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Characterization of nitrogen transformation during microwave-induced pyrolysis of sewage sludge

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ABSTRACT

The distribution of pyrolysis products and transformation of nitrogen in the char, tar and gas fractions at different temperatures were investigated during microwave-induced pyrolysis of sewage sludge. The results showed that under the temperature ranges investigated, the thermal decomposition of sewage sludge was faster in the microwave pyrolysis than in the conventional pyrolysis. At temperatures above 500 °C, microwave pyrolysis gave rise to a larger yield of bio-gas fraction (above 10%) and less bio-tar yield (below 15%) compared with those in the conventional pyrolysis. In addition, NH_3 and HCN were the main nitrogenous gas during microwave pyrolysis, in which HCN yields were nearly half of those of NH_3. FTIR and GC–MS analysis revealed that the pyrolysis of sewage sludge produced three nitrogen-containing compounds, including the amine/amide, heterocyclic-N and nitrile compounds, in the char and tar products. The pyrolysis temperature played significant roles on the transformation of nitrogen in the char, tar and gas products during microwave pyrolysis.

1. Introduction

Sludge constitutes the waste in the largest volumes at wastewater treatment plants: in China, for example, over 30 million tons (dry solids, DS) of treated sewage sludge are produced each year [1]. Consequently, the handling and disposal of sewage sludge is an issue of particular concern. Recently, there has been increasing attentions in the thermo-chemical conversion of sewage sludge into bio-fuels (bio-gas, bio-tar and bio-char) through pyrolysis technology due to environmental considerations and the increasing demands of energy worldwide [2,3]. Pyrolysis bio-gas and bio-tar can be utilized as fuels, which are now considered as the alternative energy resources replacing fossil fuels [2,4]. Moreover, pyrolysis bio-char can be converted into the adsorbent or solid fuel, reducing the sludge volume and concentrating the heavy metals in the carbonaceous residue significantly [5–7].

The conventional pyrolysis is usually conducted in the electric furnace and regenerative gas heater, where the thermal energy is externally applied to heat the substances in the reactor resulting in significant energy losses [8,9]. For recovering energy efficiently, microwave-induced pyrolysis is considered as a potential technology for the pyrolysis of biomass, coal and other wastes [4–6]. A high yield of bio-tar about 80 wt.% from coffee hulls was obtained within 15 min under the microwave input power of 130 W [10]. None of the PAHs was detected in bio-tar produced from microwave pyrolysis of sludge [11,12]. The bio-gas from the microwave had much higher syngas productions (H_2 + CO, up to 72 vol.%) than those obtained by conventional pyrolysis (51%) [10,11]. Moreover, the formation of toxic dioxins in the bio-gas was avoided under the low oxygen concentration of pyrolysis atmosphere [26]. Thus, microwave pyrolysis has many advantages with respect to its characteristics of high heating rate, low temperature of reactor wall, short heating time required and low toxic risk of pyrolysis products.

However, conversion of sewage sludge into either fuel or chemicals by pyrolysis is limited due to the presence of nitrogen in the sludge [13,14]. Pyrolysis of sewage sludge produces harmful gases such as NH_3 and HCN [15], which could be converted into nitrogen oxides (NO_x) during the combustion of bio-gas, contributing to the severe photochemical smog and acid rain pollution [13–15]. In order to develop pyrolysis process for reducing the formation of nitrogen-containing species, it is of importance to characterize the nitrogen-containing structures in the char, tar and gas products formed from the pyrolysis. Many efforts have been made to study the nitrogen conversions during the pyrolysis of coal [14,16]. However, it should be noted that the nitrogenous species in the sewage sludge are quite different from those of coal. Thus, it is considered

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Table 1
Characteristics of sewage sludge.

Proximate analysis (wt%)			Ultimate analysis (wt%, daf)							
M	A_d	V_d	FC_d	C	H	N	O	H/C	H/O	H/N
78	42	55	3	30.9	4.77	4.61	20.5	1.85	3.71	14.5

Ash analysis (expressed as wt% of metal oxides)

SiO_2	Al_2O_3	Fe_2O_3	P_2O_5	CaO	K_2O	TiO_2	ZnO	CuO	SrO
26.4	8.64	8.30	6.13	5.11	1.62	0.65	0.14	0.03	0.03

M, moisture content; A, ash content; V, volatile content; FC, fixed carbon; d, dried basis; daf, dried and ash-free basis.

that the nitrogen conversion behavior during pyrolysis of sewage sludge may differ from that of coal-N.

In this work, the product distribution and nitrogen transformation are investigated during microwave pyrolysis of sewage sludge. Our studies were focused on: (1) characterizing the nitrogen functionalities in the sewage sludge; (2) comparing the thermal decomposition behaviors of sewage sludge in the conventional and microwave pyrolysis; (3) investigating the product distributions in the char, tar and gas fractions; (4) analyzing the evolution of nitrogen-containing structures in the char, tar and gas products. This study might benefit the control of the pyrolysis process as well as the clean utilization of sludge as an energy source.

2. Materials and methods

2.1. Sewage sludge sample

The sewage sludge sample used in this study was obtained from a wastewater treatment plant in Harbin, China. The sludge had a moisture content of 78%, an ash content of 42% (dry basis) and a volatile matter content of 55%. The sludge sample was dried at 106 °C for 24 h (moisture of 0%) and then the dried sample was ground and sieved to obtain a particle size of 106–150 μm. Ultimate analysis was conducted in an Elemental Analyzer (Americas Vario EL III). X-ray fluorescence spectroscopy (XRF, Model AXIOS-PW4400, Panalytical B.V.) was employed for the rest of the elements in the sludge such as Si, Al, Fe, Ca, Zn, and Cu. The main chemical properties of sludge samples are given in Table 1.

2.2. Experimental apparatus

A sketch of the experimental apparatus for microwave-induced pyrolysis of sewage sludge was shown in Fig. 1, which mainly consisted of a microwave magnetron of 2450 MHz, a multiple mode cavity and a temperature controlling system. An infrared optical pyrometer was employed to measure the temperatures of the

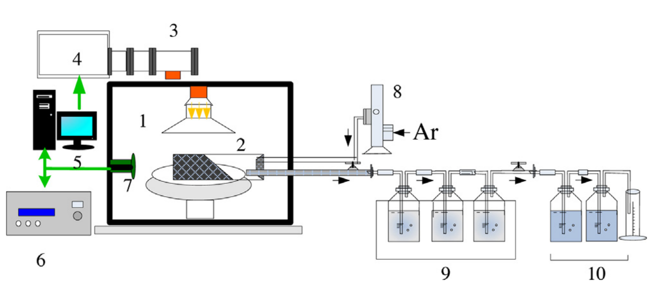

Fig. 1. A schematic of the microwave preparation reactor assembly: (1) microwave cavity; (2) quartz reactor; (3) waveguide; (4) magnetron; (5) PC with fuzzy logic algorithm; (6) power governor; (7) infrared radiation thermometer; (8) gas flowmeter; (9) tar products collection unit; (10) gas products collection unit.

samples during the experiments. The infrared optical pyrometer was calibrated by shutting off the microwaves and immediately introducing a thermocouple in the center of the sample at different times. All the experiments were repeated at least three times and the average results were used with a standard deviation of maximum 5%. Therefore, the average of the sample surface temperature and the internal temperature was obtained by taking the average of optical pyrometer and thermocouple results. When the required pyrolysis temperature was reached, detected temperature signals were passed by a network to a fuzzy logic algorithm calculating the proper power. The instruction was feedback to a controller to adjust the output power of the magnetron automatically and continuously to maintain the stability of desired temperature.

Pyrolysis experiments were carried out by placing sludge samples in a fixed-bed quartz reactor (16 cm length, 6 cm outer diameter) which was placed inside the microwave cavity. The samples were heated from room temperature to a final temperature of 100–1000 °C in an increment of 100 °C. The temperature profiles with activated carbon as microwave receptor were detected in preliminary experiments [26]. The heating rate in the pyrolysis experiment was closed to 800 °C/min. After the arrival of required temperatures, the samples subjected to microwave radiation were held for 10 min until no significant release of gas was observed. It is noted that sewage sludge has a high transparency to microwave. It was necessary to mix it with microwave receptor for reaching the required temperatures during the pyrolysis. Four different microwave receptors, including the graphite, activated carbon, silicon carbide and pyrolysis char, were tested to determine their effects on the heating rate, final temperature and bio-gas productions during microwave pyrolysis of sewage sludge [26]. Activated carbon (Tianjin Benchmark Chemical Reagent Co., Ltd., China) was selected as the optimal microwave receptor in the pyrolysis experiments. In each experiment, the activated carbon (ca. 2.5 g) was homogenously mixed with 24 g dried sludge (moisture of 0%) before microwave heating. The reducing gases CO and H_2 would not be generated after the addition of activated carbon in the sludge due to the negligible inherent moisture content of sludge. To ensure an inert atmosphere, argon (Ar) was injected into the system with a constant flow rate of 10 L/min for 20 min and then taken off before the commencement of the experiment. The microwave generator was turned off after the arrival of designated reaction time. The carrier gas was reinjected into the system to purge out the residual gas for 20 min.

In each experiment, the volatile substances evolved from the sludge pyrolysis passed through a number of dichloromethane-containing condensers placed in ice bathes. Then the bio-gas was carried out from the tar trap to the bubbling solutions. HCN and NH_3 in the bio-gas were collected by bubbling through NaOH (0.2 mol/L) and H_2SO_4 (0.1 mol/L) solutions, respectively. The tar products would be recovered from the condensers by evaporating the dichloromethane solvent in a water-bath at 60 °C for 24 h and then retrieved. The residual chars in the reactors were collected and stored in airtight containers until they were cooled to room temperature. The yields of char and tar were calculated from the weight of each fraction, while the gas yields were evaluated by difference. The elemental compositions (C, H, O, N and S) of the tar and char samples were measured in an Elemental Analyzer (Americas Vario EL III). The distributions of the main elements (C, H, O, N and S) in the char, tar and gas products were shown in Figs. S1–S5 (Supporting Information). According to the procedures reported previously [16], HCN and NH_3 absorbed in the solutions were quantified with a Dionex 500 ion chromatograph with separation columns of A Supp 1-250 for anion CN^- and C 4-100 for cation NH_4^+. All of the experiments were repeated three times, and the average values of these results were taken as final results.