed as a density homogeneous sphere and the conversion can be obtained as a shrinking particle.

The relationship between the particle diameter (d_t) and crosssectional area (A_t) at time *t* was:

$$d_t = 2\sqrt{\frac{A_t}{\pi}} \tag{1}$$

For a spherical particle with uniform density, the carbon conversion can be calculated as

$$x = 1 - \frac{m_{\rm t}}{m_0} = 1 - \frac{\rho V_t}{\rho V_0} = 1 - \left(\frac{A_{\rm t}}{A_0}\right)^{3/2} \tag{2}$$

where A_0 is the initial particle cross-sectional area, μm^2 .

3. Results and discussion

3.1. Char combustion on the molten slag surface

The combustion process of SF char particles on the slag surface with different K contents is shown in Fig. 2. Under the slag-free condition, the average complete combustion time was about 3.5 s. When the particles floated on the slag surface, as shown in Fig. 2b, the reaction time increased to 4.8 s, bubbles were formed on the slag surface simultaneously. The reaction time increased slightly, as part of the particles were immersed in the slag with no addition of K at 1300 °C which hindered the diffusion and contact of the gas with char particles. Meanwhile, with the increase of K content in the slag, as shown in Figs. 2c to e, the complete reaction time of coal char particles gradually decreased. The complete reaction time of particles was reduced to 3.8 s on the slag surface, of which the slag was added 5 wt.% K_2CO_3 . With the increase of K content in the slag, bubbles were getting larger, proving that the burning rate increased.

However, when adding 15 wt.% K_2CO_3 to the slag, the promotion effect was weakened instead, and the complete reaction time was 3.5 s. This phenomenon was named the "saturation effect" of potassium catalysis, which was also consistent with the previous study [24]. As the AAEMs content increased, the promotion effect on combustion reached an extreme value and stabilized. The fundamental mechanism of alkali metal catalysis was the binding of AAEMs to the active sites present on the coal char surface thereby leading to a reduction in activation energy [38]. Hence, a continuous increase in potassium content will not lead to a continuous increase in coal coke combustion rate.

The combustion process of RS char particles is shown in Fig. 3. Unlike SF coal char, due to the loose and porous structure of biomass char [4] and high potassium content in Table 2, the combustion time of the RS char sample was shorter than the time for SF char sample. However, during the combustion of RS char particles on the molten slag surface, the complete combustion time was prolonged from 1.7 s to 3.5 s, and this influence was similar to the combustion of coal chars in Fig. 2. The combustion of biomass char particles on the slag surface was inhibited by covered area of the molten slag with less K content, which resisted the gas diffusion to the interface between char and slag.

3.2. Effect of K_2CO_3 addition on combustion

The evolutions of cross-sectional area shrinkage rate and carbon conversion of SF char particles on the surface of slag at 1300 °C are shown in Fig. 4. At the initial stage of the combustion (<2 s), SF char shrank slowly at all experimental conditions in Fig. 4a. Then, particles shrank rapidly, owing to the increasing temperature of the particle from the heat supply of combustion. The carbon conversion curves were calculated and shown in Fig. 4b. The results displayed that the carbon conversion of coal char particles at the same combustion time was lower than the time of other conditions. However, although the combustion occurred on the slag

surface, the carbon conversion of char particles on the surface of the slag with adding K was close to the time without slag. From Fig. 4b, it is found that the carbon conversion below 20% accounted for about 50% of total combustion time and the time faction for the rest carbon conversion was about 50% for all experimental conditions, corresponding to the results of the shrinking area shown in Fig. 4a. Meanwhile, it was found that with the addition of 5 wt.% K_2CO_3 , the reaction rate of coal char pellets significantly increased in the initial stage of the reaction, thus accelerating the whole reaction stage. The promotion effect was increased with the increase of K content. Moreover, to compare the combustion rate of char particles at different conditions, the average combustion rate below and above 20% carbon conversion was calculated, and the Equation was denoted as:

$$\alpha = \frac{1/t_{i,0.2} - 1/t_{0,0.2}}{1/t_{0,0.2}} = \frac{t_{0,0.2} - t_{i,0.2}}{t_{i,0.2}}$$
(3)

$$\beta = \frac{1/t_{i,1} - 1/t_{0,1}}{1/t_{0,1}} = \frac{t_{0,1} - t_{i,1}}{t_{i,1}} \tag{4}$$

where α is the average combustion rate within 20% conversion and β is the total average combustion rate. *t* is the combustion time, subscript *i* is the additional amount of K₂CO₃ in the slag, subscript 0.2 means the conversion is 0.2, and subscript 1 is the complete carbon conversion.

The calculated results of total combustion time, average combustion rate (x < 20%), and average combustion rate (x from 0 to 100%) are given in Fig. 4c. The results showed that the potassium had a strong promoting effect on the particle combustion on the slag surface in the early stage (x < 20%), and the addition of 5 wt.% K₂CO₃ to the slag can significantly shorten the complete reaction time to 34%. It was found that the increment of the average reaction rate was linearly correlated with the K content in the initial reaction stage within 20% of conversion. When the addition of potassium was increased from 5.0 to 15.0 wt.%, reaction rates were increased by 39.02%, 83.87%, and 119.20%, respectively. However, this promotion in the rest reaction process was much lower than in the initial stage. The increments for the average reaction rate of the total process were 37.96%, 48.93% to 45.81% for the K₂CO₃ additions of 5.0 wt.% 10 wt.%, and 15.0 wt.%, respectively. Less promotion on the combustion from K addition (>5 wt.%) in the slag attributed to the decreases of mass and heat transfer efficiency from a certain amount of contact area between char and slag.

For the combustion of biomass char on the molten slag surface, the results in Fig. 4d show different evolutions of conversion curves, with the comparison of chars without slag surface. Besides, the conversion curve of the RS char sample was different from the results of SF chars in Fig. 4b. The conversion of the RS char particle increased sharply and then slowly during the combustion process. However, the conversion curve increased slowly and then rapidly for the RS char on the slag surface. The results from Fig. 4b and d indicated that the slag with less K would inhibit both combustion rates of SF chars and RS chars on the surface, owing to the covered interfacial area between char and slag. Nevertheless, more K in the slag was proved to increase the combustion of coal char particles on its surface.

3.3. Distribution and migration of element

Figure 5 shows the morphologies of SF char particles on the slag surface at different conversions. The carbon conversion was calculated based on the cross-sectional area. The elemental distribution on the interface between char and slag after the removal of particles was analyzed and shown as well. The slag was added 5 wt.% K_2CO_3 and the temperature was 1300 °C. From Fig. 5, the left column shows the slag morphology and elemental distribution



Fig. 2. Photographs of the combustion processes of SF char particles and chars on the slag surface with different contents of K at 1300 °C.

on the slag surface, including K, Al, Ca, Fe, Si, and Na. These elements were uniformly distributed on the slag surface at the initial stage at high temperatures. A little bit of difference in the distribution of the elements, such as Na, K, Al, and Fe on the slag surface shown in Fig. 5 on the left column was affected by the cooling process after the combustion experiment. These elements were proved to show different enrichment characteristics on the crystal and non-crystal surfaces after the slag was cooled [39].

When an SF char particle was on the molten slag surface, exhibited on the second column from the left side, porous structures were found on the initial particle surface. At this condition, K, Al, Ca, Si, and Na were mainly on the slag surface and less on the interface of char particles and slag, while Fe was found on both sur-

faces. When the char particle combustion began on the slag surface, carbonaceous matter on the char particle was consumed and porous structures were found on the particle surface, which can be seen from SEM images, corresponding to the carbon conversion from 24.2% to 100%. Formation of porous structures is mainly attributed to different active carbonaceous matters on the surface of coal char particles and their combustion rates. From the results of elemental distribution at different carbon conversions, it is clearly found that K was rich in the interface of char particles and slag, with similar findings on Al. The enrichments of K and Al on the interface were manifested in bright colors. However, Ca, Fe, Si, and Na gave different distribution characteristics on the interface these were mainly on the slag surface out of the interface zone. The re-



(a) RS char



(b) RS char-SF slag

Fig. 3. Photographs of the combustion processes of RS char particles and RS chars on the SF slag at 1300 °C.



Fig. 4. Evolution of cross-sectional area, carbon conversion, and combustion rate increment of coal char and biomass char particles with or without molten slag surface. (a) the cross-sectional area of the SF char sample, (b) carbon conversion of SF char at 1300 °C, (c) complete combustion time (*t*) and combustion rate increment (α : *x*<20% and β : *x*~100%) with different amount of K₂CO₃ addition, and (d) carbon conversion of RS char at 1300 °C.

Molten slag 50µm	<i>x</i> =0.0%	<i>x</i> =24.2% 50µm	<i>x</i> =68.7% 50µm	X>99% Mixed 25µm zone
К 50µm	50µm	<u>50μm</u>	<u>50µm</u>	25µm
А1 50µт	50μm	<u>50µm</u>	50μm	25µm
Si 50µт	<u>50μm</u>	<u>50μm</u>	50µm	25µm
Са 50µm	<u>50µm</u>	<u>50µт</u>	<u>50μm</u>	<u>25μm</u>
Fe 50µm	<u>50µm</u>	<u>50µт</u>	50μm	25µm
Na 5 <u>0μm</u>	50µm	50μm	50µm	<u>25μm</u>

Fig. 5. SEM images of SF char particles and elemental distribution on the interface between char and slag at different carbon conversions. The slag was added 5 wt.% K_2CO_3 and the temperature was 1300 °C.

sults of the elemental distribution before and after the combustion proved that K gradually migrated from the slag side to the reaction interface of char and slag and enriched to this zone as the reaction proceeded. Al elements appeared to migrate and enrich on the reaction interface, but the intensity was weaker than K, which may be due to the influence of the stability of the silicaaluminate structure. While Na did not demonstrate significant migration properties as its low content. The morphology and elemental distribution of the RS char sample were investigated and the results are given in Fig. 6. Similar results showed that K was enriched on the interface between the slag and RS char after the particle was stripped. However, a different finding was that the color intensity of Al on the interface was weaker than the value on the slag. Si showed a higher color intensity on the interface. The distributions of Ca and Fe were mainly on the slag surface and less on the interface. Another finding was

x=0%	K	Al Provincial	Si	Ca	Fe	Na
2 <u>0µ</u> m	2 <u>0µ</u> m	2 <u>0µ</u> m	20µm	20µm	2 <u>0µ</u> m	2 <u>0µ</u> m
x=30.0%						
2 <u>0µm</u> char	2 <u>0µ</u> m	20µm	2 <u>0µm</u>	2 <u>0µ</u> m	20µm	20µm
x>99%	and the second second	Charles and	-	1 Contraction		- All State
5 <u>0μm</u> slag	5 <u>0µm</u>	50µm	5 <u>0μm</u>	5 <u>0μm</u>	5 <u>0μm</u>	5 <u>0μm</u>

Fig. 6. SEM images of RS char particles and element distribution on the interface of char and slag at different carbon conversions.



Fig. 7. Schematic diagram of the char particles combustion at the slag interface.

that the color intensities of all tested elements maintained stable throughout the combustion process. The RS char particle contained a higher content of K than SF coal char. K in the RS was fixed on the interface zone of the combustion reaction and did not spread outward before and after combustion, which was different from the migration behavior of K during the coal char combustion on the interface. The low content of Na (< 4%) in both RS char and SF ash resulted in lower color intensity and inconspicuous migration.

3.4. Heat transfer analysis

The SF and RS coke combustion at the slag surface exhibited a certain temperature distribution on the particle surface, and temperature is a crucial factor affecting the combustion and migration process. In this study, the heat transfer process and particle temperature of coke on the slag interface were analyzed, and the schematic diagram was shown in Fig. 7. During this process, the coke combustion heat was primarily consumed via radiation, convection, conduction, and particle temperature rise. More specifically, the energy balance equation is formulated as shown in Eq. (5).

$$Q_t = Q_r + Q_c + Q_h + Q_d \tag{5}$$

where Q_t is the combustion heat, J/s; Q_r is the radiant heat with the gas, J/s; Q_c is the heat absorption of the char particle, J/s; Q_h is the convective heat exchange with the reaction gas, J/s; Q_d is the heat conduction with the slag, J/s.

It is noteworthy that the gas flow, under the experimental conditions, obtained a laminar state with a low Reynolds number (Re<1), whereas the Nussle number was about 2. The convective heat transfer effect on the reaction was negligible in the quasistatic state. Thus, each of the above heat transfer rates used in this study can be expressed separately as follows.

$$Q_t = \frac{\varphi_c \cdot \Delta m_t \cdot \Delta H}{M_c} \tag{6}$$

$$Q_{\rm r} = \sigma \cdot \varepsilon_{\rm p} \cdot A_{\rm p,t} \cdot (T_t^4 - T_g^4) \tag{7}$$

$$Q_{c} = C_{c} \cdot \varphi_{c} \cdot \Delta m_{t} \cdot (T_{t} - T_{t-1})$$
(8)

$$Q_{\rm d} = \lambda A_{h,t} \frac{T_t - T_{\rm s}}{2h_t} \tag{9}$$

where φ_c is the ash content of SF char; Δm_t is mass loss of char at time t, g; ΔH is the enthalpy of the char combustion, kJ/mol; σ is the Stefan-Boltzmann constant; ε_p is the emissivity of char; $A_{p,t}$ is the surface of char exposed in the gas, m²; while $A_{h,t}$ is the surface of char submerged in the slag, m²; T_t is the particle average temperature at time *t*, K; T_g is the environmental temperature, K; T_s is the slag temperature, K; C_c is the specific heat capacity of char, J·kg⁻¹·K⁻¹; λ is the thermal conductivity of ash, W·m⁻¹·k⁻¹; h_t is the depth of particle submergence in the slag, m.

The experiment assumed that the particles were spherical particles with uniform density. The coke particles were submerged in the slag. Based on the force balance, h_t can be calculated by Eq. (10).

$$\frac{\rho_{\rm c}}{\rho_{\rm s}} = \frac{V_{cs}}{V_p} = \frac{h_t^2 (3r_{\rm p,t} - h_t)}{4r_{\rm p,t}^3} \tag{10}$$

Further, based on the above assumption, the mass loss of char particle (Δm_t) versus diameter (d_t) was shown in Eq. (11).

$$\Delta m_t = \frac{\pi}{6} \rho_c \left(d_{t-1}^3 - d_t^3 \right) \tag{11}$$

By associating Eq. (5) to Eq. (11), we can obtain the temperature of the char during combustion for different potassium contents. The parameters used to analyze the heat transfer process during the combustion on the interface between char and slag are given in Table 3.

Figure 8 illustrated the correlation between the char maximum average temperature and potassium addition during combustion. As the K content increased from 0% to 15%, the temperature difference between the particle and the molten slag increased to 54 K, 73 K, 90 K, and 83 K, respectively. The temperature initially increased and then slightly decreased with higher K content, which

Table 3

Value of the hea	t transfer par	ameters used in thi	s study [40].
Parameter	Value	Parameter	Value
$C_c(J \cdot g^{-1} \cdot K^{-1})$	1.2	φ	0.096
$m_0(g)$	0.608	$\rho_{\rm c}(\rm kg\cdot mol^{-3})$	1200
$M_c(g \cdot mol^{-1})$	12	$\rho_{\rm s}(\rm kg\cdot mol^{-3})$	3380
$R_0(m)$	5.0×10^{-4}	ε _p	0.83
$T_g(K)$	1573	$\lambda_s(W \cdot m^{-1} \cdot K^{-1})$	0.23
$T_s(K)$	1573	$\sigma(W \cdot m^{-2} \cdot K^{-4})$	5.67×10^{-8}

incfer parameters used in this study [40]



Fig. 8. Relationship between maximum average temperature difference of char particles and potassium content during combustion.

was related to the effect of K on the gasification rate. In the molten slag, the temperature distribution between the char particle and the slag during melting may be a significant factor that contributed to the enrichment of K ions in the reaction zone. It should be noted that the model results presented the overall temperature rise of the char particles. In fact, the temperature difference between the particles and surroundings or inside the particles could be much higher, reaching several hundred Kelvins with high local gradients, due to the distribution of active sites at the char surface [41,42]. The high-temperature difference led to a more pronounced

structural difference between the reactive and non-reactive zones in the molten slag.

3.5. Structure and mineral phase on the interface

To further understand the elemental migration behavior during combustion on the interface between the slag and char sample, minerals of SF coal slag before and after the addition of K₂CO₃ was analyzed via X-ray diffraction (XRD). The spectra of SF slag samples with adding different amounts of K₂CO₃ are given in Fig. 9a. The main mineral phase in the initial SF slag was gehlenite (2CaO·Al₂O₃·SiO₂), which was due to the high content of calcium in the initial sample. Other minerals were phyllosiloxide($KMg_2AlSi_4O_{12}$) and calcium iron oxide($CaFe_6O_8$) with less peaks in the spectrum after the slag was cooled down. When adding K₂CO₃ (5 wt.%) to SF slag, langbeinite(K₂Mg₂(SO₄)₃]) was found in the XRD spectrum. Kalsilite (KAlSiO₄) formed after the SF was added 10 wt.% K_2CO_3 and more aluminosilicate were found when the addition content of K₂CO₃ increased to 15 wt.%, the additional potassium tended to form eutectoid combined with silicon and aluminum [43]. The weakening of reaction promotion by high potassium additions may be related to the increased content of kalsilite, as the presence of kalsilite was detrimental to both coal ash melting and potassium ion activation [44]. Besides, the number of gehlenite peaks decreased. With the increasing content of K in the slag sample, minerals that precipitated from the cooling slag transferred from the calcium-based phase to the potassiumbased phase. Thus, a possibility that the migration of K occurred in the slag melts was related to the interfacial combustion.

The elemental migration proved in Figs. 5 and 6 during the combustion process changed the chemical composition of the slag surface, which further influenced the slag structure [45]. In this study, Raman spectroscopy was used to determine the structure and its evolution on the interface, and the results were given in Fig. 9b. The correspondence of Raman shift and vibration modes used in this study was given in Table 4. Peaks at the Raman shifts of 323, 512, and 654 cm^{-1} were found on the reaction interfaces of SF char and RS char and the non-reaction zone of SF slag, regardless of measurement error. The band around 323 cm⁻¹ denoted the bending vibration between metal and oxygen. The band at 512 cm⁻¹ is attributed to the internal deformation of Si-O-Si [46-48]. Thus, combining the results from Fig. 9a, silicate structures would form at the slag interface with char particles. Bands at 1350 and 1614 cm⁻¹ on the reaction interface of SF char and slag



Fig. 9. Raman spectra (a) and XRD spectra (b) of SF slag under different conditions. (1-Gehlenite((2CaO·Al₂O₃·SiO₂), 2-Phyllosiloxide(KMg₂AlSi₄O₁₂), 3-Calcium Iron Oxide(CaFe₆O₈), 4-Langbeinite(K₂Mg₂(SO₄)₃]), 5-Kalsilite(KAlSiO₄).

Table 4

The correspondence of Raman shift and vibration modes used in this study.

Band	Raman shift (cm^{-1})	Vibration mode
Si-O	800~1200	Non-bridge oxygen symmetric stretching vibration [46-48]
Al-O	700~800	Symmetrical stretching vibration [46–48]
Si-O-Si or Si-O-Al	400~800	Bending vibration or expansion of bridge oxygen [46–48]
M-0	<400	Bending vibration between metal and oxygen [46–48]
Carbon	~1350	Disordered graphitic lattice (graphene layer edges, A _{1g} symmetry) [49,50]
Carbon	~ 1620	Disordered graphitic lattice (surface graphene layers, E_{2g} -symmetry) [49,50]



(a) Coal char particle combustion on the K-rich slag surface



(b) Biomass char particle combustion on the slag surface



Fig. 10. Schematic diagram of K migration process and its influence on the combustion of char particles on the char-slag interface.

corresponded to the disordered graphitic lattice of graphene layer edges, A_{1g} symmetry, and surface graphene layers, E_{2g} -symmetry [49,50]. The carbon structure found on the interface of SF char and slag was from the residual carbon after the char particle was removed.

However, on the non-reaction zone of the SF slag surface, a broad and weak Raman band at 931 cm^{-1} corresponded to the stretching vibration of Si-O in the SF slag phase was found, while Raman bands on the reaction interfaces of SF char and RS char were 976 and 953 cm^{-1} , respectively. Besides, the Raman band at

749 cm⁻¹ on the non-reaction zone of SF slag changed to 770 and 769 cm⁻¹ on the reaction interface of SF char and RS char with slag, respectively. From the data shown in Table 4, Raman shifts from 400 to 800 cm⁻¹ corresponded to bands of Si-O-Si or Si-O-Al, of which the vibration mode was bending vibration or expansion of bridge oxygen [46–48]. Raman shift ranging from 700 to 800 cm⁻¹ was the band of Al-O that corresponded to the symmetrical stretching vibration mode [46–48]. Thus, from the Raman spectra in Fig. 8b, the band tended to transfer from Si-O to Al-O during the combustion process on the interface with the effect of K. K would

migrate as potassium aluminosilicates from the slag, which contained higher contents of K, to the interface with less K content, during the coal char combustion process.

3.6. K migration mechanism on char-slag interfacial combustion

During the combustion of char particles on the interface of slag, it was found that K migrated to the combustion zone and influenced the combustion. The structures of the slag melt during the combustion were determined via Raman spectroscopy. The intensity of all peaks in the Raman spectrum migrated to the highfrequency region as shown in Fig. 9b, and it was presumed to be due to the influence of the silica-aluminate structure [51–53]. Raman band for the peak at 749 cm⁻¹ was the presence of tetraligand Al (Al^{IV}) The tetra-ligand Al-O bond between symmetric stretching vibration and symmetric bending vibration led to the formation of a spectral peak at 749 cm⁻¹ versus 323 cm⁻¹, while the vibration peak at 649 cm⁻¹ was presumed to be a symmetric bending vibration of Al-O-Si. The aluminum-oxygen tetrahedra connected with the silica-oxygen tetrahedra to form a threedimensional shelf-like structure. In contrast to a study by You et al. [54], the vibrational peak of silica-oxygen tetrahedra was lower than the value in the literature. It can be explained that the main mineral phase was gehlenite, and Al³⁺ in the melt structure mainly entered the silicate network in the form of tetra-coordinated Al^{IV,} with the effect of K. AAEMs were found to be the key factor in the depolymerization of aluminosilicates during the phase transformation [18]. Thus, with the effect of K addition or high content of K in the biomass, the small force constant of Al^{IV}-O vibrations and coupling of Al^{IV}-O and Si-O vibrations lead to the vibration frequency of the original silica-oxygen tetrahedral structural unit in the highfrequency region to the low-frequency region migration [46].

In addition, the temperature increased at the reaction interface leading to the formation of more tetra-coordinated $\mathrm{Al}^{\mathrm{IV}},$ when Al replaced Si to form aluminum-oxygen tetrahedra, and this structure simultaneously bonded to metal cations to achieve charge balance [47,48]. Based on a study by Charlie et al. [18], the diffusion rate of alkali metal (K) in the melt was higher than other metals (e.g. Ca, Mg, Fe) in the silicate network, changing the concentration distribution of the whole system. Thus, at the macroscopic level, a tendency for potassium ions to be enriched on the char/slag interface was performed from the results in Figs. 5 and 6. On the contrary, Ca²⁺ migrated to other positions previously occupied by K⁺, showing a departure from the combustion reaction zone. Meanwhile, in the molten slag phase, when $K^+/Al^{3+} < 1.0$, Al³⁺ was partly tetra-ligated (Al^{IV}) in the structure as network formers and partly hexa-ligated (AlVI) in the structure as network modifiers [51,52]. Inside the silica-alumina tetrahedra, Al^{VI} had a stronger migration tendency than the network-forming Al^{IV}. The enrichment of alkali metal promoted the shift of Al³⁺ to higher coordination (Al^{VI}), which made Al³⁺ distributed in the octahedral pores between Si(T)-O tetrahedra and played the role of network modifier. The presence of Al^{VI} leads to the migration of the stretching vibration frequency of the non-bridging oxygen in the Si-O tetrahedra to a higher wave number. Hence, the stretching vibration of Si-O migrated from 931 cm⁻¹ to 953 and 976 cm⁻¹ at the interfacial reaction, and the peak internal deformation of the Si-O v2 type migrates from 512 cm^{-1} to 515 and 521 cm^{-1} in Fig. 9b [55,56]. In addition, with the formation of more Al^{IV} oxygen tetrahedra, the symmetric bending vibration of the Al-O bonds (323 cm^{-1}) is enhanced. The migration of Al with K from the slag side to the interface of slag and SF char particle can be explained. For the combustion of RS char particles on the slag surface, due to the higher content of K from the particle side, K⁺ would be present in the reactive region without further diffusion to the low concentration of SF slag, as shown in Fig. 6.

A schematic diagram of the elemental migration process is shown in Fig. 10. For the combustion of SF char particles on the slag surface, with more K in the slag, the increase of the temperature in the combustion zone led to a transformation of the silica-aluminate structure, which in turn attracted the migration and aggregation of potassium on the interface. The addition of K and its migration behavior would promote the combustion of char particles on the slag surface. In contrast, when a biomass particle with a high content of potassium was burning on the slag surface with low K content, potassium ions remained within the combustion zone. K was attracted to the silica-aluminate structure rather than diffusing to the slag zone, while this scenario would inhibit the combustion reaction of a biomass particle on the slag surface.

4. Conclusions

The migration behavior of K during the combustion of char particles on the char/slag interface was investigated in this study. and its influence on the combustion was evaluated as well. It was found that potassium still has a promoting effect on the coal char combustion on the high-temperature slag surface. Potassium as the ionic state in the liquid slag was not deactivated. When the content of K₂O was below 5 wt.%, the high-temperature slag surface can increase the average combustion rate of coal char particles by 39%. The promoting effect was not further increased with the increasing potassium content. Further study found that the promoting influence of K on coal char combustion was mainly found in the initial stage of the reaction (x < 0.2). Nevertheless, the combustion rate of rice straw char with a high content of K was inhibited on the slag surface, which contained less K. Surface analytical technique was used in this study and the results showed a tendency that K to migrate and aggregate toward the coal char and slag interface during the combustion process, while other elements were enriched on the slag side out of the combustion zone. Inversely, K⁺ in the rice husk char particle would aggregate in the combustion zone with no diffusion to the slag side. On the combustion interface, the increase in temperature lead to the depolymerization of aluminosilicates, with alumina replacing silicon to form aluminum tetrahedra while adsorbing K⁺ to the interface and promoting the combustion.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationship that could have appeared to influence the work reported in this paper.

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