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IR and kinetic study of sewage sludge combustion at different oxygen concentrations

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ABSTRACT

Thermal degradation of sewage sludge disposal is attracting more attention due to the increase in municipal wastewater treatment. In this work the performance of the thermochemical processes of sewage sludge at different oxygen concentrations was investigated by thermogravimetric (TG) and Fourier transform infrared analysis (FTIR) study. The oxygen concentrations were varied systematically from 0 to 20%, representing heating process from pyrolysis to full combustion. The evolutions of surface functional groups in these processes were also investigated by *in situ* diffuse reflectance infrared Fourier transform spectra (DRIFT), which helped to understand the reaction mechanism during the thermal degradation, especially when the reaction conditions were different. The heating process was divided into four stages, dehydration (below 200 °C), devolatilization (200–400 °C), char combustion (above 400 °C), and secondary devolatilization (above 650 °C). Reaction mechanism and kinetic model was proposed based on the stages of heating process. Oxygen concentration was presented explicitly in the reactions and kinetic equations. The model was then developed for the heating processes at different oxygen concentrations, followed by fittings of kinetic parameters. Some of the parameters in the model were fixed as constants to minimize the number of variations. The fitted model agreed well with the TG curves at different oxygen concentrations and could illustrate the evolution of intermediates and products during the heating process. The developed kinetic model could be further applied for the modeling of sewage sludge pellets combustion considering oxygen diffusion process.

1. Introduction

Sewage sludge disposal is attracting more attention due to the increase in municipal wastewater treatment. Owing to the land limitations and stringent regulations, the traditional methods for the disposal of sewage sludge including landfills and agricultural application are suffering from more and more pressure. Thermal conversion methods such as pyrolysis, gasification, hydrothermal carbonization, liquefaction and incineration appear to be quite promising for sewage sludge treatment (Yu et al., 2017; Xu et al., 2017; Thomsen et al., 2017). Thermal technologies can not only sterilize the sludge, but also achieve considerable volume reduction and energy recovery. Incineration is the most widely used method in many countries. Sewage sludge incineration is an attractive option because it minimizes odor, significantly reduces the volume of the starting material and thermally destroys organic and toxic components (Kijo-Kleczkowska et al., 2016; Chan and Wang, 2016; Kijo-Kleczkowska et al., 2016). However, direct sewage sludge incineration is unacceptable because of its high cost and large amount of gaseous pollutants caused by unstable combustion. This problem could be overcome by combining sewage sludge with biomass or coal to produce densified solid fuel pellets (Xu et al., 2017; Jiang et al., 2016; Ruiz-Gomez et al., 2017).

The thermochemical properties of sewage sludge are different with the conventional fuels like coal and biomass, due to its high ash content, serious fouling problems, and low carbon conversion efficiency. It is necessary to understand the mechanism and kinetics of the heating process of sewage sludge. Further understanding about the combustion behaviours and kinetics is of great importance.

Up to now, enormous research works were conducted to understand to the thermochemical process of sewage sludge (Shana et al., 2013; Hayhurst, 2013; Lin et al., 2016) and such works were extensively reviewed (Manara and Zabaniotou, 2012). Both pyrolysis and combustion of sewage sludge were extensively studied

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by thermogravimetric analysis (TGA) (Lin et al., 2016; Shao et al., 2008; Conesa et al., 1998). The gaseous products during the thermochemical process, such as H_2, CH_4, CO_2, and H_2O, are identified by FTIR and mass spectrometry (MS) (Lin et al., 2016; Shao et al., 2008; Magdziarz and Werle, 2014). The properties of pyrolysis and/or combustion of sewage sludge are also frequently compared with coal and biomass (Kijo-Kleczkowska et al., 2016; Magdziarz and Wilk, 2013) and it was concluded that the thermal and kinetic behaviours of the main components of sewage sludge are similar to those reported for hemicellulose, cellulose, and lignin present in lignocellulosic biomass (Manara and Zabaniotou, 2012; Barneto et al., 2009). Co-combustion of sewage sludge and biomass/coal is also extensively studied and was found to be beneficial for the combustion process (Jiang et al., 2016; Magdziarz and Wilk, 2013; Otero et al., 2002).

When co-combusted with biomass and/or coal, pellets are always made to densify the fuels and to facilitate the transportation and combustion process (Kijo-Kleczkowska et al., 2016; Jiang et al., 2016; Li et al., 2015). It has also been reported that the addition of sewage sludge could help to reduce the diversity of pellet hardness caused by the heterogeneity of biomass (Jiang et al., 2014). During the application of the combustion process, kinetic model is a useful tool to help with the design and operation of furnaces. It is necessary to develop the kinetic model for sewage sludge. Mass transfer of oxygen is a very important factor during the modeling of pellet combustion since the oxygen concentration may vary a lot inside the pellets. Effect of mass transfer is expected to be more important for the co-combustion of sewage sludge with coal/biomass since ash contents in sewage sludge is very high. The large amount of ash may block the pores in the pellets where oxygen is diffused. Therefore, it's necessary to develop a kinetic model for sewage sludge which fully involves the effect oxygen.

There are numerous kinetic models developed in literature to study the thermal degradation characteristics of fuels. Generally, there are two types of methods to correlate thermogravimetric results with kinetic models, i.e., model-fitting method and model-free method (mostly iso-conversional). For model-fitting methods, different reaction models are first proposed and then the kinetic parameters are fitted from the experimental data (Branca and Di Blasi, 2013; Conesa and Domene, 2011; Anca-Couce et al., 2014). The model-free methods require several kinetic curves to perform the analysis. A significant number of analytical methods have been developed to calculate the kinetic parameters of activation energy (Ea) and pre-exponential factor A in the Arrhenius equation. Depending on the type of data used, the methods could be divided into two groups, differential methods, such as Friedman method (Friedman, 1969), and integral methods, such as Kissinger-Akahira-Sunose method (Kissinger, 1956), Flynn-Wall-Ozawa (Ozawa, 1965; Flynn and Wall, 1966) method and Coats-Redfern method (Coats and Redfern, 1964). For most of these available models, only effect of temperature considered in the fitted Arrhenius Equations. However, the effect of oxygen is seldom included as a parameter in these models.

We previously developed a kinetic model for the combustion of biomass (spruce, sophora, wheat straw, and peanut straw), where effect of oxygen was included explicitly in the char combustion step (Cheng et al., 2017). The kinetic model consisted of three devolatilization reactions (for cellulose, hemicellulose, and lignin) and one char combustion reaction. In the devolatilization steps, char and gas were formed as products and oxygen was not involved in the reactions. A power law dependence of oxygen was assumed for the char combustion stage. But this model could not be applied directly for sewage sludge due to the different combustion behaviour and composition of the fuels. The devolatilization reactions could not be classified as cellulose, hemicellulose, and lignin for sewage sludge. The behaviour of sewage sludge combustion should be carefully studied first and then the kinetic model could be proposed and developed based on the experimental observations.

In this paper, the performance of the thermochemical processes of sewage sludge at different oxygen concentrations is studied by TG and FTIR study. The oxygen concentrations are varied systematically from 0 to 20% (close to the oxygen concentration of air), representing heating process from pyrolysis to full combustion. The evolutions of surface functional groups in these processes are also investigated by *in situ* DRIFT. Based on the observed combustion behaviour, kinetic models, with oxygen presented explicitly in the reaction and kinetic equations, are then developed for the heating processes at different oxygen concentrations, followed by fittings of the kinetic parameters.

2. Material and methods

2.1. Material

The material used in this study is municipal sewage sludge obtained from Guozhen Wastewater Treatment Company in Changsha, China. The received wet sludge contains over 80% moisture and was then dried in air at 40 °C for 48 h. The size range of the sample powders is 80–120 μm, with an average of 96 μm. Other properties of the air-dried sewage sludge are provided in Table 1.

2.2. Thermogravimetric experiments

The thermogravimetric experiments were performed using thermogravimetric analyzer TGA/DSC1/1600HT from Mettler-Toledo. Prior to thermogravimetric tests, sewage sludge samples have been pre-dried for 10 h at 100 °C. All thermal degradation experiments were carried out from ambient temperature to a final temperature of 800 °C. The heating rate was 40 ± 0.5 °C/min and the gas flux was 100 ± 1.5 ml/min. For each experimental run, 5 mg of samples was used. In order to examine the effect of oxygen on degradation, oxygen concentrations applied in the carrying gas of the TG test were 0, 5%, 10%, 15% and 20%. Each thermogravimetric test has been made in triplicate, controlling the deviations to be within 0.5%-0.8%.

2.3. IR study

The gases released during heating process of sewage sludge were monitored online by the FTIR spectrometer (Nicolet 6700 FTIR spectrophotometer) coupled with TG, in which the range of FTIR spectra was from 4000 to 400 cm^{-1}. The temperature of the connecting line was heated and stabilized at about 180 °C to avoid gas condensation during transfer. The spectra were collected at a resolution of 4 cm^{-1}. Samples were scanned 32 times per minute.

In situ diffuse reflectance infrared Fourier transform spectra (*in situ* DRIRTs) was collected from 650 cm^{-1} to 4000 cm^{-1} at a spectral resolution of 4 cm^{-1} on the same Nicolet 6700 FTIR spectrophotometer equipped with a high-sensitive MCT detector cooled by liquid N_2. The DRIFT cell (Pike) was fitted with a ZnSe window and a heating cartridge. The samples (ca. 25 mg) were placed on a sample holder and carefully flattened to enhance IR reflection. The sample background of each target temperature was collected at room temperature. At each desired temperature, the sample is exposed to a controlled stream with the flow rate of 100 ml/min. The IR spectra were recorded at target conditions by subtraction of the corresponding background reference.

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