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Synergetic effect of sewage sludge and biomass co-pyrolysis: A combined study in thermogravimetric analyzer and a fixed bed reactor

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ABSTRACT

Much attention has been given to the valuable products from the pyrolysis of sewage sludge. In this study, the pyrolysis of sewage sludge, biomass (wheat straw) and their mixtures in different proportions were carried out in a thermogravimetric analyzer (TGA) and fixed-bed reactor. The effects of pyrolysis temperature and percentage of wheat straw in wheat straw–sewage sludge mixtures on product distributions in terms of gas, liquid and char and the gas composition were investigated. Results indicate that there is a significantly synergetic effect during the co-pyrolysis processes of sewage sludge and wheat straw, accelerating the pyrolysis reactions. The synergetic effect resulted in an increase in gas and liquid yields but a decrease in char yield. The gas composition and the synergetic effect degree are strongly affected by the wheat straw proportions, and the strongest synergetic effect of sewage sludge and wheat straw co-pyrolysis appears at the biomass proportion of 60 wt.%. With an increase of temperature, the gas yield from the pyrolysis of sewage sludge increased but the liquid and char yields decreased. Moreover, the required heat of co-pyrolysis is significantly reduced compared with the pyrolysis of sewage sludge and wheat straw pyrolysis alone, because of the exothermic reactions between the ash components in two fuel samples.

1. Introduction

Sewage sludge is the solid waste generated in the municipal and industrial wastewater treatment plants worldwide. With the rapid development of urbanization and industrialization, the production of sewage sludge has been dramatically increased. The improper disposal management of sewage sludge increases many environmental and economic problems and causes air, water and soil pollutions. This is because of the presence of harmful and toxic substances existed in sewage sludge, such as viruses, bacteria, dioxins, nonbiodegradable organic compounds, heavy metals,and so on [1]. In addition, high nitrogen content in sewage sludge will cause a serious concern for combustion processes and produce NO_x waste gases [2]. The composition of sewage sludge depends on the sewage disposal systems in the wastewater treatment plant, but the sewage sludge generally contains high levels of organic matters and proteins, which endow the capability to produce hydrogen [3]. After drying, the sewage sludge contains around 5–10 wt.% of water, 15–30 wt.% of carbohydrates, 2–17 wt.% of fats or lipids, 10–21 wt.% of proteins and 30–50 wt.% of inorganic matter [4]. Dried sewage sludge can be regarded as a kind of biomass fuel, largely because of its considerable volatile content (30–88 wt.%) and calorific value (typically 11–25.5 MJ kg^{-1}) [5].

There are many conventional methods used to treat sewage sludge, such as farmland application and sewage sludge disposal in landfills and oceans. However, these methods can also cause serious pollution accidents or need high treatment costs, and are not environmentally friendly or cost-effective. Among the various sewage sludge management options, pyrolysis is a kind of effective and potential methods to solve these problems, through producing gas, bio-oil and char while avoiding the formation of toxic organic compounds [6]. Bio-oils from pyrolysis are referred to as pyrolysis liquids, pyrolysis oils or bio-crude oils [7]. Pyrolysis can produce clean gas and bio-oils compared to incineration. However, the single pyrolysis of sewage sludge can hardly produce high quality fuels due to high moisture and ash contents. In the pyrolysis gas, the sizeable proportion of CO_2 greatly decreases the heating value [8]. The high moisture yield obtained from the pyrolysis of sewage sludge also causes the low quality of bio-oil [9]. Compared with the

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other solid fuels, the solid residues (char) from the pyrolysis of sewage sludge have relatively low heating values due to the high content of ashes existed in sewage sludge [10].

In contrast, biomass is a valuable renewable energy resource because of its high volatile matters and low ash content. Considering the high contents of moisture and ash in sewage sludge, the co-pyrolysis of sewage sludge and biomass might be an effective method because biomass addition enhances the energy utilization of sewage sludge and improves the properties of different pyrolysis products [11]. Under a series of proper cleaning treatments, these pyrolysis products can be directly used in electro-heat equipments, such as gas turbines, boiler and fuel cells. The liquid produced by the pyrolysis of sewage sludge is a complex mixture including the nitrogen- and sulfur-containing compounds. If the liquid is used as fuel, it may lead to NO_x and SO_2 emission problems. These problems would be relieved if sewage sludge and lignocellulosic biomass were co-pyrolyzed [12]. Moreover, the heating value of bio-oil from co-pyrolysis would be also improved due to the higher heating value of biomass. There have been many studies on the pyrolysis of sewage sludge and biomass mixtures to investigate the existence of synergetic effects [13,14]. Samanya et al. [15] studied the upper phase with high organic compound contents in bio-oil obtained from the co-pyrolysis processes of sewage sludge with wood, rapeseed and straw. It was found that the effect of co-pyrolysis on bio-oil was strongly affected by the biomass fuel types. Huang et al. [16] observed that the addition of rice straw increased the performance of microwave heating and proposed that the reason could be attributed to the synergetic effect. Zhu et al. [17] presented that there was no significant synergetic effect existed during the thermal decomposition of mixed sewage sludge and pine sawdust by thermogravimetric analysis. Salleh et al. [18] reported that the co-cracking of sewage sludge and rice waste did not significantly reduce the bio-oil yield from the individual rice waste samples in a fluidized-bed pyrolytic reactor. It can be seen that there is still no unified conclusion on the synergetic effects existing in co-pyrolysis process of sewage sludge and biomass due to the differences of pyrolysis conditions such as reactor types, temperature, fuel types and heating rate. The studies on the caloric requirement of the co-pyrolysis of sewage sludge with biomass are few, despite the fact that it is important for the energy balance design in the potential co-pyrolysis facilities.

The aim of this work is to convert sewage sludge into valuable products and therefore find a potential solution for sewage sludge management. In this work, the co-pyrolysis experiments of sewage sludge and biomass (wheat straw) were carried out in a TGA and fixed-bed reactor to study the synergetic effect and to determine the optimum operating conditions of the co-pyrolysis processes by measuring the three-phase (gas/liquid/solid) product distributions, the gas composition, and the pyrolysis heat required.

2. Samples and methods

2.1. Samples

Sewage sludge used in this study was obtained from a wastewater treatment plant in Xi'an, Shaanxi Province, China. The wastewater contains municipal wastewater and industrial wastewater. The industrial wastewater which comes from the textile, printing, dyeing, and mechanical working industries accounts for 55.3%, while municipal wastewater which comes from residential, institutional and commercial establishments accounts for 44.7%. Wheat straw was taken as the representative material of biomass. The wheat straw was collected from a farm around Xi'an in Shaanxi Province, China. Sewage sludge and wheat straw were dried at 105 °C for 24 h in the oven. The ultimate and proximate analysis is shown in Table 1. The dried sewage sludge and wheat straw samples were milled and sieved into 50–200 μm in diameter. Dried sewage sludge and wheat straw were well mixed together, with wheat straw weight percentages of 20, 40, 60 and 80 wt.%, respectively.

2.2. Experimental apparatus and procedure

Thermogravimetric analysis on the co-pyrolysis of sewage sludge and wheat straw was conducted in a STA-409PC thermal analyzer (NETZSCH, German). For each test, approximately 10 mg of material sample was placed into a alumina crucible and heated from 30 °C to 1000 °C at a constant heating rate of 20 °C min^{-1} in nitrogen atmosphere with a flow rate of 100 ml min^{-1}. All the samples were tested at the same conditions to be comparable. The curves of thermogravimetric mass loss (TG), differential thermogravimetric (DTG) and differential scanning calorimetry (DSC) are recorded and produced on line by using the bundled software with the analyzer.

The experiments of co-pyrolysis focusing on the product distributions and the gas composition were carried out in a fixed-bed reactor with a length of 1000 mm and internal diameter of 40 mm. The experimental system is shown in Fig. 1. This system consisted of a quartz reactor, a temperature control unit, a nitrogen control unit, a condensation unit for the condensable water and oil, a gas filter and dryer unit for cleaning and drying gases, a metering and analyzing unit for the produced gas flow rate.

The reactor was heated to the target temperatures (500, 600, 700, 800, 900 °C) at a temperature increasing slope of 20 °C min^{-1}. A quartz boat containing 1 ± 0.005 g of prepared sample was placed in the cool part of the reactor tube before each test. When the temperature reached the target value, a N_2 flow of 100 ml min^{-1} was supplied and maintained by 30 min to guarantee on air in the reactor. After that, the quartz boat was rapidly pushed into the reaction zone at the target temperature in the reactor and the gas sampling started. The pyrolysis process of each sample lasted for 10 min, after that, the quartz boat was pulled back to the cool region of the reactor, cold to room temperature in inert atmosphere, and then the solid residue was reserved for testing. The produced pyrolysis gas passed through the condensation unit to collect the condensed bio-oil and water. The total volume of the non-condensable gases was measured by a gas flow meter unit. The pyrolysis gas was collected periodically through the gas bags, and then analyzed by a gas chromatogragh (GC, Shimadzu GC-2014) to measure the concentrations of CO_2, CO, H_2, CH_4, and C_2H_m (C_2H_2, C_2H_4 and C_2H_6). After the pyrolysis process, the solid residue was collected and weighed. The absolute yield of each component in the pyrolysis gas was calculated by using the total gas volume and density of each component. The amount of the liquid fraction including condensed bio-oil and water was determined by the difference from the mass balance. All of the pyrolysis test conditions were repeated by two or three times to guarantee the repeatability. The average data were applied.

2.3. Calculations

2.3.1. Reaction heat from DSC curves

The heat from DSC curves mainly includes two parts: one is the heat necessary to heat sample, another is the heat required for the reaction [19,20]. The two parts can be presented with the following Eq. (1):

$$\frac{dQ/dt}{m_{s,0}} = \frac{m_s c_{p,s} dT/dt}{m_{s,0}} + \frac{Q_P}{m_{s,0}} \qquad (1)$$