



# Combustion characteristics and arsenic retention during co-combustion of agricultural biomass and bituminous coal



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## HIGHLIGHTS

- The thermochemical behavior of bituminous and biomass were evaluated.
- The kinetic properties of their blends were obtained.
- The arsenic retention behavior during co-combustion were studied.

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## ABSTRACT

A combination of thermogravimetric analysis (TG) and laboratory-scale circulated fluidized bed combustion experiment was conducted to investigate the thermochemical, kinetic and arsenic retention behavior during co-combustion bituminous coal with typical agricultural biomass. Results shown that ignition performance and thermal reactivity of coal could be enhanced by adding biomass in suitable proportion. Arsenic was enriched in fly ash and associated with fine particles during combustion of coal/biomass blends. The emission of arsenic decreased with increasing proportion of biomass in blends. The retention of arsenic may be attributed to the interaction between arsenic and fly ash components. The positive correlation between calcium content and arsenic concentration in ash suggesting that the arsenic–calcium interaction may be regarded as the primary mechanism for arsenic retention.

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## 1. Introduction

Arsenic is known as environmentally sensitive toxic element and is of greatly concern due to its environmental and health impacts. Arsenic in environment is derived from both natural sources and anthropogenic activities (Contreras et al., 2009). Among them, coal combustion is regarded as the primary contamination sources of arsenic (Al-Abed et al., 2008). The average concentrations of arsenic in Chinese coal and coal Clarke value are 3.79 mg/kg (Dai et al., 2012) and 8.3 mg/kg (Ketris and Yudovich, 2009), respectively. During high temperature combustion, arsenic as a semi-volatile metalloid can volatilize partly and release from coal to the lower temperature flue gas (Diaz-Somoano and Martinez-Tarazona, 2004). Arsenic in the oxidizing flue gas is mainly presented as arsenic trioxide (As<sub>2</sub>O<sub>3</sub>) (Zhang et al., 2015).

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The gaseous arsenic in flue gas can turn to supermicron particles and submicron aerosols, or remain in gas phase (Miller et al., 2002). Both types of arsenic species are difficult to remove by using currently conventional air pollution control device (APCDs), i.e. electrostatic precipitators, fabric filters, cyclone and desulphurization device, and partially emitted into environment (Yan et al., 2001). The removal efficiency of currently APCDs for arsenic and the total emission of arsenic for China's coal-fired power plants were 43–99% and 335.45 tons, respectively (Tian et al., 2014). In addition, many studies reported that gaseous arsenic (As<sub>2</sub>O<sub>3</sub>) in flue gas could rapidly reduce selective catalytic reduction (SCR) catalyst activity by both block the catalyst pores and react with active V<sub>2</sub>O<sub>5</sub> sites (Senior et al., 2006). Therefore, the development of alternative technologies to improve emission control of arsenic is of extreme significance.

The transformation behaviors of toxic elements in coal combustion processes had received fairly intensive study (Furimsky, 2000; Vassilev et al., 1999). These studies show that the partitioning behaviors of toxic elements, to a large extent, were attributed by

the solid/gas phase transformation in the combustion system, and in turn determined by the composition of the fuel, the volatility of toxic element, the mode of occurrence of toxic element in coal, combustion conditions, and the reaction with different ash components (Miller et al., 2003; Wang et al., 2014). Many studies reported that the chemical interactions with the main inorganic components (Fe, Ca, Al) in fly ash may play an important role in determine toxic element partitioning between the gas phase and particulate phases (Lopez-Anton et al., 2006). Based on this mechanism, various solid sorbents, i.e. limestone, silica sand, kaolinite, bauxite, aluminum oxide, CaO, Si-Al-based sorbent, Ca-based sorbents and apatite were emerged and mixed with coal as an additive in fixed bed, drop tube furnaces, and fluidized bed incinerators (Chen et al., 1998; Yao et al., 2004). Among these sorbents, the Ca-based sorbents are effective in reducing in toxic element during combustion processes by addition of the sorbent to combustion boiler, or by sorbent injection into the gases (Mahuli et al., 1997). The adsorption process of Ca-based sorbents was regarded as a combination of chemical reaction and physisorption (Mahuli et al., 1997). Biomass is known as high alkali and alkali-earth (Ca, K, Na, and Mg) contents (Zhou et al., 2014a, 2015). Thus, the co-combustion of coal with biomass may provide an alternative control method for arsenic retention. Meanwhile, biomass is regarded as the clean and important energy due to the completely CO<sub>2</sub> neutrality, available abundantly, renewable potentially and cost-effective (Gao et al., 2016). Therefore, the co-combustion of coal with biomass may not only relieve the rapid consumption of finite fossil fuels, but also useful for arsenic retention.

The currently combustion systems are designed in accordance with the combustion characteristic and ash yield of feedstock. The combustion behavior is far different from coal as the large differences of volatile matter, fixed carbon, mineral composition and ash component (Zhou et al., 2014a). Many investigations reported that the combustion behaviors were various among different biomass samples (Gil et al., 2010; Idris et al., 2010). Therefore, in order to investigate the combustion characteristics in currently real combustion systems, the thermochemical behaviors of coal/biomass blends should be studied.

Soybean stalk and wheat straw are regarded as the typical agricultural biomass residues, which are abundant and cost-effective. Thus, these biomass were selected as the biomass fuels in this study. The main objectives of the present study were to determine (1) the combustion characteristics of coal/biomass blends via thermogravimetric analysis, (2) the partition behaviors of arsenic during coal co-combusted with biomass, (3) the As retention mechanism during co-combustion of the blends. The outcome of this study is expected to provide important information for arsenic capture and utilization of biomass rationally.

## 2. Material and methods

### 2.1. Sample preparation

The bituminous coal (BC) was from Huainan Coalfield and was collected from Pingwei Coal-fired Plant. The ash yield of bituminous coal was approximately 13.1 wt.% and regarded as the medium-to-low ash. Soybean stalk (SS) and wheat straw (WS) were sampled from the farmland at Huainan. Both the selected coal and agricultural biomass samples were kept in the sealed plastic bags immediately to avoid contamination. The samples were air-dried, grinded and sieved into 100–150 μm for subsequent analysis. The heating values, proximate and ultimate analysis of the selected samples were measured according to ASTM standards and results were presented in Table 1. The blend samples were prepared by mechanical mixing of biomass and coal for the weight ratio of 10:90, 20:80, 30:70, and 50:50, respectively. The chemical compositions of the selected samples were summarized in Table 1.

### 2.2. Thermogravimetric analysis

The thermochemical behaviors, including thermogravimetry (TG) and differential thermal analysis (DTA) of the selected fuels were conducted by using the SDT Q600 thermal analysis system. The microbalance sensitivity and precisions of temperature measurement are ±0.1 μg and ±0.1 °C, respectively. In order to prevent the mass and heat transference interference, 20 mg powdered samples were conducted under dynamic condition from room temperature to 1000 °C at the air flow and heating rate of 100 ml/min and 15 °C/min, respectively. Each sample was measured in triplicate to guarantee the repeatability. The results show that the TG and DTA curves superposed greatly, indicated that the error was supposed to acceptable.

### 2.3. Toxic element analysis

The laboratory-scale circulated fluidized bed furnace with a height of 1500 mm and an inside diameter of 50 mm was applied to investigate the retention characteristics of toxic elements during co-combustion coal with biomass. The furnace is made of stainless steel and wrapped by electrically resistant material packed with ceramic fibers to thermal insulation. The reaction temperature set at 1000 °C with the feeding rate, the excess air ratio (relative to the theoretical air), the fluidizing air flow, the secondary air flow and the fuel/air ratio of 0.20 kg/h, 40%, 1 Nm<sup>3</sup>/h, 0.5 Nm<sup>3</sup>/h and 0.714, respectively. The feedstock, bottom ash and fly ash were collected at each site simultaneously. Meanwhile, in order to investigate the concentrations of toxic elements in different particle size

**Table 1**

The physico-chemical properties of the selected bituminous coal (BC), soybean stalk (SS) and wheat straw (WS) samples.

Proximate and ultimate analysis	Proximate analysis, db (wt.%)					Ultimate analysis, daf (wt.%)				HV (MJ/kg)
	A	VM	FC	M	C	O	H	N	S	
BC	13.1	29.0	52.9	1.80	71.5	9.86	4.75	1.38	0.93	27.8
SS	7.96	74.2	17.8	7.96	40.8	45.3	6.23	0.59	0.58	17.5
WS	8.78	66.4	18.1	8.78	37.3	36.3	5.75	1.17	0.55	16.0
Ash analysis (wt.%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	MgO	TiO <sub>2</sub>	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
BC	53.1	32.7	3.13	4.31	1.32	1.71	1.18	1.40	0.07	0.05
SS	28.5	2.01	31.1	0.78	17.6	0.85	9.20	0.05	1.08	2.45
WS	55.8	4.93	8.47	2.18	13.0	3.61	6.22	0.25	0.08	1.19
Trace element (mg/kg)	As	Se	Cr	Cu	Pb	V	Zn			
BC	3.24	3.05	22.7	24.5	7.53	56.2	82.8			
SS	1.48	0.22	2.55	6.86	1.04	1.15	22.1			
WS	0.12	0.17	2.58	28.6	3.62	7.17	8.73			

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