



# Comparative thermogravimetric analyses of co-combustion of textile dyeing sludge and sugarcane bagasse in carbon dioxide/oxygen and nitrogen/oxygen atmospheres: Thermal conversion characteristics, kinetics, and thermodynamics

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## ABSTRACT

Thermodynamic and kinetic parameters of co-combustion of textile dyeing sludge (TDS) and sugarcane bagasse (SB) were studied using thermogravimetric analysis in CO<sub>2</sub>/O<sub>2</sub> and N<sub>2</sub>/O<sub>2</sub> atmospheres. Our results showed that the comprehensive combustion characteristic index (CCI) of the blends was improved by 1.71–4.32 times. With the increased O<sub>2</sub> concentration, co-combustion peak temperature decreased from 329.7 to 318.2 °C, with an increase in its maximum weight loss rate from 10.04 to 14.99%/min and its CCI by 1.31 times ( $\beta = 20 \text{ °C}\cdot\text{min}^{-1}$ ). To evaluate the co-combustion characteristics, thermodynamic and kinetic parameters (entropy, Gibbs free energy and enthalpy changes, and apparent activation energy) were obtained in the five atmospheres. The lowest apparent activation energy of the TB64 blend was obtained in oxy-fuel atmosphere (CO<sub>2</sub>/O<sub>2</sub> = 7/3).

## 1. Introduction

On average, textile dyeing sludge (TDS) is being generated at a rate of about 25 m<sup>3</sup> per million tons from textile wastewater treatment plants (Huang et al., 2011). TDS has complex chemical compositions, with large amounts of toxic organic matters such as perishable organic matter, parasites, microorganism, dyeing agents, additives, PAHs, and heavy metals (Cd, Zn, Cu, and Cr) (Liu et al., 2017a, 2017b; Xie et al., 2018b; Jiang and Liu, 2015; Zhang et al., 2017). TDS disposal is therefore posing a serious threat to the environmental and human health. In China, landfills and incinerations are the two main approaches used for the TDS disposal. Due to the limited space, and the risks of soil and water pollution, landfills become increasingly difficult to implement. Therefore, there is an urgent need to find out an appropriate treatment method for TDS.

Such advantages as waste reduction, flame stabilization, sanitation, and energy generation generally make incineration an efficient alternative for the TDS disposal (Xie et al., 2018a; Zhuo et al., 2017). Since the combustion efficiency of TDS is low due to its high moisture content, it is difficult to burn TDS alone, thus rendering co-combustion

feasible. The co-combustion characteristics of TDS with biomass or coal have been studied to increase co-combustion efficiency. For example, Huang et al. (2016) found an interaction between sewage sludge and water hyacinth in CO<sub>2</sub>/O<sub>2</sub> atmosphere. Otero et al. (2008) reported that the co-combustion characteristics of coal and sewage sludge remained similar to those of coal.

Blending biomass with other substances can increase volatile content of the blend, thus promoting the co-combustion reaction (Gil et al., 2015; Huang et al., 2016; Chen et al., 2017). When compared to other solid fuels, biomass is low in carbon and calorific value but high in O<sub>2</sub> content, and thus, more biomass to be burned is required to gain the same energy output (Zhuo et al., 2018; Huang et al., 2018; Chen et al., 2018). Sugarcane bagasse (SB) is composed mainly of cellulose, hemicellulose, and lignin and generally used in thermal power generations and fermented alcohol industries (Ramajo-Escalera et al., 2006). Globally, China was the third largest sugarcane producer, with annual output of 70 million tons, and its bagasse production as the byproduct of sugar industry was about 7 million tons in 2014 (Wang et al., 2010; FAOSTAT, 2014). Co-firing TDS with SB may be a feasible way to dispose them both. However, there still exist a few studies about co-

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combustion of TDS and SB, and their thermodynamics and kinetic parameters.

Oxygen-fuel combustion is a technology to reduce CO<sub>2</sub> emissions from coal-burning (Farrow et al., 2015). Compared to the air (N<sub>2</sub>/O<sub>2</sub>) atmosphere, the combustion characteristic indices of coal such as ignition temperature, burning temperature, and ash content conversion were reported to reduce NO<sub>x</sub> and SO<sub>2</sub> emissions in the O<sub>2</sub>-enriched atmosphere (Gil et al., 2015). Co-firing biomass with coal in the O<sub>2</sub>-enriched atmosphere in fluidized bed combustors may potentially reduce anthropogenic CO<sub>2</sub> emissions (Anthony and Hoteit, 2010). Meanwhile, (co-)combustion in the O<sub>2</sub>-enriched atmosphere can reduce the reaction loss of chemical energy converted into heat energy as well as the concentrations of organic pollutants in the exhaust (Yu et al., 2008). The O<sub>2</sub>-enriched combustion is faster, more secure and more competitive than the other combustion technologies.

Zhuo et al. (2017) found that the co-combustion characteristics of TDS and coal were improved in the CO<sub>2</sub>/O<sub>2</sub> atmosphere with the increased O<sub>2</sub> concentration up to 30% beyond which the reaction produced a negative effect. Kayahan and Ozdogan (2016) reported more NO and SO<sub>2</sub> emissions following the co-combustion of lignite and biomass in the O<sub>2</sub>-enriched atmosphere using a 30 kWth fluidized bed. Rathnam et al. (2009) illustrated that the release of volatile matters from the fuel was more efficient in the CO<sub>2</sub>/O<sub>2</sub> atmosphere than in the N<sub>2</sub>/O<sub>2</sub> atmosphere using four coal types in a drop tube furnace. Burning in the CO<sub>2</sub>/O<sub>2</sub> atmosphere was reported to boost combustion performance (Zhuo et al., 2017). The co-combustion characteristics of TDS and SB in the O<sub>2</sub>-enriched atmosphere have not been studied thus far. Therefore, there still remains a knowledge gap about impacts of different O<sub>2</sub> concentrations on combustion performance (Zhuo et al., 2017).

The objective of this study was to quantify the thermochemical conversion rates and co-combustion characteristics of TDS and SB in the N<sub>2</sub>/O<sub>2</sub> and CO<sub>2</sub>/O<sub>2</sub> atmospheres, and their thermodynamic and kinetic parameters such as apparent activation energy (*E<sub>a</sub>*), pre-exponential factor (*A*), entropy change (*ΔS*), Gibbs free energy change (*ΔG*), and enthalpy change (*ΔH*) using thermogravimetric analysis (TGA), and the methods of Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS).

## 2. Materials and methods

### 2.1. Experimental materials

TDS samples were collected from a sludge dewatering workshop of a printing and dyeing textile factory in Dongguan, while SB samples were obtained from a vegetable market in Guangzhou, Guangdong Province, China. Both were air dried, grounded in a grinder and screened on a mesh with a size of 75 μm. All the samples were dried in an oven at 105 °C for 24 h and stored in a desiccator. The blends of TDS and SB were prepared at the following ratios of 9:1, 8:2, 7:3 and 6:4 on a dry weight basis coded as TB91, TB82, TB73, and TB64, respectively. Their ultimate and proximate analyses are presented in Table 1 (Xie et al., 2018a). Since the most obvious interaction was found for TB64 from among the different blend ratios studied by Xie et al. (2018a), TB64 was chosen as the blend ratio to evaluate the co-combustion characteristics.

### 2.2. Experimental methods

Thermogravimetric analysis was conducted using a NETZSCH STA 409 PC simultaneous analyzer in the five atmospheres (CO<sub>2</sub>/O<sub>2</sub> = 8/2, CO<sub>2</sub>/O<sub>2</sub> = 7/3, CO<sub>2</sub>/O<sub>2</sub> = 6/4, CO<sub>2</sub>/O<sub>2</sub> = 4/6, and N<sub>2</sub>/O<sub>2</sub> = 7/3). The sample (10 ± 0.5 mg) was loaded into an alumina crucible and then put into the furnace where it was heated up from room temperature to 1000 °C with the three heating rates (10, 20 and 30 °C·min<sup>-1</sup>) at a gas inflow rate of 50 mL·min<sup>-1</sup>. Before the experiment started, blank tests were carried to obtain the baseline to eliminate the systematic errors of

**Table 1**

Ultimate and proximate analyses of textile dyeing sludge (TDS) and sugarcane bagasse (SB).

Analysis	TDS	SB
<i>Ultimate analysis (%)</i>		
Carbon	20.20	44.48
Hydrogen	6.08	6.057
Oxygen	25.32	40.69
Nitrogen	3.22	0.19
Sulfur	2.76	0.047
<i>Proximate analysis (%)</i>		
Moisture content	11.84	6.44
Volatile content	50.74	86.01
Ash content	37.46	2.09
Fixed carbon content	4.2	5.47

the instrument. In order to decrease the experimental errors, repeated tests (three times) were also performed. The NETZSCH-T4-Kinetic2 software was used to provide the thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of the samples.

### 2.3. Co-combustion characteristic parameters

The characteristic parameters used to evaluate co-combustion performances in the five atmospheres were ignition temperature (*T<sub>i</sub>*), peak temperature (*T<sub>p</sub>*), burning temperature (*T<sub>b</sub>*), maximum weight loss rate (*R<sub>max</sub>*), average weight loss rate (*R<sub>a</sub>*) (Meng et al., 2013; Chen et al., 2015), ignition performance index (*D<sub>i</sub>*) (Li et al., 2011), stationary combustion performance index (*C*) (Yan et al., 2007), and comprehensive combustion characteristic index (*CCI*) (Liu et al., 2013).

$$D_i = \frac{R_{max}}{T_i \times T_p} \quad (1)$$

$$CCI = \frac{R_{max} \times R_a}{T_i^2 \times T_b} \quad (2)$$

$$C = \frac{(dw/dt)_{max}}{T_i \times T_b} \quad (3)$$

A higher *D<sub>i</sub>* implies a better ignition performance. A *C* estimate measures whether or not the fuel (co-)combustion is stable, reflecting both its degree of difficulty and its situation after the ignition. A high *CCI* value indicates a superior (co-)combustion performance.

### 2.4. Interaction indices

Interactions between TDS and SB during co-combustion were analyzed using the following theory TG curves (Deng et al., 2016):

$$TG_{CAL} = x_{TDS} \cdot TG_{TDS} + x_{SB} \cdot TG_{SB} \quad (4)$$

where *x<sub>TDS</sub>* and *x<sub>SB</sub>* were regarded as mass fractions of TDS and SB, while *TG<sub>TDS</sub>* and *TG<sub>SB</sub>* represent TG curves of pure TDS and SB, respectively.

To further explore interactions between TDS and SB, deviations were calculated as follows (Haykiri-Acma and Yaman, 2010):

$$Deviation = (TG_{EXP} - TG_{CAL}) / TG_{CAL} \quad (5)$$

where *TG<sub>EXP</sub>* refer to TG curves of the blends. *DTG<sub>EXP</sub>* and *DTG<sub>CAL</sub>* were the curves of differential *TG<sub>EXP</sub>* and *TG<sub>CAL</sub>*, respectively.

### 2.5. Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods

To describe the kinetic processes of TDS and SB burned alone and simultaneously, the two model-free solutions, the FWO and KAS methods, for apparent reaction activation energy (*E*) were applied.

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