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Pyrolysis and combustion kinetics of sludge–camphor pellet thermal decomposition using thermogravimetric analysis

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ABSTRACT

The pyrolysis and combustion characteristics of sludge pellet (SP), camphor pellet (CP) and sludge–camphor pellet (SCP, 50% sludge ratio) were studied via thermogravimetric analysis. The samples were heated from ambient temperature to 1073 K at various heating rate (5, 10, 20, 40 K/min) in nitrogen and air atmosphere. Heating rate had a substantial effect on mass loss and mass loss rate in both pyrolyzing and oxidizing conditions. The thermal behavior of SCP was the integration of SP and CP. Onset and offset temperatures of SCP lay between that of CP and SP in various heating rate. The kinetic parameters of the process were evaluated using two iso-conversional models (Flynn–Wall–Ozawa and Starink). Kinetic analysis results showed that activation energy was highly depended on conversion which indicated the existence of a complex multi-step mechanism. E_α value for the sludge–camphor pellet (SCP) was lower than the single pellet (SP and CP). Some synergistic effects happened between sludge and camphor during pyrolysis.

1. Introduction

Recently, more and more scientists and organizations urge to research alternative sources of energy due to the serious energy shortage problem and environmental issues. On the other hand, the treatment and disposal of sewage sludge have become environmental problems in China. It was reported that the amount of sewage sludge (at a moisture content of 80%) would increase from 30 million metric tonnes in 2012 to 34 million metric tonnes in 2015 [1]. In order to reuse the sludge effectively, pelletization has been applied as a processing technology for further pyrolysis and combustion [2].

Refuse derived fuel (RDF) is a recent developing technology of an alternative energy from the waste [3–7]. The RDFs can be divided into seven categories according to the American Society for Testing and Materials (ASTM) classification for RDFs. RDF-5 is defined as the dense or compressed combustible waste fraction in the form of pellets, slugs, cuvettes, or briquettes. The prime characteristics of RDF-5 are its size, high and constant heating value (usually two-thirds of coal), low level of pollution, and that it does not emit a stink [8]. In addition, as it is shrank to one-tenth of its original size after extruding, it can reduce the costs of storage, transportation and logistic handling. The conventional method for sludge RDF production is to mix the sludge with auxiliary fuel (coal, refuse, sawdust, etc.), desulfurizer and binder. Chen et al. [8] mixed sludge and sawdust with asphalt as binding agent to produce RDF-5. It concluded that the ash content of derived fuel made from organic sludge was less than 20% and its calorific value reached 5000 kcal/kg which was higher than the derived fuels standards. Zhao et al. [9] used dewatered sewage sludge with moisture content about 80% and the leaves of Chinese parasol as raw materials. The steam explosion pretreatment was applied as a thermo–mechanical–chemical process to improve sewage sludge dewaterability and thus to enhance the heating value of solid fuel. Jiang et al. [2] investigated the effects of pressure, die temperature, moisture content, sludge ratio and biomass size on the pellet properties for co-pelletization of sludge and biomass (Chinese fir, camphor and rice straw, respectively). It suggested that sludge RDF could be a suitable method for energy recovery and environmental protection.

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Nowadays, pelletized recovered solid waste fuel is often applied in pyrolysis, gasification and incineration systems to provide feedstock with a stabilized quality and high heating value [3,10–13]. The utilization of solid pellet fuel as an alternative fuel has attracted more and more attention. However, prior knowledge of reaction kinetics would be crucial before any attempt to utilize solid pellets for thermo-chemical processes. A kinetics study is very helpful for understanding the devolatilization/degradation mechanisms, rate of reaction, reaction parameters and to predict the products distribution. It could in turn facilitate the design of reactors and the optimization of the operating conditions. Thermogravimetric analysis (TGA) has been widely used for the evaluation of kinetic parameters in thermal degradation of biomass. Several studies have been conducted, focusing on the pyrolysis or combustion kinetic analysis for biomass pellet [14–17]. For example, major decomposition of switch grass pellet occurred with 40–75% conversion with an activation energy of 314 kJ/mol during pyrolysis. In air, the main decomposition occurred at 30–55% conversion with an activation energy of 556 kJ/mol [15]. However, the information on pyrolysis and combustion kinetic analysis of sludge–biomass pellet has been still very limited so far.

In this paper, the thermogravimetric analysis was applied to evaluate the pyrolysis and combustion behaviors of sludge pellet, camphor pellet and sludge–camphor pellet with sludge ratio of 50%. The kinetic parameters of sludge–biomass pellets in inert and oxidation atmosphere were calculated by two iso-conversional methods: the Flynn–Wall–Ozawa (FWO) method and the Starink method. The current study can potentially contribute to deeper understand the pyrolysis and combustion characteristics of sludge–biomass pellets.

2. Materials and methods

2.1. Raw materials

In this study, sewage sludge labeled as SS coming from Guozhen wastewater treatment plant in Changsha, Southern China. Camphor (*Cinnamomum camphora* (L.) J. Presl) was acquired as the wood material from a furniture factory. The ultimate analysis, proximate analysis, chemical analysis and higher heating values of the raw materials were presented in Table 1. The methods applied for the above analysis have been reported in our previous paper [2,18].

2.2. Pelletization

The sludge and camphor were dried, pulverized and screened into fractions of particle diameter less than 0.45 mm, respectively. After then, 15% moisture content samples were obtained by adding predetermined amounts of deionized water onto the particles uniformly. Sludge sample and camphor samples were weighed and mixed manually to produce the required blends. In this study, sludge pellet (SP), sludge–camphor pellet (wt. 50%) (SCP), and camphor pellet (CP) were produced using a single pellet press unit which has been described in our previous papers [2,18]. For each experimental trial, approximately 0.80 g of samples was fed into the die channel and compressed with a predefined procedure controlled at 69 MPa and 110 °C. The higher heating values of SP, SCP and CP were 15.86 MJ/kg, 17.25 MJ/kg, and 18.52 MJ/kg, respectively.

2.3. Thermogravimetric analysis (TGA)

To verify if the sludge–biomass pellet could be used as substitute fuel, SP, SCP and CP were selected to conduct the thermogravimetric analysis to investigate the combustion and pyrolysis characteristics [9,15]. The instrument was periodically calibrated using indium (In), tin (Sn) and calcium oxalate (CaC_2O_4) to ensure accurate results of the TGA. Nitrogen and air were used as carrier gases at a flow rate of 100 mL/min. Experiments were carried out from ambient temperature to 1073 K at four heating rates of 5, 10, 20, and 40 K/min. Each run was done in triplicate. The relative error among the data of TGA was controlled to less than 5%.

2.4. Kinetic modeling

Iso-conversional methods were applied for the determination of activation energy (E_α) and pre-exponential factor (A). These are model-free methods which depend on thermogravimetric data set based on multiple heating rates at a particular fraction of conversion. The basic rate equation applied in all kinetic studies is described by Eq. (1).

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where α is fuel conversion, and is given by

$$\alpha = \frac{W_i - W}{W_i - W_f} \tag{2}$$

where W_i, W, W_f is the initial, instantaneous and final weights of the sample, respectively. The temperature dependence rate constant is expressed in terms of the Arrhenius equation as in Eq. (3).

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E_\alpha}{RT}\right)f(\alpha) \tag{3}$$

where A, pre-exponential frequency factor (min^{-1}); E_α, activation energy (J/mol); R, gas constant (8.314 J/mol K); T, absolute temperature (K); $f(\alpha)$, reaction model.

At constant linear heating rate $\beta = dT/dt$, integrating Eq. (3) by separation of variables gives:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta}\int_{T_0}^{T} \exp\left(\frac{-E_\alpha}{RT}\right)dT \tag{4}$$

Let $x = -E_\alpha/RT$, Eq. (4) becomes:

$$g(\alpha) = \left(\frac{AE_\alpha}{\beta R}\right)\left\{-\frac{\exp^x}{x} + \int_0^\infty \left(\frac{\exp^x}{x}\right)dx\right\} = \left(\frac{AE_\alpha}{\beta R}\right)P(x) \tag{5}$$

The term $P(x)$ is the temperature integral and has no exact analytical solution. Therefore, only numerical integration or approximations can be used to solve the complex integral. The difference

Table 1
Properties of raw sewage sludge and camphor sample.

Analysis	Ultimate analysis (d.b. wt.%)				Proximate analysis (r.b. wt.%)				Chemical analysis (d.b. wt.%)				HHV (MJ/kg)
	C	H	N	S	Moisture	Volatile	Fixed Carbon	Ash	Protein	Hemicellulose	Cellulose	Lignin	
Sludge	36.11	5.25	6.50	1.03	5.42	57.22	6.09	31.27	35.5	–[a]	–[a]	–[a]	15.59
Camphor	48.18	6.09	0.70	0.00	6.67	79.02	12.53	1.78	–[a]	20.82	38.87	24.40	18.40

d.b. dry basis, r.b. received basis.
[a] Not measured.