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# The thermal behaviour of the co-combustion between paper sludge and rice straw



### Zeqiong Xie<sup>a,\*</sup>, Xiaoqian Ma<sup>b</sup>

<sup>a</sup> Guangzhou Academy of Energy Testing and Inspection, No. 1 Miaoqian Street of Xishan, Dongfeng Road West, Guangzhou City, Guangdong Province, PR China <sup>b</sup> School of Electric Power, South China University of Technology, 381 Wushan Road, Guangzhou 510640, PR China

#### HIGHLIGHTS

- The combustion of paper sludge could be improved by blending rice straw.
- There existed significant interaction between rice straw and paper sludge.
- The interaction improved the thermal decomposition of the blends.
- The activation energy of initial fuel first decreased and then increased.
- The average activation energy was the minimum by blending 80% rice straw.

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#### 1. Introduction

Paper sludge is the residue produced by pulp and paper plants, which contains a large amount of toxic and harmful chemicals, such as heavy metals, viruses, bacteria and parasites, etc. (Ahluwalia and Goyal, 2007; Nicholson et al., 2003). It will bring serious pollution to the environment and endanger human health if paper sludge is discharged directly into the environment without suitable treatment (Beauchamp et al., 2002). There are different treatments for paper sludge at present, such as landfill, agricultural application, composting and incineration, etc. (Lee et al., 2003). The sludge incineration was one of the methods widely applied for the sludge treatment, because it has many advantages compared to other methods. For example, the sludge incineration can greatly reduce the volume and weight of sludge and convert it into the electrical or heat energy. However, the sludge has the following

#### ABSTRACT

The thermal characteristics and kinetics of paper sludge, rice straw and their blends were evaluated under combustion condition. The paper sludge was blended with rice straw in the range of 10–95 wt.% to investigate their co-combustion behaviour. There was significant interaction between rice straw and paper sludge in high temperature. The combustion of paper sludge and rice straw could be divided into two stages. The value of the activation energy obtained by the Friedman and the Ozawa–Flynn–Wall (OFW) first decreased and then increased with the conversion degree rising. The average activation energy did not monotonically decrease with increasing the percentage of rice straw in the blends was 80%, the value of the average activation energy was the smallest, which was 139 kJ/mol obtained by OFW and 132 kJ/mol obtained by Friedman, respectively.

characters: high moisture content, high ash, high density, high viscosity and low calorific value, which has a bad impact on its incineration. So it is necessary to use auxiliary fuel to ensure the steady combustion of its incineration. The ash content of rice straw is lower than that of paper sludge, the heat value of the blends can be increased by adding rice straw in paper sludge. In addition, the low density of rice straw makes it easy to escape from the combustion zone. Then blending sludge with rice straw can increase the density of rice straw, which ensures the fully combustion of rice straw. Therefore, the co-combustion of paper sludge and rice straw can avoid the drawbacks with each other and increase combustion efficiency.

The combustion characteristics of the biomass fuel are quite different from that of sludge. Biomass has a high volatile and a low ash content compared to sludge, so the addition of biomass to sludge can affect the entire combustion process and improve the combustion efficiency. Thermogravimetric analysis (TGA) has been widely used to evaluate the combustion characteristics of coal and biomass, as well as the combustion behaviour of sludge. The characteristic parameters, such as the ignition temperature, the



<sup>\*</sup> Corresponding author. Tel.: +86 20 81097291; fax: +86 20 81099177. *E-mail address:* xiethanks@126.com (Z. Xie).

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burnout temperature and the activation energy, can be obtained by TGA, which can be used to understand the combustion process and provide a reference for the application of sludge. Many authors have studied its thermal behaviour and co-firing paper sludge with coal or other fuels. The devolatilization of paper sludge occurred earlier with a higher rate, but its high ash content inhibited its combustion. The combustion process of paper sludge could be described by a single reaction and a power law model might be the best model for its combustion (Vamvuka et al., 2009). It was found that the entire decomposition of paper sludge could be divided into four stages, which were drying, pyrolysis, medium and combustion (Yu et al., 2002). Previously, the kinetic parameters of paper sludge had been calculated by iso-conversional methods, such as Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose (Liao and Ma, 2010; Xiao et al., 2010). However, most of the literature focuses on the co-combustion of sludge and coal or biomass and coal at present. the research about the co-combustion characteristics between biomass and sludge is relatively rare. Only a few researchers have studied the emission characteristics of their co-combustion (Tsai et al., 2002). Therefore, further study is still essential to research the co-combustion behaviour and the interaction between sludge and biomass.

In this paper, the thermogravimetric analysis was used to evaluate the combustion behaviour of rice straw, paper sludge and their blends at different heating rates. The interaction between rice straw and paper sludge was also investigated under the different mixture ratios. The kinetic parameters during the combustion process were calculated by two iso-conversional methods: the Friedmen and the Ozawa–Flynn–Wall (OFW). The results obtained in this paper could lead to deeper understand the combustion characteristics of sludge and rice straw and provide reference for the incineration of paper sludge and rice straw.

#### 2. Methods

#### 2.1. Materials and measurements

The paper sludge was obtained from the dewatering shop of the paper mill, which was natural dried 7 days. And the rice straw was provided by the Zhanjiang biomass power plant. The paper sludge and rice straw were dried at 105 °C for 7 h in a drying oven. All the samples were pulverized and sieved to ensure that the particle size of the samples was smaller than 178  $\mu$ m. The ultimate analyses and proximate analysis of the initial materials were shown in Table 1. The raw materials were named RS (rice straw) and PS (paper sludge), and the percentage of RS in the blends was named PRS. Different mixtures of both materials were prepared, which included 10, 20, 30, 50, 70, 80, 90 and 95 wt.% of rice straw (10RS90PS, 20RS80PS, 30RS70PS, 50RS50PS, 70RS30PS 80RS20PS, 90RS10PS and 95RS5PS, respectively).

The experiments were carried out by the NETZSCH simultaneous thermal analyzer with the accuracy of 0.001 g and 0.1 °C, model STA 409 PC Luxx. The flow rate of the gas mixture was 100 ml/min, which was mixed by high purity nitrogen and high purity oxygen with the ratio of 8:2. The mass of the samples located in the  $Al_2O_3$  crucible for all runs was  $6 \pm 0.2$  mg. The experiment temperature was increased from 40 °C to 1000 °C at a heating

rate of 10, 20 or 40 °C/min. In order to decrease experiment error, all the experiments were carried out at least twice, which was found that the reproducibility was very good.

#### 2.2. Kinetic theory

The combustion process of all samples could be described by the following equation:

$$d\alpha/dt = k(T)f(\alpha) \tag{1}$$

According to the Arrhenius equation:

$$k(T) = A \exp(E/RT) \tag{2}$$

where  $\alpha$  was conversion degree, *A* was the pre-exponential factors, *E* was the activation energy, *T* was the reaction temperature and *R* was the universal gas constant. The conversion degree  $\alpha$  was expressed as (Liao and Ma, 2010; Zuru et al., 2004):

$$\alpha = (m_0 - m_t)/(m_0 - m_\infty) \tag{3}$$

where  $m_0$  and  $m_\infty$  were the initial mass and the final mass of the samples, respectively.  $m_t$  was the mass of samples at time *t*.For the non-isothermal experiments, the heating rate  $\beta$  could be described as dT/dt. So Eqs. (1) and (2) could be combined into the following equation:

$$\beta d\alpha/dt = A \exp(-E/RT) f(\alpha) \tag{4}$$

The activation energy of the samples in this paper was estimated by the iso-conversional method. In this work, the Friedman and the Ozawa–Flynn–Wall (OFW) were used to calculate the activation energy. The Friedman method was based on the following equation (Friedman, 1964; Vrandečić et al., 2010):

$$\ln(\beta d\alpha/dT) = \ln[Af(\alpha)] - E/RT$$
(5)

For  $\alpha$  was a constant,  $\ln[Af(\alpha)]$  was also a constant value. Then  $\ln(\beta d\alpha/dT)$  vs. 1/T at different heating rates yields a straight line whose slope allowed evaluation of the apparent activation energy.

The Ozawa–Flynn–Wall (OFW) method was based on the following equation (Grause et al., 2010; Ounas et al., 2011):

$$\ln(\beta) = \ln[AE/RG(\alpha)] - 5.33.5 - 1.0516E/RT.$$
(6)

For  $\alpha$  = constant, *E* could be obtained by the slope of the straight line by plotting ln( $\beta$ ) vs. 1/*T*.

#### 3. Results and discussion

#### 3.1. Thermogravimetric analysis of PS and the RS

As shown in Table 1, rice straw (RS) has less ash content and more volatiles than paper sludge (PS), and it also has a lower nitrogen content and sulphur content. These characteristics favour clean combustion conditions (Vamvuka et al., 2003b). In comparison with PS, the combustion characteristics of RS are better than that of PS due to its high volatile matter and high oxygen content. Both raw materials have a high volatile matter/fixed carbon (VM/ FC) ratio. In this work, the VM/FC ratio for RS is approximately 5.0 and for PS 33.6. Consequently, for RS and PS, the predominant form of combustion will take place via the gas phase oxidation of the volatile species (Gil et al., 2010).

Table	1
Table	1

The ultimate analyses and	proximate analyses of	PS and RS on dry basis.
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Samples	Ultimate analyses (wt.%)					Proximate analyses (wt.%)		
	С	Н	0	Ν	S	V	Fc	Α
PS	22.69	3.32	18.02	1.44	1.42	47.08	1.40	51.52
RS	39.09	9.31	34.51	0.72	0.38	70.35	13.73	15.92

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