Journal of Analytical and Applied Pyrolysis 106 (2014) 86–91

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Influence of catalyst types on the microwave-induced pyrolysis of sewage sludge

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ARTICLE INFO

Article history:
Received 21 September 2013
Accepted 1 January 2014
Available online 9 January 2014

Keywords:
Sewage sludge
Microwave-assisted pyrolysis
Catalyst
Pyrolytic gas

ABSTRACT

The effect of six catalysts (CaO, $CaCO_3$, NiO, Ni_2O_3, γ-Al_2O_3 and TiO_2) on the pyrolysis of sewage sludge under the microwave irradiation was investigated. The wet sewage sludge was used and the pyrolysis experiments were performed in a laboratory-scale microwave heating apparatus to check the variations of temperature evolution, product distribution and gas composition with catalysts introduction. Four pyrolytic products, char, water and hydro-soluble compounds, oil and non-condensable gas, were carefully collected; and the gas components were analyzed by gas chromatography. The presence of catalysts not only affected the temperature evolution of sewage sludge but also changed the pyrolytic product distribution and gas composition. Except CaO, the catalyst addition increased the temperature rise rates of sewage sludge, and the decreasing order for the temperature rise rate is as: $Ni_2O_3 \approx$ γ-$Al_2O_3 > TiO_2 > NiO > CaCO_3$. Ni-based catalysts including NiO and Ni_2O_3 presented the higher activities towards the decomposition of organic matters in sewage sludge, and remarkably increased the yields of bio-oil and pyrolytic gas, especially with the case of Ni_2O_3 catalyst. CaO favored the production of H_2-rich syngas, while CO-rich syngas was generated over Ni-based catalysts. γ-Al_2O_3 and TiO_2 also promoted the decomposition of organic matters to produce higher organic volatiles, but they almost showed no impact on the percentage of combustible gas and the ratio of H_2/CO.

1. Introduction

The new disposal of sewage sludge must be considered since dumping in the ocean, direct landfill and agricultural utilization have been limited or prohibited [1]. Owing to its rich in volatile matter and potential application as fuels, the use of sewage sludge as a biomass for renewable energy source via direct combustion [2], gasification [3,4] and pyrolysis [5,6] has been continuously developed over the last 40 years. Among the three conversion technologies, pyrolysis received the significant attention because of the higher energy recovery and less emissions of NO_x and SO_x [7]. Meanwhile, the formation of toxic organic compounds, such as dioxins, can be avoided [8].

Pyrolysis is the thermal degradation of material in the absence of air or in an oxygen-deficient atmosphere, leading to the production of gas, liquor (bio-oil) and carbonaceous residue [9]. Most of the pyrolysis processes have been carried out by means of conventional heating. It is notable that microwave heating has been considered as an alternative for the pyrolysis of sewage sludge in recent years [10–14]. The clear advantages of microwave systems are the high energy efficiency and the short heating time needed to achieve high temperatures in several minutes if the raw sludge is mixed with an effective microwave receptor, such as graphite, char or activated carbon [10,11].

Many works in the literature focused on the production of bio-oil, syngas and char from the direct microwave-assisted pyrolysis of sewage sludge. It was observed that microwave heating could achieve the greater proportion of syngas and higher quality of bio-oil compared with the conventional pyrolysis [12,13]. However, the studies on the control of product composition using suitable catalysts for the pyrolysis of sewage sludge under microwave radiation were very limited [14], and there was no published data reported on the catalytic upgrading (or reforming) of pyrolytic gas produced from the pyrolysis of sludge sample. Considering the aspects of biomass pyrolysis, it would be desirable that the distribution of pyrolytic products can be effectively regulated by catalysts [15]. Nickel-based catalysts has been used in polymeric wastes gasification due to its high effectiveness in tar removal [16,17], along with the additional advantages of CO_2 reforming, steam reforming and water gas shift activity [18–20]. Moreover, some non-noble metal oxides such as CaO, Al_2O_3 and TiO_2 were also considered as catalysts in catalytic degradation and steam reforming during the pyrolysis of biomass [21–23].

The application of microwave heating to the pyrolysis process is of interest due to the appearance of "hot spots", which may be more favorable for the catalytic conversion of organic matter in

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http://dx.doi.org/10.1016/j.jaap.2014.01.003

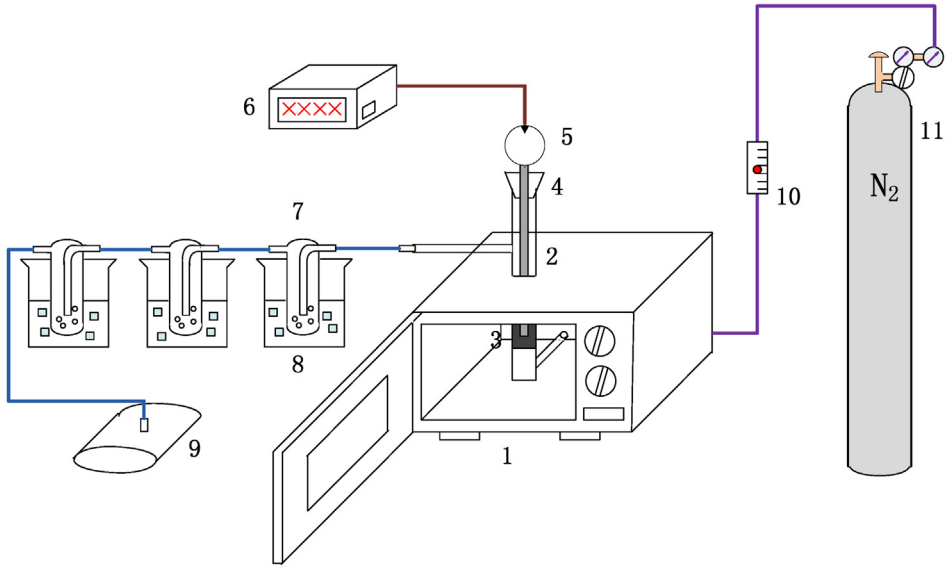

Fig. 1. Experimental apparatus for the microwave-induced pyrolysis of sewage sludge.

swage sludge and the catalytic upgrading of bio-oil and syngas. The present paper focused on achieving a better understanding of the role of the catalysts on the process of the microwave-induced pyrolysis of sewage sludge. The detailed objectives were: (1) to gain an insight into the possible influence of the catalysts on the yields of pyrolytic products; (2) to evaluate the effects of the catalysts on the composition of pyrolytic gas by means of gas chromatography (GC); (3) to explain the relationship between the characteristics of the catalysts and the catalytic reactions.

2. Materials and methods

2.1. Materials

A representative sample of wet sewage sludge dewatered with belt filter press was obtained from a municipal wastewater treatment plant sited in Dalian city, Liaoning province (in the Northeast of China). This plant carries out a Cyclic Activated Sludge Technology (CAST) process which is a type of modified Sequencing Bath Reactor (SBR). Moisture content of the wet sewage sludge was determined to be wt.76.8%, and pH value was 6.5 (wet sewage sludge:distilled water = 1:10). A small part of wet sludge sample was dried at 105 °C for 24 h and then pulverized by hand-mill through 80 mesh sieve for the composition analysis. X-ray fluorescence (XRF) analysis indicated that the main chemical composition of dry-bass sewage sludge was (wt.%): C 57.7%, O 19.8%, Si 8.7%, Al 4.0%, Fe 2.6%, Ca 2.0%, P 1.8%, K 1.0%, Mg 0.7% and S 0.6%. The organic matter content in the dry-bass sewage sludge was determined to be 83.1 wt.% by dichromate potassium oxidation method.

Wet sewage sludge has a very high transparency to microwaves. It is therefore necessary to mix it with an appropriate microwave receptor to achieve the high temperatures required for pyrolysis. For this purpose, a commercial activated carbon made from coconut shell was used for all the treatments in the experiments. To determine the effect of catalysts on the production of syngas, different catalysts including CaO, $CaCO_3$, NiO, Ni_2O_3, γ-Al_2O_3 and TiO_2 were added into the wet sewage sludge, respectively. All the catalysts used in this study are analytical reagent.

2.2. Experimental apparatus and procedure

Pyrolysis experiments were conducted using an apparatus comprised of microwave oven, quartz reactor, thermocouple specialized for microwave, temperature displayer, liquid collective unit, Tedlar® gas sampling bag, float ball gas flowmeter and N_2 gas cylinder, as shown in Fig. 1.

A domestic microwave oven (LG WP700, MS-2079TW, frequency 2450 MHz) was refitted as the test microwave apparatus, on the top and back of which a 30 mm and a 5 mm diameter holes were digged, respectively. A quartz reactor (28 cm length, 28 mm outer diameter) and its N_2 inlet tube (3 mm) were inserted into these two holes. A diversion trench connecting with the steam outlet tube was built around the inner wall of quartz reactor in order to avoid the reverse-flow of condensed liquid. Approximately 30 g of the wet sewage sludge on the layer of quartz wool were placed at the bottom of the quartz reactor. The top end of the reactor was sealed with a polyfluoretraethylene plug. The microwave treatments consisted of subjecting the samples to microwave action for 60 min. The constant input power of 700 W was used in the experiments. In order to maintain an inert atmosphere during the treatments, a N_2 flow of 100 mL min^{-1} was passed through the reactor for 5 min prior to the commencement of the experiment, then being reduced during the pyrolytic experiment to 15 mL min^{-1}. Accurate measurement of temperature evolution was monitored by a thermocouple specialized for microwave, which was inserted into the center of hot zone of the sludge sample. The pyrolytic products were swept out from the reactor and passed through three consecutive condensers immersed in ice bath. The non-condensable gas was collected by 2 L Tedlar® gas sampling bags with a polypropylene fitting for sampling. The collection process of non-condensable gas was divided into two stages, i.e., low temperature pyrolysis stage (sludge temperature ≤300 °C) and high temperature pyrolysis stage (sludge temperature >300 °C).