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Research Paper

Study of the pyrolysis of municipal sludge in N_2/CO_2 atmosphere

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HIGHLIGHTS

- The pyrolysis properties of wet and dried municipal sludge are studied.
- With the existence of moisture, the releasing of volatiles is enhanced and a large amount of CO_2 and NH_3 generates earlier.
- CO_2 makes a difference to the pyrolysis behavior in high temperature.
- Kinetics parameters are calculated by using Coast-Redfern method.

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ABSTRACT

The present study aims to explore the pyrolysis characteristics and gaseous product of municipal sludge including dry sample (DS) and wet sample (WS). The experiments were performed under atmospheres of different N_2/CO_2 ratios using TG-FTIR. All of the thermal process could be divided into two stages. With the existence of moisture, the releasing of volatiles was enhanced and a large amount of CO_2 and NH_3 generated earlier. CO_2 was inert in first stage and became reactive in second stage. The char gasification by CO_2 resulted in more mass loss and macropores generation. As the CO_2 concentration increased, the corresponding peak shifted to lower temperature. The kinetic parameters were calculated by Coast-Redfern method and agreed with the pyrolysis properties observed. The activation energy and pre-exponential factor increased (or decreased) simultaneously, illustrating kinetic compensation effect.

1. Introduction

Municipal sludge is the inevitable by-product of municipal wastewater treatment process. Along with the urbanization process, the yield of municipal sludge is increasing rapidly. It is estimated that the total production of municipal sludge in China will have reached 60 million–90 million tons by 2020. Municipal sludge is a heterogeneous mixture, rich in organic matter and N, P, K nutrient elements, also containing heavy metals and pathogenic organisms. Due to its content of hazardous substances, it would result in environmental problem and human disease without proper disposal.

The disposal of sludge is a great challenge. The common used methods such as landfill and dumping possibly caused secondary pollution to groundwater and soil. As the laws and regulations of sludge management is getting stricter, their application would be limited [1]. Pyrolysis is regarded as one of the most promising treatment of sludge. Its distinct advantages reflect in generating valuable product including syngas, bio-oil and biochar as well as reducing volume, eliminating pathogens. The syngas and bio-oil of high caloric value with further processing can be used as fuel [2,3]. Bio-char also has many application such as soil conditioner, adsorbent and construction materials [4,5]. In addition, the majority of heavy metals are concentrated in pyrolysis residues except volatile elements Hg and Cd [6,7]. The pyrolysis of sludge have already been implemented. The Sewage sludge utilization plant in Balingen, German has been in continuous operation since 2002 [8]. The plant converts 1250 tons sludge per year into syngas that is used as fuel for a thermal power plant and thus recovers energy as heat and electricity.

The relevant research about pyrolysis of sludge has intensified in recent years. In most of these experiments, dried sludge was usually used as the object of study [9,10]. However, initial sludge contains a large amount of moisture. And it consumes a lot of energy to remove the moisture content [11]. In the process of pyrolysis, the existence of moisture in wet sludge would make a difference to pyrolysis characteristics. As pointed out in several papers [12,13], the presence of water in the sludge increases the

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production of gases and also favors the generation of hydrogen. So far little information is available about the thermal decomposition characteristics of wet sludge. Therefore, both wet and dry municipal sludge are taken as experiment samples in our work to explore the possibility of combining cost reduction and pyrolysis characteristics improvement together.

Many research have reported that the pyrolysis process and product were affected by many factors such as particle size, temperature, heating rate and the composition of sludge [14–17]. However, few studies focused on the effect of CO_2 atmosphere on sludge pyrolysis. CO_2 accounts for a large fraction of the pyrolytic gas. Recycling gas product stream and then providing CO_2 as carrier gas instead of N_2 would result in the enrichment of CO_2 in the flue gas, which helps carbon capture and storage (CCS) and reducing the greenhouse gas emission [18–20]. Such study also could assess a better understanding to oxy-fuel combustion, which is one of the most primary technologies for CO_2 capture. Some research about coal, biomass have shown that the participation of CO_2 made a great difference to the pyrolysis behaviors. TG-FTIR analysis of coal pyrolysis showed that replacing N_2 with CO_2 enhanced the volatile releasing rate and prevented the calcite from decomposing [21]. The study of lump coal pyrolysis indicated that CO_2 atmosphere was favorable to the release of H_2O and absorbing gases. The fast pyrolysis process of biomass showed that CO_2 impacted the final gas yield and composition, as well as the char yield and properties [22]. The reaction between CO_2 and the nascent char above 600 °C occurred at a considerable high rate correlated with thermal cracking and resulted in an extra mass loss [23]. In other words, CO_2 may play the role as reactant or product and thus changes the pyrolysis behavior. It is worthy to study the impact of CO_2 concentration on the sludge pyrolysis further.

The objective of the present work is to explore the pyrolysis characteristics and gaseous product of municipal sludge in different N_2/CO_2 atmosphere. The experiments of the wet/dry sludge in different atmospheres were carried out using Thermogravimetric Analyzer and Fourier Transform Infrared Spectrometry (TG-FTIR). TG is widely applied to monitor mass change of a solid sample as function of temperature at given heating rates, reflecting the reaction process. The recorded TG data was used to study pyrolysis characteristics and evaluate the kinetic parameters, which is useful for optimization of actual operation condition. FTIR could identify the evolved gas with time and deepen the understanding of the pyrolysis process. Furthermore, Scanning Electron Microscopy and Energy Dispersive Spectrometer (SEM-EDS) were used as auxiliary means to get the surface morphology and element distribution of the solid residue.

2. Methods

2.1. Material

The municipal sludge from Liede Wastewater Treatment Plant in Guangzhou city, Guangdong province of China was used as the raw material. The dry sludge sample was prepared at 105 °C in an air dry oven for 24 h until the mass no longer changed. The wet sludge sample after drying in the same oven for 4 h was obtained with moisture content of 30%. The samples were abbreviated to DS and WS respectively. The ultimate and proximate analyses of the sample on dry basis were shown in Table 1.

2.2. Experiment

The pyrolysis experiments were carried out in a Thermogravimetric Analyzer (METTLER TOLEDO TGA/DSC 1/1600). According to the moisture content, the initial weight of sample was maintained at 7 ± 1 mg for DS and 10 ± 1 mg for WS respectively to ensure the same quality of dry basis. To investigate the effect of the atmosphere, the carrier gases were N_2, CO_2, $75\%CO_2 25\%N_2$, $50\%CO_2 50\%N_2$, $25\%CO_2 75\%N_2$ respectively, with a total flow rate of 80 mL/min^{-1}. The samples were heated from ambient temperature to 1000 °C at the rate of 10/30/50 °C/min, and then remained at 1000 °C for 5 min to complete reaction. Blank experiments were carried out using empty crucible under different atmosphere at different heating rate to obtain the baselines, which would be deducted in the experiments with sample.

Gaseous products from TGA passed through a transfer line into Fourier Transform Infrared Spectrometry (Nicolet™ iS™ 10 FT-IR spectrometer). The transfer line should be preheated to 225 C and kept at the temperature during the experiment, in order to prevent gas condensation. FTIR scan wave number range is from 4000 to 500 cm^{-1}, with resolution better than 0.4 cm^{-1}. FTIR spectra was used to analyze the evolved gas under N_2 atmosphere in real time. Before FTIR scanning, pass N_2 for 5 min and correct the background baseline. In CO_2 atmosphere, however, the high absorbance of CO_2 would cause interference due to the limitation of FTIR technique and thus the untrusted result should be discarded.

2.3. Kinetic analysis

The basic dynamic equation for heterogeneous solid-state reactions is generally given by:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} k(T) f(\alpha) \quad (1)$$

where α is the conversion rate of the sample, t (min) is time, β is the heating rate, T (K) is the absolute temperature, $k(T)$ is the temperature-dependent constant, $f(\alpha)$ is the reaction mechanism function. Expression of conversion rate is as follows:

$$\alpha = m_o - m_t / m_o - m_f \quad (2)$$

where m_o, m_t, m_f are initial mass, mass at time t and final mass of the sample respectively. $k(T)$ is usually described by the famous Arrhenius equation:

$$k = A\exp(-E/RT) \quad (3)$$

where A is the pre-exponential factor, E is the apparent activation energy, R is the universal gas constant.

For nth-order reaction, $f(\alpha)$ is expressed as $f(\alpha) = (1-\alpha)^n$. Integration of the function $f(\alpha)$ is defined as:

$$G(\alpha) = \int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT \quad (4)$$

$G(\alpha)$ has no analytical solution and only get numerical and approximate solutions. An approximate equation can be obtained by Coats-Redfern method and rearranged into the following form [24,25]:

Table 1
Ultimate and proximate analyses of sample on dry basis.

Sample	Ultimate analyses (wt%, d)					Proximate analyses (wt%, d)		
	C	H	O	N	S	Volatile	Fixed carbon	Ash
Municipal sludge	26.52	4.556	19.434	4.32	0.6	48.82	6.61	44.57