



Research Paper

Assessing thermal behaviors and kinetics of (co-)combustion of textile dyeing sludge and sugarcane bagasse



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HIGHLIGHTS

- Co-combustion performance of textile dyeing sludge & sugarcane bagasse was assessed.
- Positive interaction effects occurred with the co-combustion.
- Evolved-gas-analysis was quantified using TG-MS.
- Blended samples evolved less SO₂ but more NO_x, NH₃ and CO₂ emissions.
- E_a estimates by FWO and KAS showed lower activation energy for blended samples.

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ABSTRACT

Thermogravimetric and mass spectrometric (TG-MS) experiments were carried out using textile dyeing sludge (TDS), sugarcane bagasse (SB) and their blends with different ratios. (Co-)combustion kinetic parameters of each sample were calculate by using TG-derivative curves. CO₂, NO_x, NH₃ and SO₂ emissions were also quantified. The addition of SB to TDS lowered SO₂ but enhanced NO_x, NH₃ and CO₂ emissions. Calculated activation energies (*E*) of the pure TDS and SB, and their blend (TB64) according to the Flynn-Wall-Ozawa method were on average in the range of 185.6–253.9 kJ·mol⁻¹, 152.9–235.9 kJ·mol⁻¹ and 111.1–161.8 kJ·mol⁻¹, respectively. Based on the Kissinger-Akahira-Sunose method, *E* estimates of the pure TDS and SB, and the blend ranged from 183.1 to 251.0 kJ·mol⁻¹, 152.1 to 237.2 kJ·mol⁻¹ and 108.2 to 160.1 kJ·mol⁻¹, respectively. Our results indicated that the blend *E* was affected by the interactions between TDS and SB.

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1. Introduction

With the rapid development of textile-related industries, the production of textile dyeing sludge (TDS) rich in heavy metals with strong biological toxicity has increased as a result of their waste water treatment, thus exerting adverse effects on the environment [1,2]. According to the *China Environmental Statistics Yearbook*, the amount of TDS with 80% moisture content reached about 5.38 million tons in China in 2013 [3]. Incineration/co-combustion of TDS is more conducive to environmentally benign reduction, reuse and recycling than landfill and agricultural disposal methods [4–7]. Due to the high moisture and low calorific contents of TDS itself,

mono-combustion consumes a large amount of fuel and energy, while co-combustion with other materials usually costs less and is more environmentally friendly. Moreover, the use of TDS with biomass materials can render the co-combustion process more stable and complete [8,9].

As an alternative clean energy, biomass can improve the performance of TDS combustion and reduce related CO₂ emissions [10]. However, there are still few studies about the co-combustion behaviors of TDS with biomass collected from different sources. For example, the pyrolysis characteristics and reaction kinetics of five kinds of biomass quantified on the basis of thermogravimetric experiments showed that the major reaction stage was related to decomposition of hemicellulose, cellulose and lignin [10,11]. When wood was co-fired with oily sludge, the co-combustion of oily sludge was improved by which ignition temperature and reaction

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rate increased, and maximum weight loss rate was enhanced, with the char playing a catalytic role in the residue decomposition of oily sludge [12]. Co-combustion of microalgae with TDS was reported to enhance the co-combustion performance owing to the catalytic function of alkali/alkaline metals of the incineration [13].

China grows large amounts of sugarcane and sugarcane bagasse (SB) as the main byproduct at rates of over 70 and 7 million tons per year, respectively, following Brazil (the largest producer with over 730 million tons in 2014) and India [14]. Sugarcane bagasse usually consists of cellulose, hemicellulose and lignin and can be regarded as an important renewable biomass resource owing to its high lignification degree [15]. Due to the residual fiber, SB is usually burned to generate electricity [16]. So far, co-combustion behaviors and kinetics of TDS and SB have not been quantified. In this study, evolutions of gaseous (co-)combustion products during thermal transition as well as thermal stability of TDS and SB were quantified using thermogravimetric analysis (TGA) and mass spectrometry (MS) under the four heating rates (10, 20, 25 and 30 °C·min⁻¹) and the four blending ratios of TDS to SB (9:1, 8:2, 7:3 and 6:4). Such attributes as blend ignition, burnout, comprehensive combustion characteristics (CCI), and kinetics were also assessed for the (co-)combustion processes. Activation energies (*E*) for the fuel materials were analyzed using the methods of Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO).

2. Materials and methods

2.1. Experimental materials

Textile dyeing sludge was collected from a sludge dewatering workshop of a printing and dyeing textile factory, Dongguan, Guangdong Province, China, while sugarcane bagasse was collected from a vegetable market in Guangzhou Higher Education Mega Center, Guangzhou, Guangdong Province, China. Both materials were air-dried, grounded by a grinder and then screened over a mesh size of 75 μm. All the samples were oven-dried at 105 °C for 24 h and stored in a desiccator. In this experiment, we aimed at determining which SB ratio of blends would improve the TDS co-combustion significantly, and thus, a gradually changing ratio of blends (blend gradient) was chosen. The blending of TDS and SB was prepared using the following four ratios of 9:1, 8:2, 7:3 and 6:4 on a weight basis coded as TB91, TB82, TB73, and TB64, respectively. The ultimate and proximate analyses of TDS and SB are presented in Table 1.

2.2. Experimental methodology

Thermogravimetric analysis was conducted using a NETZSCH STA 409 PC simultaneous analyzer under the air atmosphere (21% O₂ / 79% N₂). The sample (8 ± 0.5 mg) was loaded into an alumina crucible and then placed into a furnace. The sample in the furnace was heated up from room temperature to 1000 °C at the four heating rates of 10, 20, 25 and 30 °C·min⁻¹ under the gas inflow of 50 mL·min⁻¹. Before the start of the experiment, blank tests were conducted to obtain the baseline to eliminate

the systematic errors of the instrument. In order to reduce the experimental errors, repeated tests were performed in three replicates. The NETZSCH-T4-Kinetic 2 software was used to obtain thermogravimetry (TG) and derivative thermogravimetry (DTG) curves.

TG-mass spectrometry (MS) analysis was conducted using a TG-MS analyzer (Rigaku Thermo Mass Photo, Japan). Samples of about 3 ± 0.5 mg were measured in argon atmosphere (20% O₂ / 80% He) at a flow rate of 300 mL·min⁻¹. The samples were heated at a rate of 20 °C·min⁻¹ from 30 °C to 950 °C in an alumina crucible under the flowing gas. The ions of characteristic interest were *m/z* = 17 (NH₃), *m/z* = 30 (NO_x), *m/z* = 44 (CO₂), and *m/z* = 64 (SO₂).

2.3. Kinetic and thermodynamic parameters

So as to obtain accurate results to describe and compare the kinetic processes of TDS, SB, and their blends, the two apparent reaction activation energy (*E*) model-free solutions were employed using the Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods. According to the Arrhenius law, the combustion kinetics equation of the non-isothermal solid phase reaction can be expressed thus:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = f(\alpha)k(T) = A \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (1)$$

where α is conversion rate of the solid reactant; $k(T)$ is reaction speed constant; $f(\alpha)$ is modal function of the thermodynamic reaction mechanism; A is apparent pre-exponential factor (min⁻¹); E is reaction activation energy (J·mol⁻¹); R is the ideal gas constant (8.314 J·mol⁻¹·K⁻¹); T is absolute temperature (K); t is reaction time (min); and β is heating rate (°C·min⁻¹).

The term “ α ” can be derived from the TG curves:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (2)$$

where m_0 , m_t and m_f represent sample weights at the initial moment, moment t and the end of reaction.

The integration form of the Eq. (1) can be expressed as follows:

$$\begin{aligned} g(\alpha) &= \int_0^\alpha \frac{d(\alpha)}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) d(T) \\ &= \frac{AE}{\beta R} \int_x^\infty \frac{\exp(-x)}{x^2} dx = \frac{AE}{\beta R} p(x) \end{aligned} \quad (3)$$

where $x = \frac{E}{RT}$, $p(x)$ cannot be obtained exactly because it is a temperature integration function.

The FWO method [17–19] uses the following Doyle [20] approximation method:

$$\lg \beta = \lg \frac{AE}{Rg(\alpha)} - 2.315 - 0.4567 \frac{E}{RT} \quad (4)$$

With any given conversion degree (α), $g(\alpha)$ can be assumed as a constant. Plotting “ $1/T$ ” against $\lg \beta$, the slope becomes $-0.4567E/R$, thus enabling the activation energy of the reaction at a given conversion rate to be calculated.

Table 1
Proximate and ultimate analyses of TDS and SB.

Sample	Ultimate analysis (%)					Proximate analysis (%)			
	C _{ad}	H _{ad}	O _{ad}	N _{ad}	S _{ad}	M _{ad}	V _{ad}	A _{ad}	FC _{ad}
TDS	20.20	6.08	25.35	3.22	2.76	11.84	50.74	37.46	4.2
SB	44.48	6.057	40.69	0.19	0.047	6.44	86.01	2.09	5.47

ad, air-dried; M, moisture content; V, volatile content; A, ash content; and FC, fixed carbon content.

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