Quantifying thermal decomposition regimes of textile dyeing sludge, pomelo peel, and their blends

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ABSTRACT

Thermal decomposition behaviors of textile dyeing sludge (TDS), pomelo peel (PP), and their blends (TP) were detected using TG-FTIR. The blend ratios of TDS to PP ranged from 10 to 40 wt% and were subjected to heat above room temperature up to 1000 °C under four heating rates. Our results pointed to four stages for TDS combustion and three stages for PP combustion. The interactions between TDS and PP exerted inhibitive effects during the co-combustion process. Releases of CO_2 and light organics occurred less with a TP ratio of 70%—30% (TP73) than with the individual fuels. Apparent activation energy (E_a) was obtained using Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods. The FWO-based E_a estimates were in the range of 59.7—122.2 kJ·mol^{-1} for TDS, 84.4—243.5 kJ·mol^{-1} for PP, and 94.3—142.1 kJ·mol^{-1} for TP73.

1. Introduction

Textile printing and dyeing industries are among the most heavily polluting sectors that not only require large quantities of freshwater but also generate large volumes of wastewater and sludge after the treatment. The total amount of wastewater from textile printing and dyeing industries in China reached about 2.15 billion tons (t), with the resultant generation of textile dyeing sludge (TDS) of 5.38 million t (including 80% water content) [1]. Given rapidly growing rates of TDS, its high toxicity and low degradability, and limitations of the conventional disposal technologies such as landfill, sea disposal, and fertilizers, there is an urgent need to develop environmentally and economically effective ways of its disposal [2—5]. Sludge (co-)combustion appears to be a promising way to maximize sludge reduction [6]. For example, most European Union countries have promoted sludge (co-)combustion and incineration as the mainstream treatment technology for TDS [7]. However, as the mono-combustion of TDS is unstable and incomplete due to its high ash content and low calorific value [8], seeking co-combustion alternatives for TDS is of pivotal significance to minimization of environmental issues and maximization of useful energy.

Thermogravimetry (TG) analysis used to explore thermal regimes and reaction kinetics of mono- and co-combustions of sludge, coal, and biomass under different conditions showed that co-combustion performance of sludge improved significantly with the concurrent use of biomass [9—11]. For example, Font et al. [12] quantified TG curves of two sludge types at different heating rates, proposing a kinetic model with three independent but parallel reactions. Liu et al. [13] explored combustion regimes of different sludge sources and their physicochemical properties. The blend of coal and sludge (50 wt%) was reported to show reactivity similar to that of sludge in the low temperature region (<350 °C) and similar to that of coal in the high temperature region (>350 °C) [14]. The combustion regimes of miscanthus, poplar wood, and rice husk were found to increase ignition and burnout temperatures with the increased heating rate [15]. Wang et al. [16] determined significant synergistic effects during the co-pyrolysis of sewage sludge and

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straw. The synergistic effect of the TDS and microalgae co-combustion was reported to improve both char catalytic effect and alkali metal melting-induced effect [8]. Deng et al. [17] related the interaction effect of oil sludge and wood primarily to co-combustion temperature.

Over 2 million t pomelos, a characteristic fruit of China, are produced annually with the generation of a large amount of pomelo peel (PP) as a byproduct [18]. Thus far, PP has been used to extract pectin, flavonoids, essential oils, natural pigments, a variety of other active ingredients, and biosorbents [19–22]. However, the present utilization of these value-added byproducts is very limited and massive amounts of PP are frequently dumped in garbage. In line with the sludge treatment and disposal policies of China, the co-combustion of garbage and sludge is highly encouraged. PP is rich in organic matter, cellulose and lignin [18]; however, it has never been used as a potential biofuel source in a (co-)combustion process for energy utilization. Instead, thermal decomposition behaviors of TDS and orange peels were quantified combining TG analyzer-Fourier transform infrared spectroscopy (TG-FTIR) techniques, with no report on the analysis of evolved gas [23,24]. However, it is necessary to probe variations in gaseous products during the co-combustion process in order to predict the possible differences among thermal decomposition behaviors of blended versus individual samples. There exists a knowledge gap as to the quantification and understanding of the potential co-combustion of PP and TDS, and the shortcomings of mono-combustion of TDS.

The objectives of the present study were to (1) explore thermal decomposition regimes of TDS and PP co-combustion using the combined TG-FTIR technique under the air atmosphere (composed of 21% O_2 and 79% N_2), (2) compute various characteristic combustion indices to evaluate impact of PP on the combustion characteristics of TDS under four heating rates and four blend ratios, and (3) quantify kinetics and evolution of gaseous products during (co-)combustion of PP and TDS. The Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) iso-conversional methods were applied in the kinetic analysis to estimate apparent activation energy (E_a).

2. Methods

2.1. Sample preparation

The block-shaped TDS used in this study was obtained from a textile printing and dyeing plant from Dongguan in the Guangdong Province, China. Pomelo peel was collected from a fruit market of Guangzhou University Mega Center. After being milled and sieved into particles of 74 μm diameter, TDS and PP samples were dried in the oven at 105 °C for 24 h. The TDS and PP samples were blended with the following PP weight (wt) percentages of 10%, 20%, 30% and 40% coded as TP91, TP82, TP73 and TP64, respectively.

2.2. TG-FTIR experiments

The (co-)combustion characteristics of TDS and PP were analyzed using a TG analyzer system (NETZSCH STA 409 PC Luxx, Germany) coupled with a FTIR spectrometer (TENSOR 27 FTIR, Germany). The transfer line and gas cell of the FTIR spectrometer were heated at 200 °C to prevent the condensation of evolved gases. FTIR spectra from 4000 to 650 cm^{-1} were recorded at a resolution of 4 cm^{-1}. The test data were processed using the OMNIC software (Thermo Electron, USA).

In the TG experiments, all the samples (10 ± 0.5 mg) were heated at temperatures up to 1000 °C using the four heating rates of 15, 20, 25 and 30 °C·min^{-1} under the air atmospheric condition composed of 21% O_2 and 79% N_2, at a flow rate of 50 mL·min^{-1}. Each test was conducted three times to ensure reproducibility, accuracy, and that errors of results were within ±2%.

2.3. Mineral composition of samples

Mineral compositions of the individual fuels were characterized using an energy dispersive X-ray fluorescence spectrometer (EDX-7000, SHIMADZU, Japan).

2.4. Performance index

For an integrative evaluation of the (co-)combustion characteristics of TDS and PP, the comprehensive combustion index (S) was used and was defined as follows [25]:

$$S = \frac{(dW/dt)_{max}(dW/dt)_{mean}}{T_i^2 T_f} \tag{1}$$

where $(dW/dt)_{max}$ is the maximum mass loss rate, while $(dW/dt)_{mean}$ is the average mass loss rate (%·min^{-1}). The higher the S values are, the better the combustion properties of the samples are.

2.5. Interaction indices

In order to confirm the possible existence of interaction effects (accelerative or inhibitive) between TDS and PP during the co-combustion, the TG curves were obtained from the mass loss of the individual samples which were in contrast to the experimental values. The estimated TG (TG_{cal}) values for the TP blends were defined as follows [9]:

$$TG_{cal} = \gamma_{TDS}TG_{TDS} + \gamma_{PP}TG_{PP} \tag{2}$$

where γ_{TDS} and γ_{PP} were the mass fractions of TDS and PP in the blends, respectively, while TG_{TDS} and TG_{PP} were the corresponding weight losses of the individual samples.

To gain further insight into the degree and variation of the interaction effects on the co-combustion, deviations from the TG_{cal} values were introduced using the following equation [26]:

$$Deviation(\%) = \left[\frac{TG_{exp} - TG_{cal}}{TG_{cal}}\right] \times 100\% \tag{3}$$

2.6. Kinetics

According to the Arrhenius equation, the general kinetic equation for the solid-state thermal transformation can be expressed thus:

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = f(\alpha)k(T) = A\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \tag{4}$$

where α is the degree of conversion for the solid reactant; $k(T)$ is the constant of reaction rate; $f(\alpha)$ is the reaction model of the thermodynamic mechanism; A (min^{-1}) is the apparent pre-exponential factor; E_a (J·mol^{-1}) is activation energy; R is the universal gas constant (8.314 J·mol^{-1}·K^{-1}); T (K) is the absolute temperature; t (min) is the reaction time; and β (°C·min^{-1}) is the heating rate.

The mass loss fraction was estimated from the corresponding TG curves and defined as follows: