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Characterization of particulate matter formed during sewage sludge pyrolysis

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ABSTRACT

Particulate matter (PM) formation during sludge pyrolysis was investigated under different operating conditions. The impact of inert gas flow rate, heating rate, and sludge types on PM generation was examined. PM generated during sewage sludge pyrolysis varied with tested conditions and ranged from 1.14 wt% to 6.33 wt%. A PM characterization study revealed that carbon content decreased, but oxygen, sulfur, and phosphorus contents increased with increasing temperature. It was considered that the PM formation mechanism varied with different temperature ranges. The increase of inert gas flow and volatile content of sewage sludge promoted PM generation. The formation of PM could be reduced by a low inert gas flow rate, and with lower volatile content of sewage sludge.

1. Introduction

With rapid urbanization in China, the production of sewage sludge containing heavy metals, microorganisms and pathogens has increased dramatically [1]. Improper sewage sludge management practices have become a serious environmental concern [2]. Pyrolysis has emerged as a potential option to handle sewage sludge with advantages including large volume reduction, pathogen elimination, and valuable end products: biochar, bio-oil and syngas [3–6]. Biochar has been studied for agricultural applications and environmental purposes [4,7–11], while syngas and bio-oil can be used as alternative fuels with proper refinery processes [12–15]. Pyrolysis gas is mainly composed of H_2, CH_4, and CO and also contains air pollutants, such as, NO_x, NH_3, H_2S, tar, polycyclic aromatic hydrocarbons (PAHs), and particulate matter (PM), etc. [15–17].

PM is composed of soot, liquid, and solid phase materials. PM is developed from the precursors via nucleation, coalescence, and agglomeration processes [18]. PM is also considered to be a carrier for some toxic substances including heavy metals, PAHs, and others [19,20]. PM not only presents a risk to human health when released in the air [21] but also downgrades the quality of pyrolysis gas when used as a fuel by increasing cleaning cost and contaminating downstream equipment and processes [15,22]. Pyrolysis gas quality also can affect the formation of PM in its combustion process. Dunnigan et al. [23] reported variations during PM formation in the combustion of syngas and bio-oil mixtures produced under different pyrolysis conditions.

A few studies on fuel gas pyrolysis revealed that PM formation depended on pyrolysis operation factors, such as temperature, heating rate, and gas residence time and/or fuel types [24–26]. Dandajeh et al. [24] showed soot concentration increased from 16 mg/m^3 to 1282 mg/m^3 with temperature rising from 1050 °C to 1250 °C using C_2-C_3 fuel pyrolysis. Viteri et al. [25] also indicated that soot mass concentration increased from 138.3 mg/g to 630 mg/g while temperature increased from 1000 °C to 1200 °C in their butanol pyrolysis study. Oh, et al. [26] observed that the concentration of soot particles was enhanced ten-fold with decreasing gas residence times from 693 ms to 277 ms at 1300 °C in their diesel pyrolysis study. In contrast, Sánchez, et al. [27] showed that soot formation in acetylene pyrolysis increased when residence time increased from 1.28 s to 2.28 s but decreased when the residence time increased from 2.28 s to 3.88 s at both 900 °C and 950 °C. PM or soot formation in pyrolysis gas in these studies utilized relatively simple gas fuel. The property of feeding stock can be influential in the formation of PM in pyrolysis gas but PM study with a complex feeding stock like sewage sludge is rare. In addition, PM or soot in pyrolysis gas with slow pyrolysis conditions is not often discussed. Understanding PM formation in pyrolysis gas is required to determine favorable conditions for optimizing the pyrolysis of sewage sludge and designing the gas cleaning system.

Sewage sludge is not only a complex mixture with various percentages of volatile matter, fixed carbon and ash contents but also contains various inorganic compounds. Many studies have been conducted in the field of sewage sludge pyrolysis but PM formation in pyrolysis gas during pyrolysis is little understood. In this study, PM formation during sludge pyrolysis was investigated under different operating conditions

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Table 1
Proximate and ultimate analyses of three types of sewage sludge.

Parameters	BH	NS	LH
Ultimate analysis (wt%[a])			
C	47.97	32.53	35.53
H	8.12	8.49	8.57
N	7.38	5.39	5.80
S	1.18	1.04	0.76
O[c]	35.35	52.56	49.34
Proximate analysis (wt%[b])			
Volatile matter	57.9	43.4	36.2
Fixed carbon[c]	8.4	2.6	1.8
Ash	33.7	54.0	62.0
Ash composition (wt%[b])			
Al_2O_3	11.26	13.10	15.87
SiO_2	9.65	21.05	25.65
P_2O_5	5.30	5.18	3.92
Fe_2O_3	2.57	4.27	6.92
CaO	1.92	2.20	2.09
K_2O	0.83	1.89	1.76
TiO_2	0.24	0.46	0.28
ZnO	0.18	0.13	0.15
MnO	0.029	0.069	0.085
CuO	0.014	0.031	0.033
Cr_2O_3	0.012	N.D.[d]	N.D.
PbO	0.004	0.007	0.008
SrO	N.D.	0.018	0.015
ZrO_2	N.D.	0.017	0.013
BaO	N.D.	N.D.	0.47

[a] On dry-ash-free basis.
[b] On dry basis.
[c] Determined by the difference (Fixed carbon = 100% – Moisture – Volatile matter – Ash).
[d] Not detected.

including inert gas flow rate, heating rate, and sludge types. A quantification and characterization study was conducted for the collected PM.

2. Materials and methods

2.1. Sewage sludge

Sewage sludge samples were collected from Binhe (BH), Nanshan (NS) and Longhua (LH) municipal wastewater treatment plants (WWTPs) in Shenzhen, China. The collected sludge samples were dried at 105 °C in a dry oven. The dry sludge samples were ground manually and then sieved. Sludge particles between 0.15 mm and 0.45 mm were used for pyrolysis. The physicochemical properties of the sludge samples were determined with proximate analysis (GB/T 17664-1999), element analysis (PerkinElmer 2400, USA) and ash composition analysis (EDX-LE, Shimadzu, Japan). The properties of three sludge types are presented in Table 1.

2.2. Sludge pyrolysis

Sewage sludge pyrolysis was carried out using a laboratory scale horizontal furnace (Sanli Inc., China). As illustrated in Fig. 1, the pyrolysis system is comprised of a gas supply unit, a reactor tube (inner diameter: 74 mm, length: 1000 mm (400 mm in the heating zone)), a PM collection unit, and a condensation unit with a heat exchanger. In each run, a 10 g (± 0.01 g) dried sludge sample was loaded into a corundum crucible and introduced into the furnace. For an oxygen-free atmosphere, N_2 (99.99%, V/V) was purged into the furnace at a flow rate of 1 L/min for 15 min before heating. The furnace was heated up to 1000 °C with a desired heating rate. Three heating rates (5°C/min, 10 °C/min and 20 °C/min) were used. When the furnace temperature reached 1000 °C, the temperature was maintained for two hours. Various gas residence time was used by controlling the flow rate of N_2 (inert gas) with a mass flow controller (MFC). The selected inert gas flow rates were 200, 400, and 800 mL/min corresponding to the gas residence time of 187 s, 94 s, and 47 s, respectively. Table 2 shows the summary of parameters examined in this study.

2.3. Sampling PM in flue gas

A PM collection unit comprised of a PM impactor and a tape heater was used to collect PM. The temperature of the PM impactor was maintained at 200 °C to avoid hot volatile condensation and the secondary cracking of tar while sampling PM [28,29]. A quartz filter (Ø47 mm, Whatman Inc.) was placed in the impactor to collect PM. The filter was heated in a muffle furnace at 550 °C for 5 h to remove potential organic contaminants prior to installation. PM collection started when the furnace temperature reached 200 °C. The quartz filter was replaced at 400 °C, 600 °C, 800 °C, and 1000 °C during heating, and every 30 min (0.5, 1.0, 1.5, and 2 h) during the holding time at 1000 °C. PM mass was determined with the weight difference of the filter before and after collecting PM. The sampling flow rate in the PM impactor was adjusted to 1000 mL/min by an MFC and a gas pump at the end of the exhaust outlet. At the front of the PM impactor unit, the dilution gas (clean air) was supplied with a pipe connected to the exhaust gas pipe. Total dilution gas volume was measured by a mass flow totalizer (MFT). The volume of pyrolysis gas (at 293 K and 1 atm) was determined by the equation below:

$$V_{Pg} = (v_S - v_I)t - V_{TD} \quad (1)$$

where, V_{Pg} = total pyrolysis gas volume; v_E = sampling flow rate; v_I = inert gas flow rate; V_{TD} = total dilution gas volume; t = time.

2.4. Characterization of PM

PM collected on each quartz filter was investigated using an FEI Magellan 400 field emission XHR-SEM (Oxford Instruments) at 5 kV and 6.3–25 pA using a through-lens detector (TLD). Elemental composition measurement was carried out using an 80 mm^2 X-Max Silicon Drift Detector (Magellan 400 instrument) and a Quantax 70 EDS system (TM3030 Plus instrument) at 20 kV, 0.8 mA and 15 kV, 38.1 mA, respectively. Chemical functional groups of PM were characterized using Fourier Transform Infrared (FT-IR) spectra with IR Tracer 100 (Shimadzu, Japan). The FT-IR spectra were obtained in the wavenumber range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and scanning frequency of 20 scans.

2.5. Thermogravimetric analysis of sludge

Thermogravimetric analysis was conducted with a thermogravimetric analyzer (TGA-50H, Shimadzu, Japan). A 5.0 mg dry sludge sample was used for each pyrolysis run in triplicate. Each sample was heated to 100 °C and retained at the temperature for 20 min to remove adsorbed moisture. Then these were heated to 1000 °C with 2 h holding time with a heating rate which corresponded to the pyrolysis conditions in the furnace experiment. N_2 gas (99.99%) was purged into the thermogravimetric analyzer (TGA) at a flow rate of 40 mL/min during pyrolysis.

3. Results and discussion

3.1. PM formation during sludge pyrolysis

PM generated during sewage sludge pyrolysis varied with testing conditions and ranged from 1.14 wt% to 6.33 wt%. In Table 3, PM generation in this study was compared with the ranges of PM generations reported in the literature. Trubetskaya, et al. [30] showed that PM (referred to as soot) generation ranged from 2.66 wt% to 8.36 wt%