Applied Energy 86 (2009) 1741–1745

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Isoconversional kinetic analysis of co-combustion of sewage sludge with straw and coal

Han-min Xiao *, Xiao-qian Ma, Zhi-yi Lai

School of Electric Power, South China University of Technology, 381 Wushan Road, Guangzhou 510641, PR China

ARTICLE INFO

Article history:
Received 25 February 2008
Received in revised form 14 November 2008
Accepted 16 November 2008
Available online 23 December 2008

Keywords:
Co-combustion
Sewage sludge
Straw
Thermogravimetry
Isoconversional

ABSTRACT

In this paper, the co-combustion behaviour of sewage sludge with straw and coal were carried out in a thermogravimetric analyzer under different atmospheres and at different heating rates (10, 20 and 40 K min^{-1}) in the temperature range from ambient temperature to 1000 °C. TG and DTG curves were analysed. The Flynn–Wall–Ozawa's (FWO) and Kissinger–Akahira–Sunose's (KAS) isoconversional methods were used to yield dependency of the activation energy of reduction process on the degree of conversion. The values of E_α were obtained. The results indicate that: with the increase of heating rate, the maximum weight loss rate of samples increase obviously. The activation energy is practically constant in the $0.2 \leqslant \alpha \leqslant 0.9$ range, with the average values of $E_\alpha = 137.27$ and 132.38 kJ mol^{-1} calculated by FWO and KAS methods, respectively.

1. Introduction

Treatment of municipal wastewater results worldwide in the production of large amounts of sewage sludge [1]. Sewage sludge is harmful for human and environment if not be dealed with. Recycling in agriculture, landfilling, dumping into sea and incineration are the four sludge disposal methods which are currently used. The limitations facing landfilling and recycling, and the planned ban on sea disposal lead to the expectation that the role of incineration will increase in the future [2]. The co-combustion of sewage sludge together with coal, under the appropriate control, may be a secure outlet and generate profits through energy [3]. In the literature there are some recent works on the co-combustion of sewage sludge and coal [4–19]. The 50 wt% sludge–coal blends show two different regions of reactivity. In the lower temperature region (about $T < 350$ °C), the blend reactivity is similar to that of sludge, while in the higher temperature region ($T > 350$ °C), it is similar to that of coal [5]. Combustion of sewage sludge may be a viable solution for its management in some cases and so is its co-combustion with coal [6].

With the development of world industry, the supply of energy and the problem of pollution are getting more and more serious. It is necessary to generate energy from renewable resources to reduce both greenhouse gas emissions and the consumption of fossil fuels. Biomass is a suitable candidate for greater use. Co-firing of coal and biomass is an area worthy of exploration to improve the energy output. It can be a practical and attractive approach to increase the use of renewable energy while maintaining similar power supply from fossil fuels and reducing greenhouse gas emissions [20]. Several authors have studied the behaviour of the co-combustion of coal and biomass [21–24]. The co-combustion behaviour of coal with wastes and biomass and the related toxic gaseous emissions were investigated [25]. Co-firing biomass with coal in existing power plants offers a relatively inexpensive and efficient option for increasing near-term biomass energy utilization [20]. There is also a literature to study effect of the co-combustion of sewage sludge and biomass on emissions and heavy metals behaviour [26].

The analysis of the co-combustion already had been investigated by numerous of studies, however, there are fewer literatures to study the co-combustion of sewage sludge with straw and coal.

In this work, thermogravimetric analysis was employed to investigate the co-combustion characteristics of sewage sludge with straw and coal. The aim of this work is to use a simple set of TGA to give an appraisal to the co-combustion sewage sludge together with straw and coal. The Flynn–Wall–Ozawa's (FWO) and Kissinger–Akahira–Sunose's (KAS) isoconversional methods were use to analysis of co-combustion of sewage sludge with straw and coal. Sewage sludge is an injurant. Straw is a renewable resource. Coal is still the most popular fuel, and this situation will not be changed in near future. There are many old coal-fired heat-generating plants in China, which now need urgently the capital for modernization. It is, therefore, very significant to research the combustion of sewage sludge with straw and coal.

* Corresponding author. Tel.: +86 020 87110232.
E-mail address: xhanmin@sohu.com (H.-m. Xiao).

0306-2619/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.apenergy.2008.11.016

2. Experimental

2.1. Materials and measurements

The experimental material of straw was collected from a rural area of Xuzhou city Jiangsu Province in China. The sewage sludge was obtained from the wastewaters treatment plant of Guangzhou city Guangdong Province in China. The materials' ultimate and proximate analyses are shown in Table 1. The initial coal and straw sample was milled and sieved. The coal particle diameter is less than 74 μm, the straw particle diameter is less than 200 μm. The sewage sludge sample be dried in oven at 105 °C for 5 h, and then was milled and sieved. The particle is less than 200 μm in diameter. Finally, the sewage sludge was mixed with straw and coal in the proportion of 20, 10 and 70 (wt%).

Thermogravimetry (TG) tests were carried out on NETZSCH STA 409 Pc simultaneous analyzer. The TG baselines were corrected by subtraction of predetermined baselines run under identical conditions except for the absence of a sample. Sample (10 ± 0.5 mg) was placed in an Al_2O_3 ceramic pan. To simulate the combustion and pyrolysis processes, six different atmospheres were used, all with a flow of 100 ml min^{-1} at heating rate 40 K min^{-1}. These were 80% nitrogen/20% oxygen, 70%nitrogen/30% oxygen, 60% nitrogen/40% oxygen, 40% nitrogen/60% oxygen, 30% nitrogen/70% oxygen and were, respectively, designated Nit80, Nit70, Nit60, Nit40 and Nit30. Other three samples were heated from ambient temperature to 1000 °C at heating rate 10, 20 and 40 K min^{-1} under artificial air (20/80 in O_2/N_2) flow rate of 100 ml min^{-1}.

2.2. Kinetic theory

The kinetic equation of common type can be generally written as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)P^n(O_2) \tag{1}$$

where α is the conversion degree of sample, t is time, T the absolute temperature, $f(\alpha)$ is a function, the type of which depends on the reaction mechanism, $P(O_2)$ is the oxygen partial pressure, n is the power dependency of the oxygen partial pressure, $k(T)$ the temperature dependent rate constant. $k(T)$ usually described by the Arrhenius equation

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where k_0 is pre-exponential or frequency factor, E is the activation energy, R is the universal gas constant.

The degree of conversion of the reduction process is expressed as

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{3}$$

where m_0 is the initial mass of the sample, m_t the mass of the sample at time t, m_∞ the final mass of the sample in that reaction.

It was considered that the apparent pre-exponential factor consists of two terms: a typical Arrhenius kinetic constant and the partial pressure of oxygen with the power of a coefficient n, the equation is

$$A = k_0P^n(O_2) \tag{4}$$

Inserting Eqs. (2) and (4) into Eq. (1), its form is changed to

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{5}$$

An integration function is shown as below

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right)dT \tag{6}$$

where $g(\alpha)$ is the integral kinetic function or integral reaction model when its form is mathematically defined, $\beta = dT/dt$ the heating rate of combustion.

There are different methods to carry out the analysis of kinetic data. According to the mathematical model, there are two possible approaches: model-fitting and isoconversional (free model). According to the results of the ICTAC kinetics project, isoconversional methods can up to this challenge among a few methods [27]. In non-isothermal kinetics, the Friedman (FR), Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO) and Vyazovkin (V) methods are the most popular representatives of the isoconversional methods. The methods of Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) were used in this investigation.

The Flynn–Wall–Ozawa (FWO) method [28,29] based on the following equation:

$$\ln\beta = \ln\left[\frac{AE_\alpha}{Rg(\alpha)}\right] - 5.331 - \frac{E_\alpha}{RT} \tag{7}$$

For α = const., $\ln\beta$ vs. $1/T$ obtained at several heating rates yields a straight line whose slope allows evaluation of the apparent activation energy.

The Kissinger–Akahira–Sunose (KAS) method [30] based on the following equation:

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left[\frac{AR}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{RT_\alpha} \tag{8}$$

The E_α for different conversion values can be calculated from a plotting $\ln\left(\frac{\beta}{T_\alpha^2}\right)$ vs. 1/T.

3. Results and discussion

3.1. TG results

3.1.1. TG and DTG analysis of fuels

Figs. 1 and 2 show TG and DTG profiles of coal, sludge, straw and their blend, respectively. The blend is the mixing of sewage sludge, coal and straw, which were mixed with straw and coal in the proportion of 20, 10 and 70 (wt%). Four samples were heated from ambient temperature (30 °C) to 1000 °C at heating rate 40 K min^{-1} under artificial air (20/80 in O_2/N_2) flow rate of 100 ml min^{-1}. Table 2 shows the results of thermogravimetric analysis for coal, sludge, straw and their blend.

Table 1
Ultimate (wt%, daf.) and proximate analyses (wt%, dB) of sewage sludge, coal and straw.

Samples	Ultimate analyses (wt%, daf.)					Proximate analyses (wt%, dB)			
	C	H	O	N	S	M_{ar}	V_{ar}	A_{ar}	FC
Sewage sluage	10.12	1.79	5.29	1.53	0.58	53.85	16.74	26.84	2.57
Coal	58.84	5.70	8.21	0.73	0.38	13.43	26.90	12.72	51.33
Straw	44	5.9	49.5	0.7	0.15	4.4	66	13.6	13.6