



The investigation of co-combustion of sewage sludge and oil shale using thermogravimetric analysis



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ABSTRACT

The co-combustion behaviors between sewage sludge and oil shale were investigated in this study. The TGA experiment was given a temperature spanning from 105 °C to 1000 °C by setting the heating rates 10, 20 and 30 °C/min. The combustion characteristics, characteristic index, co-combustion interactions, activated energy and DAEM of blends were studied in this paper. The ignition temperature shifted to an earlier temperature when adding sludge. An inhibition interaction of co-combustion occurred at low temperature and the proportion of sludge with 10% showed the best promoting effects. The average activated energy reached the minimal also when the ratio of sludge was 10%. The average fractional residuals were less than 1.3%. Models showed a good recuperation with experimental data.

1. Introduction

Due to the growth of such facilities, sludge production by the urban wastewater treatment process has been increasing rapidly. Sewage sludge (SS) is formed during wastewater treatment. Over 30 million tons of SS was generated annually in China and this number will rise to 50–60 million per year for 2020 [1]. In Europe, sludge production had reached 10 million tons in 2010 and will be expected to be increased 30% for 2020 [2]. 80% of the sludge does not reach the standards of harmlessness and stability [3]. Therefore, how to hand of this great amount of SS has become an urgent environmental issue. Today, landfill remains as one of the predominant methods of waste disposal worldwide. However, there are no longer available for traditional disposal routes which have the limitation of existing filling capacities and high cost of disposal and suffer from a variety of problems such as noxious gas emission, dust, and leachate production, rodent infestation, etc. [4]. Excess activated sludge is the final form of sewage sludge in the process of waste-water disposal. The excess activated sludge weight proportion of volatile is less than 50%, but it is easy to be ignited due to its low ignited temperature [5]. So the sewage sludge, collected from excess activated sludge, can be used to improve some low-rank fossil fuels by conditioning management.

Oil shale (OS) is an organic-rich, carbonaceous fine-grained sedimentary rock containing significant portions of kerogen and small amounts of bitumen, linked dispersedly within a mineral matrix [6]. Over 10000 billion tons of OS was found all over the world and was

about 40% more than coal [7]. In Estonia, over 90% of its electricity was generated from OS [8]. China is also one of the countries where oil shale has been found rich enough to be mined. The oil-shale resources in China rank No. 4 in the world [9] and Maoming Mine in Guangdong Province is a main oil-shale production area. Compared to other oil-shale production regions, oil shale from Maoming is a typical high-ash fossil fuel [10,11]. It is difficult to use Maoming oil shale as a fired fuel in power plant because of its low rank of combustion property.

That conversion technologies for utilizing biomass as renewable energy resource have been studying by many scholars, such as biochemical conversion (anaerobic digestion and fermentation), thermal conversion (combustion), agrochemical conversion (oil extraction) and thermochemical conversion (pyrolysis, gasification, liquefaction, etc.) [12,13]. Due to the lower and acceptable gas emission, pyrolysis and gasification were both identified to be zero waste methods in the solution of sewage sludge [14–16]. Besides, researchers had found that sludge-based adsorbents and activated carbons were useful for the production of pollutant remediation [17,18]. However, these zero waste methods are still immature and being developed in the technique and facilities. The severe situation of sludge management needs more efficient methods to the reduction of sludge. Combustion, is arousing wide public concern because of its technology maturity and high reduction of sludge [19]. Hong-peng Liu et al. [20] had studied the co-combustion of oil shale semi-coke with torrefied cornstalk and co-combustion increased with the greater degree of heat-treated cornstalk. Limao Huang et al. [3] had searched the thermodynamics and kinetics

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parameters of co-combustion between sewage sludge and water hyacinth. After adding 10–40 wt.% sewage sludge, water hyacinth was improved 1–1.97 times as revealed by the comprehensive combustion characteristic index. There are many literatures about SS and OS co-combustion with other fuel or biomass, while there are almost no reports about the research on the co-combustion of SS and OS.

Thermogravimetric analysis (TGA) has been widely adopted to characterize the thermal process of biomass and fossil fuels and lately it has been used to investigate the thermal decomposition of municipal solid wastes [21,22]. TGA provides some information about characteristic parameters for combustion and this is of great importance to improve cognition of combustion process and to estimate combustion efficiency. The results by TGA can be used for the optimum operational adjustments in combustion process. Up to the present, a great deal of attention has been given to kinetic analysis of co-combustion technology. However, co-combustion between SS and OS has been seldom studied. Co-combustion technology had been investigated in many researches [23,24], while few of them modeled the co-firing process. Knowledge of kinetics is important in the computational fluid dynamics modeling of co-combustion process. The distributed activation energy model (DAEM) is widely used in the thermal process of biomass [25,26]. This method assumes that a large number of parallel, independent reactions take place during the thermal decomposition. The availability and accuracy of DAEM had been proved in many researches [27]. Therefore, it is possible for its application in co-combustion technology.

The aim of this work is to deal with SS and utilize OS, convert them into valuable energy, provide a way of thinking and therefore find a potential solution for management. In this paper, the co-combustion characterization, interactions, kinetic behaviors and the prediction of devolatilization curves using DAEM between SS, OS and their blends through TGA were investigated. The results afforded a theoretical groundwork for the co-combustion equipments design of sludge produced by municipal activities and the development of their resourceful utilization system.

2. Material and methods

2.1. Materials and preparation

In this study, the sewage sludge (SS) was collected from excess activated sludge, produced in Liede Wastewater Treatment Plant of Guangzhou city, Guangdong province of China. The fresh sludge was thickened and dewatered by hydraulic compression in the paper sewage treatment plant. Oil shale (OS) was from Maoming, Guangdong province of China. SS and OS were dried at 105 °C for 24 h in a drying oven to remove the moisture content. Then, the SS and OS were both crushed and sieve to less than 178 μm particle size. Finally, the final samples were stored in desiccators. The ultimate analyses, proximate analyses and higher heating value (HHV) of the dried SS and OS were shown in Table 1. The HHV was calculated by Dulong equation based on ultimate analyses:

$$HHV = 33.93C + 144.32(H - 0.125O) + 9.3S + 1.494N \quad (1)$$

where, C, H, O, S and N were the weight percentages of C, H, O, S and N in dried samples, respectively.

The SS was blended with OS at the weight ratios of 90%, 70%, 50%, 30%, 10% (named as 90SS10OS, 70SS30OS, 50SS50OS, 30SS70OS, 10SS90OS, respectively) for analysis and further experiments.

2.2. Experimental facility and method

The METTLER TOLEDO TGA/DSC1 thermogravimetric simultaneous thermal analyzer was examined experimentally for the co-combustion between SS and OS. Its temperature precision was ± 0.5 °C and microbalance sensitivity was less than ± 0.1 μg.

Table 1

The ultimate analyses, proximate analyses and the result of X-Ray Fluorescence on ash (XRF) of sewage sludge (SS) and oil shale (OS) on dry basis.

Samples		SS	OS
Ultimate analyses (wt.%)	C	21.61	12.08
	H	4.04	2.38
	O	19.42	14.40
	N	3.53	0.57
	S	0.55	1.74
Proximate analyses (wt.%)	Volatile	42.54	22.78
	Fixed carbon	6.61	8.39
	Ash	50.85	68.83
HHV(kJ/kg)		9758.45	5111.28
Ash Composition (XRF)		SS	OS
SiO ₂ (wt.%)		52.77	71.28
Al ₂ O ₃ (wt.%)		22.32	17.34
P ₂ O ₅ (wt.%)		9.65	0.13
Fe ₂ O ₃ (wt.%)		6.22	7.82
K ₂ O(wt.%)		3.21	1.69
CaO(wt.%)		2.77	0.28
MgO(wt.%)		1.19	0.42
TiO ₂ (wt.%)		0.7	0.52
SO ₃ (wt.%)		0.43	0.28
MnO(wt.%)		0.21	0.12
Na ₂ O(wt.%)		0.13	/
Cr ₂ O ₃ (wt.%)		0.09	0.06
ZnO(wt.%)		0.08	/
BaO(wt.%)		0.06	/
NiO(wt.%)		0.05	/
CuO(wt.%)		0.04	/
SrO(wt.%)		0.03	0.01
ZrO ₂ (wt.%)		0.02	0.01
Cl(wt.%)		0.02	/
As ₂ O ₃ (wt.%)		0.01	0.01
Y ₂ O ₃ (wt.%)		/	0.01

Blank experiments were carried out without samples to obtain the baselines, which were used to calibrate the experiments with samples, at different heating rates (10, 20 and 30 °C/min). Under the atmosphere of air (a flow rate of 80 ml/min), the samples for co-combustion investigations were heated from 105 °C to 1000 °C. Besides, samples were kept at 10 ± 1 mg for avoiding heat transfer limitations. All the experiments were carried out at least twice to decrease the test error and all the experiments were conducted twice and the reproducibility was satisfied.

2.3. Iso-conversional method

The kinetics of heterogeneous solid-state thermal degradation is dominated by the fundamental equation [28,29].

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(\frac{-E_a}{RT}\right)f(\alpha) \quad (2)$$

where t for time, T for the reaction temperature, A for the pre-exponential factor, $k(T)$ for the rate constant which is temperature dependent, $f(\alpha)$ for the dependence of extent of conversion (α) in relation to reaction model, E_a for the apparent activation energy at the conversion α and R for the universal gas constant (8.314 kJ/mol·K).

The conversion degree α typically reflects the progress of the transformation of a reactant to products described by equation:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (3)$$

where m_0 and m_∞ for the initial mass and the final mass, respectively; m_t for the mass of the sample at temperature T .

When heating rate $\beta = dT/dt$ is introduced, Eq. (2) can be transformed to:

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

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