

## Release and transformation of alkali metals during co-combustion of coal and sulfur-rich wheat straw



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### ABSTRACT

Co-combustion of coal and biomass is a low-cost, large-scale, and efficient way to utilize biomass energy, which has a wide range of potential applications. However, biomass, especially herbaceous fuels, contains high levels of volatile K, Na, and Cl, the use of which may result in ash-related operational problems, such as corrosion, fouling, and slagging during thermal utilization. The aim of this study is to investigate the effects of wheat straw and temperature on the release and transformation of alkali metal species during co-combustion of coal and S-rich wheat straw. Results indicate that the amounts of K and Na released during co-combustion could be reduced by the effects of Fe, Ti, S, Si, and Al from blended fuels. At lower wheat straw shares, the release of K decreased due to reactions of KCl with Fe species, and Ti species, forming  $K_2Fe_2O_4$  and  $K_2TiO_3$ . At high wheat straw shares, the release of K could be mainly captured in the form of  $K_2SO_4$ ; small amounts of  $KAlSiO_4$  were also observed in the bottom ash. When the wheat straw share was 80 wt.%, increasing temperatures enhanced the release of  $KCl(g)$  and  $NaCl(g)$  at 600–800 °C. By contrast, in the range of 800–1000 °C, the amounts of these gases released exhibited no apparent association with temperature. Compared with the release of K, fuel K was mainly retained in the bottom ash. The  $K_2SO_4$  content in the bottom ash decreased with increasing temperature in the range of 600–1000 °C, whereas the fraction of K in the form of  $KAlSiO_4$  and  $KAlSiO_6$  increased with increasing temperature, especially at temperatures between 800 and 1000 °C.

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### 1. Introduction

Co-combustion of coal and biomass for energy generation has attracted considerable attention because the technology offers a number of environmental, technical, and economical benefits [1,2]. In addition to reduction of  $CO_2$  emissions,  $NO_x$  and  $SO_2$  emissions can also be controlled during co-combustion of biomass with coal [3–5], and capital investments can be saved by using existing infrastructures. Existing coal-fired power systems may be utilized for co-combustion [6,7].

Unfortunately, biomass, especially herbaceous fuels, contains higher levels of alkali metals and Cl than coal, and its use can cause serious ash-related problems, such as agglomeration, corrosion, fouling, and slagging; these problems can result in unscheduled shut-downs and increases in operational costs [8–10]. As co-firing

biomass and coal is a promising alternative that may counteract ash-related problems through the effects of S and minerals in coal, continued developments in co-firing technology remain an urgent necessity [11]. In most existing co-firing power plants, biomass as a substitute energy source can only be co-combusted with coal at relatively low ratios to avoid severe ash-related problems. In the UK, the maximum share of biomass in pulverized fuel power plants is 10% (on an energy basis) [12]. Aho et al. [13] found that Cynara could be co-combusted with Spanish coal on an energy basis of 30% without operational problems.

The behavior of alkali metals during combustion is well known to have a direct correlation with ash-related problems and strongly depends on both fuel composition and temperature [14–16]. A large amount of information can be obtained from the release of alkali metals during biomass combustion, especially of wooden fuels. However, the physical and chemical characteristics of biomass and coal are significantly different. Despite the publication of some reports, investigations related to co-combustion of biomass and coal are usually carried out at limited biomass fractions and fixed temperatures. Research attention has generally

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focused on ash deposition and specific ash-related problems during co-firing coal with various types of biomass.

Wheat straw is one of the most important agricultural residues in China. However, most of this material is directly burned in open fields, which pollutes the environment and wastes biomass resources [17,18]. Much attention has been paid to investigating co-combustion characteristics and pollutant emissions. While the interactions of alkali metals and Cl during co-combustion of straw and coal have been reported by [19], reports regarding the release and transformation characteristics of alkali metals during co-combustion of indigenous wheat straw and coal are limited.

The aim of this study is to investigate the effects of indigenous wheat straw and temperature on the release and transformation of alkali metals during co-combustion of coal and S-rich wheat straw. The results of this work may help determine a suitable fuel mixture and temperature combination that can effectively control the formation of alkali metal species to alleviate ash-related problems. The crystalline compounds of bottom ashes were subjected to X-ray powder diffraction (XRD), and thermodynamic calculations were performed using the software HSC 6.0 to support the interpretation of the experimental data.

## 2. Materials and methods

### 2.1. Fuel preparation

Sub-bituminous coal (Tiefa Coal Ltd., Liaoning province, China) and S-rich wheat straw (Tangshan city, Hebei province, China) were chosen as co-firing fuels in this study. Samples were pulverized and sieved into particle sizes less than 0.15 mm in diameter. Prior to the experiments, samples were stored under dry conditions at room temperature. Proximate, ultimate, and ash composition analysis results of the fuels are given in Table 1. Wheat straw has observably high concentrations of S, Cl, and K compared with coal. Wheat straw–coal blends were prepared with wheat straw shares of 0 wt.%, 20 wt.%, 50 wt.%, 80 wt.%, and 100 wt.% (w/w).

### 2.2. Experimental setup

Coal, wheat straw, and their blends were combusted in a laboratory-scale fixed-bed reactor (Fig. 1). The detailed set-up diagram and experimental procedures are described elsewhere [20]. The quartz tube was 460 mm in height and had an inner diameter of 56 mm. The temperature in the reaction zone was monitored by a thermocouple.

Prior to each experiment, the reactor was purged with an air flow of 0.2 m<sup>3</sup>/h and heated to the desired temperature. In each

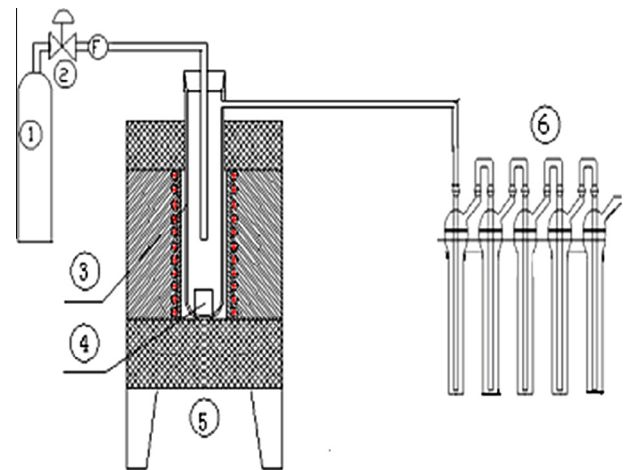


Fig. 1. Sketch of combustion reactor setup (1 – air compressors, 2 – flow meter, 3 – quartz tube, 4 – crucible, 5 – tube furnace, 6 – absorption bottle).

run, 2 g of the sample was inserted into the bottom of the quartz tube and then combusted. The residence time was 30 min. The K, Na, and Cl in the flue gas were absorbed by four bottles containing 150 mL of de-ionized water. The K, Na, Cl, and SO<sub>4</sub><sup>2-</sup> condensed inside the quartz tube were determined by rinsing with de-ionized water. The contents of these species in the bottom ash were determined by immersing ash in de-ionized water for 24 h. Water-soluble ions were analyzed by ion chromatography (IC). The bottom ash was observed using XRD to determine crystalline compounds. Three repeated experiments were performed under each condition and the results were averaged to ensure reproducibility.

## 3. Results and discussion

### 3.1. Effect of S-rich wheat straw on the release and transformation of alkali metals

During wheat straw and coal co-combustion, changes in the release of K and Na may be caused not only by physical dilution because of blending effects but also by chemical interactions of species in the wheat straw and/or coal. Thus, to differentiate between these effects, the measured versus predicted amounts of K and Na released from wheat straw/coal blends at 850 °C were plotted (Fig. 2). The predicted values were based on a linear combination of the measured values for the pure wheat straw and pure coal. The release of K and Na from the wheat straw and coal blends was lower than that from pure wheat straw. Regardless of the wheat straw share in the fuel, the predicted amounts of released K and Na were higher than the amounts measured during co-combustion, which indicates that the release of K and Na species can be inhibited by interactions between wheat straw and coal. Dayton and Belle-Oudry [6] reported that the release of KCl could be counteracted by clay minerals in coal. Robinson [21] found that the stickiness and Cl content of deposits could be reduced by reactions between alkali species from straw and S from coal during co-firing of straw and coal blends. Compared with the predicted amounts of K, the measured amounts of K decreased by 56%, 30%, and 81% in blends with 80 wt.%, 50 wt.%, and 20 wt.% wheat straw, respectively. Similar data for the amounts of Na released were also acquired. The reduction percentage of Na released from the fuels caused by synergistic reactions between two pure fuels was 32%, 63%, and 50% in fuels with 80 wt.%, 50 wt.%, and 20 wt.% wheat straw, respectively. The amounts of Na released

Table 1  
Proximate, ultimate and ash composition analysis of fuels (wt.%, air dry basis).

	Wheat straw	Coal	Wheat straw	Coal
Proximate analysis				
Ash	7.59	15.10	1.79	0.05
Volatile matter	72.32	39.06	0.11	0.10
Fixed carbon	8.84	42.48	0.14	0.43
Moisture	5.52	3.36	0.33	0.16
Ultimate analysis				
C	43.81	64.88	2.18	3.47
H	6.08	4.28	0.11	0.51
N	0.47	0.72	0.01	0.06
S	0.69	0.39		
O	35.84	11.27		
Cl	0.90	0.01		
Ash composition analysis				
K				
Na				
Ca				
Mg				
Al				
Si				
Fe				
Ti				

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