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Thermal characteristics and kinetics of refining and chemicals wastewater, lignite and their blends during combustion

Jianbiao Chen [a], Lin Mu [b,a], Jingcheng Cai [a], Hongchao Yin [a,*], Xigeng Song [a], Aimin Li [b]

[a] *School of Energy and Power Engineering, Dalian University of Technology, Dalian 116023, China*
[b] *Key Laboratory of Industrial Ecology and Environmental Engineering of Ministry of Education, School of Environmental Science and Technology, Dalian University of Technology, Dalian 116023, China*

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ABSTRACT

Co-combustion characteristics of refining and chemicals wastewater solid (RS) and Huolinhe lignite (HL) were studied through thermogravimetric analysis (TGA). The combustion behaviors of the blends at various RS to HL ratios were compared with those of the individual samples. Co-combustion experiments showed that the combustion performance of the blends would be improved with the percentage of RS rising. The interactions between RS and HL during the co-combustion could be divided into four phases, and there were no interactions below 120 °C (PH 1) and beyond 700 °C (PH 4), inhibitive effects at the temperature range of 120–700 °C (PH 2 and PH 3). The results of SEM and XRD indicated that the sintering and fusion degree of residues after combustion became more severe with the percentage of RS increasing. The iso-conversional methods, Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO), were used for the kinetic analysis of the combustion process. The results showed that the activation energy of RS was higher than that of HL, and the minimum value was obtained at 75HL/25RS.

1. Introduction

Wastewater generated from chemicals production including petroleum refining is generally characterized by a large amount of highly toxic and poorly biodegradable components, which is named as refining and chemicals wastewater (denoted as RCW) in this work [1,2]. If not properly handled, the wastewater will have some serious and harmful impacts on the ecological environment, especially surface and ground water sources [1]. The conventional wastewater treatment facilities attempt to utilize a great variety of physical, chemical, and biochemical methods to reduce the concentration of refractory organics, but the expensive operating cost and incomplete treatment effects restrict their widespread application. Recently, the incineration disposal in wastewater is getting an increasing attention. It can completely break down the toxic chemicals, greatly reduce volume, and effectively realize waste to energy [3–6].

As an important waste to energy (WTE) technology, the waste incineration can make great contribution to the environmental protection and global warming control [7]. Along with the rapid development of the world economy, the energy requirements and the environmental challenges become more and more severe. Through precisely controlling, once the quality of waste is appropriate, the technology generated energy from wastes to achieve energy recovery and emissions reduction is well worth to be popularized [8]. RCW has a high concentration of organic matters, which can produce certain heat and be seen as a resource instead of as an industrial waste. However, the high moisture content in RCW gives rise to low calorific value, high transport cost, and low burning efficiency. In the wastewater incineration process, the stability of incineration, burning rate, and flame temperature will be reduced by the evaporation of the moisture. Therefore, some favorable improvements should be explored in the thermal treatment of RCW.

Recently published works have indicated that the issue of low calorific value of the waste materials could be solved by adding some auxiliary fuels for co-combustion [8–10]. The co-disposal of wastes in existing facilities can be a practical and low-cost solution to meet the demands of ever-increasing waste productions in the short term [11,12]. Besides that, the well-trained and experienced operators and well-equipped flue gas cleaning facility are of great attractive [12]. Therefore, the co-combustion of wastes and coal are getting more and more attentions. Otero et al. [8] selected a semi-anthracite coal, two distinct sewage sludge and their blends as research objectives to evaluate the influences of the percentage of sewage sludge in the blends on the combustion behaviors and kinetics. Their work indicated that the weight loss process and

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[*] Corresponding author.
E-mail address: hcyin@dlut.edu.cn (H. Yin).

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kinetics of the co-combustion of sewage sludge and coal can be rapidly assessed by the thermogravimetric analysis (TGA). Xiao et al. [13,14] have studied the co-combustion behaviors of sewage sludge blended with various materials, such as straw and coal, coal gangue and coal. The results showed that the combustion performance of the blends was quite different from that of individual samples, signifying that some interactions occurred between raw materials. Concerning industrial wastewater, many researchers mainly focused on pyrolysis. Song et al. [15] have studied the pyrolysis behaviors and kinetics of reed black liquor (RBL) via TGA. The results showed that the pyrolysis process could be divided into three stages. Gea et al. [16] made a deep analysis about the effects of the pyrolysis temperature, CO concentration, and heating rate in N_2 atmosphere on the solid conversion and the devolatilization rate of the thermal degradation of alkaline black liquor from straw. However, the co-combustion behaviors and kinetics of wastewater and coal blends have not been reported before, especially concerning TGA. In the present work, we focused on co-combustion as a means to effectively and rapidly dispose RCW.

In this work, the combustion characteristics of refining and chemicals wastewater solid (RS), Huolinhe lignite (HL) and their blends were studied by TGA at different heating rates. The interactions between RS and HL in the process of co-combustion were investigated under different blending ratios. The kinetics parameters during the combustion process were calculated by using the Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO) methods.

2. Methods

2.1. Preparation of samples

Refining and chemicals wastewater (denoted as RCW) analyzed in the present work was gained from the concentration unit of the wastewater incinerator in Sinopec Shijiazhuang Chemical Fiber Co., Ltd, (Shijiazhuang, PR China). Huolinhe lignite (denoted as HL) provided by Dalian Power Generation Co., Ltd (Dalian, PR China) was selected as the coal sample to be blended with RCW. The ultimate, proximate analysis and lower heating value for RS and HL were performed by Vario Macro cube CHNS elemental analyzer (Elementar, Germany), SDTGA5000 proximate analyzer (SUNDY Enterprise Co., Ltd, Changsha, PR China) and SDACM5000 oxygen bomb calorimeter (SUNDY Enterprise Co., Ltd, Changsha, PR China), respectively. The ash compositions of RS and HL were analyzed by using X-ray fluorescence (XRF) (XRF-1800, SHIMADZU, Japan), and the results were presented in Table 1.

Before being detected in a thermal analyzer, the solid sample of RCW (denoted as RS) should be prepared, as well as various RS and HL blends. Firstly, the lignite sample was air dried in the 5E-MIN6150 drying oven (Kaiyuan Instrument Co., Ltd, Changsha, PR China) at 105 °C until it kept a constant weight. The lignite sample was milled in the GJ-IIA sealed grinder for sample preparation (Xinke New Technology Co., Ltd, Hebi, PR China), and then sieved to obtain the appropriate particle size of less than 178 μm (<80 mesh). With regard to RS, it was prepared using RE-52A rotary evaporator (Yarong Biochemical Instrument Factory, Shanghai, and PR China) at 55 °C, −0.09 MPa, and 150 rpm for 2 h. This dehydration approach was adopted, other than in an oven (105 °C for several hours), to effectively avoid losses of heat-sensitive and low-boiling organics in RCW. The weight percentages of RS can be estimated by the following equations: $y_{RS} = w_{RS}/w_{RCW} \times 100\%$ where y_{RS}, w_{RS}, and w_{RCW} refer to the weight percentage of RS, weight of RS, and weight of RCW, respectively. The weight percentage of moisture can be calculated from the equation: $y_{Moisture} = 100 - y_{RS}$. Therefore, the weight percentages of RS and moisture in the raw RCW are 55.50 and 44.50 wt.%, respectively.

In this study, five distinct weight percentages of RS in the RS and HL blends were taken into consideration, which included 100, 75, 50, 25, and 0 wt.% of RS (RS, 25HL/75RS, 50HL/50RS, 75HL/25RS, and HL, respectively). The binary mixtures were prepared in a magnetic stirring apparatus (Sile Instrument Co., Ltd, Shanghai, and PR China) at 600 rpm for 20 min, for the purpose of sufficient mixing. Considering the high content of moisture in RCW, and effects to achieve rapid and mild dehydration and continuous mixing, the binary mixtures were also obtained by using RE-52A rotary evaporator (Yarong Biochemical Instrument Factory, Shanghai, PR China) at 55 °C, −0.09 MPa, and 150 rpm for 2 h. To remove residual moisture, various solid samples were finally dried at 105 °C for 5 h. After above treatments, the experimental samples were kept in a desiccator until they would be tested in a thermogravimetric analyzer.

2.2. Thermogravimetric analysis and combustion characteristic parameters

Thermal analysis tests (thermogravimetry, TG; differential thermogravimetry, DTG; and differential thermal analysis, DTA) were conducted on the STA 449 C simultaneous thermal analyzer (NETZSCH, Germany). For the purpose of reducing or eliminating the heat and mass transfer limitations, a small quantity of samples (6 ± 0.2 mg) were loaded into the reactor and heated up from room temperature to 1000 °C at the heating rate of 10, 20, 30, and 40 °C min^{-1}. The carrier gas was a dry air with a total gas flow rate of 100 mL min^{-1}. For each sample, the blank experiment was carried out under identical conditions except for the absence of a sample to obtain a thermogravimetric (TG) baseline. Doing subtraction of the TG baseline predetermined, the experimental error caused by buoyancy influences could be eliminated. Each thermal analysis test was repeated at least three times to guarantee the reproducibility of the experimental results. After the combustion reaction, the surface morphology of various residues after combustion was analyzed using JSM-5600LV scanning electron microscope (SEM) (JEOL, Japan). The analysis on mineral compositions in various combustion residues was performed by using X-ray diffraction (XRD) (XRD-6000, SHIMADZU, Japan). The scans were specified from 10° to 70° with a size of 0.02°, and the scanning rate was 5° min^{-1}.

For effectively disposing RS and HL blends and realizing resource utilization as fuel, the rational design and optimal operation of the waste incinerator are essential, and data for each fuel including the influence of the blending ratio on combustion

Table 1
Ash compositions of RS and HL.

Samples	Ash compositions/wt.%											
	Na_2O	SiO_2	SO_3	NiO	Fe_2O_3	Al_2O_3	CaO	Cr_2O_3	K_2O	MgO	TiO_2	Others
RS	40.21	0.95	50.20	3.37	1.72	1.35	0.54	0.48	0.48	0.36	ud④	0.34
HL	0.46	66.80	3.66	ud[a]	3.54	16.99	4.71	ud④	1.86	0.94	0.81	0.23

[a] ud-below the limits of detection.