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Temperature influence and distribution of bio-oil from pyrolysis of granular sewage sludge

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ABSTRACT

The temperature influence on bio-oil distribution of granular sewage sludge (GSS) pyrolysis from 500 °C to 800 °C in a horizontal tube reactor was investigated. The maximum yield of bio-oil was 43.6% of weight-lost percent during GSS pyrolysis. The bio-oil mainly contained polycyclic aromatic hydrocarbons (PAHs) and long chain nitriles. The nuclear magnetic resonance (NMR) results of bio-oil indicated that PAHs were formed during pyrolysis, which were in agreement with gas chromatography-mass spectrometer (GC–MS) results that PAHs in bio-oil were mainly made up of tricyclic and tetracyclic PAHs. The yield of PAHs strongly increased with temperature, reaching a maximun value at 700 °C. The present results might be valuable for assessing sewage sludge pyrolysis as thermal treatment method and also for studying the formation mechanism of PAHs during sewage sludge pyrolysis.

1. Introduction

Sewage sludge (SS) is the major byproduct from wastewater treatment plants worldwide [1]. The increasing amount of sewage sludge has resulted in a significant environmental problem [2,3]. Common disposal methods of sewage sludge, including application to farmland, placement in landfills and incineration [4], may cause secondary pollutions to soil, ground water and air. Nowadays it is necessary to find harmless methods for treating sewage sludge.

Sewage sludge pyrolysis is commonly described as the thermal decomposition of the organic substances in sewage sludge in the absence of oxygen at mediate temperature to yield bio-oil, biochar and uncondensable gas [5–8]. During pyrolysis process part of organic compounds in the sewage sludge could release from the solid phase and formed bio-oil and uncondensable gas. The other organic compounds could form carbon in the biochar. Sewage sludge pyrolysis is considered as an effective way and develops rapidly since it is high-efficiency in reducing the volume of sludge and the product of sewage sludge pyrolysis could be used as energy source [9–11]. Before the process of pyrolysis, sewage sludge should be dried to improve the efficiency of pyrolysis process [12]. Granular sewage sludge (GSS), which sewage sludge is shaped by an extruding machine, is generated during the process of drying and it is beneficial for moisture removal in industry. GSS can be considered as a potential biomass feedstock due to its volatile content and calorific value. Particle size is known to influence the heat and mass transfer effects during pyrolysis [13]. Chun-Zhu Li reported the effects of biomass particle size on the yield and composition of bio-oil at 500 °C [14]. Gu et al. studied the influence of pyrolysis time and particle size on biomass pyrolysis inside the fluidised bed reactor [15]. Therefore, it is meaningful to investigate the pyrolysis of GSS.

Polycyclic aromatic hydrocarbons (PAHs) are organic contaminants drawing great public concern for their potential carcinogenic and mutagenic characteristics and harmful implication for human health [16–18]. The formation of PAHs during pyrolysis of sewage sludge have been generally investigated [16,19,20], while certain parameters, such as temperature and residence time[21] and sample mass and gas flow [22]. Particle size is an interesting parameter that has been studied for pyrolysis of sewage sludge [23,24]. However, the formation mechanism of different PAHs during sludge pyrolysis has not been documented.

Several analytical approaches also have been developed to investigate the pyrolysis behavior of sludge [25,26]. Fonts et al. [27] analyzed the composition of pyrolytic liquids by GC–MS and GC-FID. Ischia et al. [28] investigated the sludge pyrolysis process using thermogravimetry (TG) coupled to mass spectrometry (MS) and gas chromatography (GC), TG/MS and TG/GC/MS. Tian et al. [29] studied the N-containing components during the process of sludge pyrolysis by TG coupled to Fourier transform infrared spectroscopy and mass spectrometry (TG-FTIR-MS). In our previous reports, we have used nuclear magnetic resonance (NMR) to identify the structure of organic compounds [30,31].

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Table 1
General characteristics and constituents of the sludge and GSS600.

Items	Sludge (wt.%)	GSS600
Proximate analysis		
Moisture content (%)	76.6	0
Zeta Potential (mV)	−37.7	−57.9
Calorific value (kJ/g)	13.6	5.91
VS/DS	0.580	0.210
Chemical composition		
C	74.314	33.977
Na_2O	0.158	0.939
MgO	0.769	2.011
Al_2O_3	4.104	12.150
SiO_2	9.640	36.016
P_2O_5	2.253	1.523
SO_3	1.039	1.013
Cl	0.039	0.121
K_2O	0.612	1.302
CaO	3.892	6.905
TiO_2	0.179	0.424
Cr_2O_3	0.006	0.032
MnO	0.049	0.074
Fe_2O_3	2.857	3.399
CuO	0.006	0.017
ZnO	0.046	0.057
Rb_2O	0.003	0.006
SrO	0.012	0.019
Y_2O_3	0.001	0.002
ZrO_2	0.007	0.013

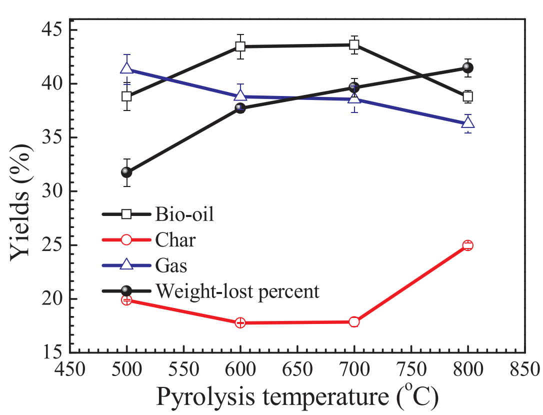

Fig. 1. Yields of the pyrolysis products at different temperatures.

In this study, we report using nuclear magnetic resonance (NMR) and GC–MS to investigate bio-oil of sludge pyrolysis. The effect of pyrolysis temperature on the yield of products was explored. The formation mechanism of different PAHs during sludge pyrolysis was proposed.

2. Methods

2.1. Materials

Sewage sludge samples were collected from a municipal wastewater treatment plant after centrifugal dewatering process in Dalian, China. Sewage sludge was shaped by an extruding machine with a φ 4 die (Pore diameter = 4 mm). After extruding the sludge was dried and cut to 4–6 mm, granular sewage sludge (GSS) was achieved.

2.2. Pyrolysis of GSS

In GSS pyrolysis process, 10 g GSS was loaded into a quartz cylindrical reactor and pyrolyzed for 4 h at 500 °C, 600 °C, 700 °C and 800 °C, respectively, with the heating rate of 3 °C/min. The bio-char obtained at the pyrolysis temperature of 500 °C, 600 °C, 700 °C and 800 °C was titled GSS500, GSS600, GSS700 and GSS800, respectively. The pyrolysis vapors were swept by high pure nitrogen (99.999 wt.%) at a flow rate of 500 mL min^{-1}, of which the condensable fraction was quenched by water to obtain bio-oil. After filtrating with 0.45 μm film, the mixture of bio-oil and char were achieved. The bio-oil and char were separated by dichloromethane (CH_2Cl_2) extraction and weighed to estimate their yields. Each pyrolysis experiment was performed twice and the results were given in average values.

2.3. Analysis

X-ray Fluorescence (XRF) was used to analyze elemental content in sludge and bio-char with Magix 601 equipment produced by PANalytical. X-ray photoelectron spectroscopy (XPS) was performed to analyze the composition and chemical state of the surface elements of bio-char. The specific surface area of bio-char was measured by the Brunauer-Emmett-Teller (BET) methods using QUADRASORB SI4 instrument produced by Quantachrome Company. Scanning electron microscopy (SEM) experiments were performed on a scanning electron microscope (Quanta 200F, FEI Company). Energy dispersive X-ray spectroscopy (EDAX's Sapphire Si(Li) Detector, USA) was carried out on an EDAX silicon-drift detector, which enabled rapid determination of elemental compositions and acquisition of compositional maps of bio-char.

For the GC–MS analysis, the bio-oil sample was extracted by dichloromethane (CH_2Cl_2), and the compounds in the CH_2Cl_2-soluble fraction were analyzed by Angilent model 7890A Gas Chromatograph (GC) equipped with a model 5975C Mass Selective (MS) detector and a capillary column (HP–5 ms, 30m × 0.25mm × 0.25 μm, Agilent J&W GC Columns) was used. The initial oven temperature of gas chromatograph was kept at 50 °C for 5 min. The oven temperature increased at a rate of 15 °C/min to reach a final temperature at 250 °C, and this temperature was held for 10 min. The injector temperature was 250 °C. The detector temperature was 280 °C.

Nuclear magnetic resonance (NMR) was used to investigate the structure of products in bio-oil. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer and chemical shift values were referred to δ_{CDCl3} = 77.16 ppm or $CDCl_3$ ($\delta(^1H)$, 7.26 ppm).

3. Results and discussion

3.1. Characteristics of the sludge and GSS600

The general characteristics and constituents of the dried sludge and GSS600 are listed in Table 1. The calorific value of GSS600 was 5.91 kJ/g measured by oxygen bomb combustion much lower than that of the dried sludge (13.6 kJ/g), indicating that a large amount of organic substances in the sludge were removal after pyrolysis process. The other characteristics of GSS600 such as ^{57}Fe Mössbauer spectra, XPS, BET, SEM, and EDAX were shown in Fig. S1–S5.

3.2. Pyrolysis products distribution at different temperatures

Pyrolysis is a very complex process due to the mixtures in the sludge. Dependent upon the pyrolysis conditions, especially the temperature, the yields and properties of pyrolysis products (bio-oil, char and gas) are quite different.

Fig. 1 shows the yields of bio-oil, char, gas and weight-lost percent at different temperatures. It can be seen that the weight-lost percent increased from 31.7% to 41.5% with the temperature increased from 500 °C to 800 °C. However, the yield of char first decreased at 500 °C to 600 °C and increased above 600 °C. It indicated that higher pyrolysis temperature (above 600 °C) is favorable for the complete