



# Synergistic behaviors of anthracite and dried sawdust sludge during their co-combustion: Conversion ratio, micromorphology variation and constituents evolutions

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## ABSTRACT

This paper studied the synergistic behaviors of anthracite and dried sawmill sludge (DSS) in the conversion ratio (CR) of combustible substances, micromorphology variation and constituents' evolutions. The results showed that the blend CRs were the highest, and CRs increased with O<sub>2</sub> and temperature. In ash formation, DSS mainly contributed to the fly ash yield, while anthracite determined the morphology of bottom ash. The carbon proportion of combusted blend decreased to 0, revealing its thorough combustion, thereby proving the synergistic effects between anthracite and DSS. The disappearances of C=C, –CH<sub>2</sub>– and O–H determined by FT-IR indicated the burning losses of kinds of hydrocarbons, meanwhile the identified enlarged bands of Si–O, Al–O and Fe–O suggested the formations of inorganic compounds. The XRD results further demonstrated the formations of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaSO<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>, the rising temperature promoted their melting/conglomeration process, thereby lowering the XRD peaks since the miscrystals generations. The oxygen-enrich atmosphere inhibited the formations of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> but promoted the generation of Fe<sub>2</sub>O<sub>3</sub>, and accelerated the formation of porous-smooth ash. The addition of CaCO<sub>3</sub> assisted the pore formation and integrated the metal-oxides crystals. Urea made the particles welly dispersed, and weakened the XRD peaks since it improved the melting process.

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## 1. Introduction

As a result of the rapid urbanization and industrialization in the past decades, a huge amount of waste was produced, which resulted in an urgent situation that the waste surrounds the cities. The waste containing kinds of hazardous substances those threat the human's health and eco-system sustainable development. Meanwhile, the progressive dwindling of fossil fuel and the need for a sustainable society presuppose the development of renewable energy resources. As a result, the development of effective technical process to utilize waste as an alternative energy is being focused

upon in recent years. The conventional methods for the energy utilization of sludge include co-combustion with coal [1–4], anaerobic digestion with producing methane [5], low-temperature pyrolysis to generate fuel oil [6], gasification to form combustible gas [7], and slurry synthesis of coal sludge [8]. Among these methods, co-combustion method is a desirable way to treat sludge which has attracted widely interest in recent years. Also the co-combustion process exhibits some other advantages such as the decreasing of sludge volume, elimination of the pathogenic organisms, thermally destroying the organic/toxic components, and conveniently disposal of the tail gas by mature air pollution control devices (APCDs).

A lot of works have been done to investigate the co-combustion of coal and sludge, such as tannery sludge and bituminous coal [2], pulp mill sludge and bituminous coal [9], dried sewage sludge pellets and coal gangue [10], semi-anthracite and paper mill sludge [11,12], rice husks and coal [13], pine sawdust and coal [14],

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bituminous coal and pickling sludge [15] and solid recovered fuel and coal [16]. The above studies confirmed the co-combustion method was a secure outlet and could generate income through energy recovery so long as the sludge proportions and operational conditions could be controlled appropriately.

Compared with the above sludges, dried sawmill sludge (DSS), a biomass-based sludge, possesses the properties of relatively high calorific value, low ignition temperature and less harmful toxicants, which is a potential resource if it is handled properly. But few works were involved to study how to effectively treat them as well as reuse this alternative energy resource. Instead, most of the scholars paid more attention to reuse the raw biomass materials. Intrinsically speaking, the property of DSS is different from raw wood because DSS is actually a removal product from wastewater treatment process, containing a large amount of adsorbed water, salts and particulate matters. Its pyrolysis behavior as well as the emission characteristics of air pollutants is different from the combustion of biomass fuel. Thus the study on reusing DSS as an alternative energy source is meaningful.

In addition, it is known that anthracite is a primary energy source with high calorific value but high ignition temperature, meaning it is difficult to be ignited and burned out. In consideration of the characteristic complementary of DSS and anthracite, we determined to combine them and study their single or synergistic behaviors during alone or co-combustion process.

Known from the existing studies, the synergistic behaviors of coal and sludge were mostly revealed in terms of the enhanced combustion efficiency, the reduction of air pollutants emission and the retention of hazardous heavy metals. Onenc et al. [17] investigated the combustion behavior and emission characteristics of different fuels (poultry litter and its char, scrap tires and its char, and blend of char/lignite) and found chars caused a decreasing of the combustion reactivity of lignite, and the  $\text{NO}_x/\text{SO}_2$  emissions were correlated to the fuel types. Zhang et al. [18] employed CaO-sludge (Sc–CaO) as a conditioner for coal-burning. Sc–CaO strengthened the devolatilization and volatiles combustion. Meanwhile  $\text{SO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{NO}$  were effectively captured by CaO. Yousaf et al. [19] investigated the combustion characteristics and the emissions of PTEs (As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Ga, Ni, Pb, Sb, Sn, V and Zn) during the co-combustion of coal and biochar produced from peanut shell and wheat straw, and pointed out that biochar-coal showed steady combustion over broad temperature range, and the combustion efficiency and the thermal characteristics were improved. The CO emission and un-burned carbon in fly ash were reduced. The volatilization potential of PTEs was decreased as biochar added. Additionally, Vekemans et al. [20] evaluated sorbent ( $\text{CaCO}_3$  or  $\text{Ca}(\text{OH})_2$ ) co-firing and waste co-combustion to reduce  $\text{SO}_2$  emissions. Kopczynski et al. [21] studied the co-combustions of hard coal and raw, torrefied biomass and biodegradable waste, and found the impact of torrefaction on the emission of CO,  $\text{SO}_2$  and  $\text{NO}_x$  depended on the biomass type. Palares et al. [22] reported coal mine waste could be used in the co-firing process. Zhou et al. [23] found in the co-combustion of bituminous coal and biomass residues (corn stalk and sawdust) that the ignition index, burnout temperature and activation energy were decreased. And the reductions of heavy metals and polycyclic aromatic hydrocarbon (PAHs) were demonstrated.

It could be found in the above works that few scholars focused on the components evolutions and micromorphology changing during the co-combustion process, which were also the key issues involved in the reaction mechanism and synergistic effects of coal and sludge. Hence, the present study attempts to investigate the alone and synergistic behaviors of anthracite and DSS in terms of the combustible substances conversion, ash micromorphology variation, the changing of elemental proportions, the functional

groups distributions and the inorganic salts evolutions under different conditions. The obtained results verified the enhanced combustion of anthracite and the accelerating thermal destroying of DSS.

## 2. Experimental

### 2.1. Materials

The anthracite and DSS used in the experiments were got from Longyan coal district and some sawmill in Fuzhou, Fujian province. Anthracite and DSS were firstly dried at  $105^\circ\text{C}$  for 24 h, then both of anthracite and DSS were ground into powders with the particle size of 200-mesh. The proximate analyses were conducted by electrothermostatic blast oven (DGG-9123AD, China), muffle furnace (5E-MF6000, China), and proximate analysis instrument (5E-MAG6700, China) according to Chinese standard GB 212-91. The ultimate analyses were carried out using an element analyzer (5E-CHN2000, China) according to Chinese standard GB 476-91. These standard methods were as efficient as ASTM standard D7582-12 and ASTM standard D5373-08 [24]. And the analyses data of anthracite and DSS are shown in Table 1.

$M_{\text{ar}}$ ,  $M_{\text{ad}}$ ,  $A_{\text{ad}}$  and  $V_{\text{ad}}$  respectively refer to the yield of vapor, ash and volatile on a dry basis; ultimate analysis was conducted on a dry basis;  $Q_{\text{net,ar}}$  refers to the lower heating value.

### 2.2. Process parameters

The combustions of anthracite, DSS and blend (1:1 of anthracite and DSS) were carried out in a horizontal tube furnace (300 mm length and 50 mm inner diameter) (SK-2-13, Yong Guang Ming Medical Instrument Company, Beijing, China) with the temperature precision of  $\pm 3^\circ\text{C}$ . In real operational conditions of coal-fired boilers, the fuels are burned at a relative stable temperature. Thus in the current study, the temperature of the tube furnace was firstly increased to the desired value, then the sample was pushed into the tube furnace. This method can avoid the increase of the furnace temperature as a result of the sample is burned in the combustion chamber. When the burning reaction was terminated, the sample was pulled out from the tube furnace to the cooling position, as described in Wang's method [25].

During the combustion process, the feeding gas composed of  $\text{N}_2$  and  $\text{O}_2$  controlled by mass flowmeter controller continuously entered into the furnace at a velocity of 1.0 L/min. A sample of 2 g ( $\pm 0.001$  g) was used for each test. The blend was prepared by physically mixing the powders of DSS and anthracite. The effects of combustion temperature,  $\text{O}_2$  content and two co-combustion additives,  $\text{CaCO}_3$  and urea, were investigated. The investigated temperatures were 800, 900 and  $1000^\circ\text{C}$ . Three atmosphere conditions, 10%, 21% and 30% of  $\text{O}_2$  content, were used. The mass proportions of  $\text{CaCO}_3$  and urea used in the experiments were 10%.

Weight loss analysis was conducted by determining the weights of solid products before and after the combustion. The experiment was conducted in triplicate, and accordingly three parallel results were obtained, and the mean value of the three parallel results was used for combustion analysis. The error between each measurement result and the mean value was less than 10%. The conversion ratio (CR) of combustible substances can be obtained by the following formula:

$$\text{CR} = \frac{(m_0 - m_t)}{m_0(1 - A_{\text{ad}})} \times 100\% \quad (1)$$

where  $m_0$  and  $m_t$  represent the initial and terminal weight of the sample, respectively, and  $A_{\text{d}}$  represents the ash yield of the sample

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