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Polycyclic aromatic hydrocarbon formation from gasification of sewage sludge in supercritical water: The concentration distribution and effect of sludge properties

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ABSTRACT

The changes in the polycyclic aromatic hydrocarbon (PAH) concentration and distribution in 10 different types of raw sewage sludge and gasified residues were investigated, and the effects of the sludge properties and the organic matter composition were determined. The results showed that the concentrations of 2-ring and 6-ring PAHs increased significantly during the gasification process. The PAHs in raw sludge were dominated by 3-ring and 4-ring PAHs, and those after gasification were dominated by 2-ring and 3-ring PAHs. The total PAH concentration increased with the increasing volatile matter content and decreased with the increasing pH value. Phenols have been considered to be important precursors for PAH synthesis. The crude fat and carbohydrate content can promote lower-molecular-weight PAH formation, while lignin and humic substance content can promote higher-molecular-weight PAH formation, which indicates that the organic matter composition in raw sludge has a high impact on the PAH distribution.

1. Introduction

Sewage sludge is the end-product of the wastewater treatment process and contains large amounts and complex mixtures of components. The treatment and disposal of waste sludge in effective and safe ways are significant environmental problems for most wastewater treatment plants (WWTPs). Sewage sludge is a useful form of bio-energy that is rich in organic matter (OM), nitrogen, and micronutrients. Using sewage sludge as a resource has therefore become of increasing interest to researchers in recent years [1–4]. Supercritical water gasification (SCWG) is a useful technology for treating sewage sludge that contains large amounts of water (greater than 80%), allowing wet sewage sludge to be gasified without it having to be dried or otherwise treated. The process allows the OM in the sludge to be converted into syngas and can reduce the environmental pollution, making it a "win-win" technology in terms of energy use and environmental protection [5–7].

However, sewage sludge is a more complex waste than other biomass types because it contains toxic and hazardous pollutants, such as heavy metals and persistent organic pollutants. Therefore, it is necessary to understand the changes that can occur in the pollutant concentrations and whether new toxic compounds can be produced through the complex chemical reactions involved in SCWG. Yildiz Bircan et al. [8] analysed polychlorinated dibenzo-*p*-dioxins and dibenzofurans (dioxins) and dioxin-like compounds produced by the hydrothermal gasification of biowastes (chicken and cattle manure) and found that the total toxic equivalent of dioxins produced by hydrothermal gasification was within the limits allowed in Japan. Zhang et al. [9] treated secondary pulp/paper-mill sludge and sewage sludge with supercritical water (SCW) to recover energy and obtained heavy oils from the liquid product, which mainly contained phenol and a variety of phenolic compounds. Phenolic compounds are considered to be important precursors for polyaromatic hydrocarbons (PAHs) [10,11]. Huelsman and Savage [12] treated dibenzofuran (the main intermediate product from phenol SCWG) in SCW and detected many PAHs produced in the liquid phase in amounts that increased with the temperature. PAHs are a group of organic compounds with two or more fused aromatic rings and are the most common contaminants in sewage sludge and thermochemical treatment products, appearing on the US EPA priority controlled pollutant list [13]. We have found that PAHs were produced during the SCWG process, and high reaction temperature,

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Table 1
Properties of the dewatered sewage sludges tested.

Type of sludge	Volatile matter (wt.%)[a]	Moisture content (wt.%)	Ash (wt.%)[a]	pH[b]	Ultimate analysis (wt.%)[a]					Proportion of industrial wastewater[d]	Sewage treatment process[e]
					C	H	N	S	O[c]		
S0	44.5 ± 0.1	77.9 ± 0.2	54.5 ± 0.1	8.1	7.60 ± 0.16	2.53 ± 0.05	0.37 ± 0.02	0.91 ± 0.06	34.09	30% E	AS
S1	41.8 ± 0.4	73.5 ± 0.4	57.8 ± 0.1	8	16.25 ± 0.01	2.29 ± 0.04	0.62 ± 0.01	2.85 ± 0.03	20.22	8% D	A/O
S2	45.2 ± 0.0	74.8 ± 0.2	54.1 ± 0.1	6.8	9.14 ± 0.03	3.94 ± 0.01	1.38 ± 0.01	1.03 ± 0.01	30.47	–	OD
S3	50.5 ± 0.2	88.5 ± 0.1	48.7 ± 0.0	6.9	18.02 ± 0.06	4.06 ± 0.03	2.79 ± 0.01	1.95 ± 0.01	24.47	6% E	A/A/O
S4	50.5 ± 0.0	84.7 ± 0.3	49.0 ± 0.1	7.6	17.14 ± 0.13	3.96 ± 0.02	2.93 ± 0.02	1.16 ± 0.02	25.78	6% D	UASB
S5	51.2 ± 0.1	86.9 ± 0.4	48.2 ± 0.1	6.6	20.39 ± 0.36	4.15 ± 0.08	3.05 ± 0.03	1.30 ± 0.01	22.93	9% R	A/A/O
S6	54.5 ± 0.2	85.4 ± 0.3	44.9 ± 0.0	7	22.08 ± 0.05	4.41 ± 0.06	3.53 ± 0.04	1.05 ± 0.03	24.02	10% E	CAST
S7	58.2 ± 0.1	86.3 ± 0.5	41.2 ± 0.1	6.4	25.05 ± 0.01	4.70 ± 0.01	3.84 ± 0.01	1.21 ± 0.01	24.02	10% E	OD
S8	61.4 ± 0.1	87.8 ± 0.6	38.2 ± 0.0	5.9	27.56 ± 0.06	5.20 ± 0.01	1.58 ± 0.02	2.49 ± 0.03	24.97	90% D	CAST
S9	74.6 ± 0.1	74.0 ± 0.2	24.3 ± 0.1	3.7	31.00 ± 0.05	6.20 ± 0.07	1.22 ± 0.01	3.34 ± 0.04	33.91	78% D&T	A/O

[a] On an air-dried basis.
[b] The ratio of water to solid was 20.
[c] By difference (O% = 100% – ash% – C% – H% – N% – S%).
[d] E: electronic wastewater; D: dyeing wastewater; R: rinse wastewater; T: textile wastewater.
[e] AS: activated sludge process; A/O: aerobic-oxic; OD: oxidation ditch; A/A/O: anaerobic-anoxic-oxic; UASB: up-flow anaerobic sludge bed; CAST: cyclic activated sludge technology.

Table 2
Organic matter composition of the dewatered sewage sludges tested.

Type of sludge	Organic matter (wt.%)[a]	Organic composition (wt.%)[a]					
		Nitrogenous compounds	Aromatic ring containing compounds		Non-aromatic ring and non-nitrogen compounds		
		Crude protein	Humic substances	Lignin	Crude fat	Hemicellulose	Cellulose
S0	29.3 ± 0.3	18.1	3.8	0.14	7.1	0.08	0
S1	30.9 ± 0.2	15.2	8.4	1.7	5.6	0.08	0.02
S2	37.4 ± 0.6	18.2	9.6	1.5	7	1.1	0.01
S3	46.1 ± 0.3	15.8	18	1.9	6.7	3.5	0.11
S4	49.6 ± 0.6	22.7	15.8	1.8	6.3	2.8	0.11
S5	51.1 ± 0.3	17.1	18.4	4.4	7.6	3.5	0.12
S6	54.4 ± 0.4	19.4	20.2	2.6	7.1	5	0.14
S7	59.5 ± 0.3	19.6	23.9	3.1	8.3	4.4	0.22
S8	63.9 ± 0.5	19	27.1	2.9	12.4	2.5	0.01
S9	73.0 ± 0.4	21.1	32	3.5	15.9	0.55	0.04

[a] On an air-dried basis.

low dry matter content, and long reaction time were demonstrated to be favourable for PAH generation in a previous study [14].

Studies have shown that organic pollutants, such as phenols, dioxins and PAHs, can be produced during the gasification of biowaste using SCW. However, the relationships between the concentrations and characteristics of organic pollutants before and after SCW treatment remain unclear. The properties of sewage sludge from different WWTPs vary greatly because of differences in the wastewater sources and sewage treatment processes [15], and the sludge properties have a great influence on the production of sewage sludge gasification in SCW [16], so the effects of the sludge properties on the concentrations of organic pollutants in gasified products also need to be assessed.

In this study, the concentrations and forms of 16 US EPA priority controlled PAHs in 10 different types of dewatered sewage sludge (DSS) and their gasified products were measured to investigate changes in the PAH distribution during the gasification of wet sludge in SCW (at 400 °C, 60 min and 23 MPa). Ten sewage sludge samples were used to assess the effects of the sludge properties on the PAH concentrations and forms in the liquid and solid residues of the SCWG of wet sludge.

2. Materials and methods

2.1. Materials

In this work, 10 different types of DSS, named S0–S9, were collected from WWTPs in Jiangsu, China. The DSSs from WWTPs usually is a mixture of primary sewage sludge and secondary sewage sludge. Besides, wastewater that treated in WWTPs is mostly a mixture of domestic wastewater and industrial wastewater. The wastewater treatment process and the proportion of industrial wastewater are listed in Table 1. The DSS samples were collected from the WWTPs and stored in the preservation box of a refrigerator at a temperature below 4 °C. The compositions, in terms of the contents of volatile matter, moisture, and ash, as well as the ultimate analyses of each type of DSS, are listed in Table 1. To investigate the correlation between the PAH concentration distribution in the residues and organics of raw DSS, the OM composition of each type of DSS was measured and is listed in Table 2.

2.2. Experimental apparatus and procedure

The SCWG of DSS was performed in a 316L stainless steel batch reactor obtained from the Songling Chemical Instrument Co., Yantai, Shandong, China. The schematic of the reactor has been described in detail previously [16]. Our experimental records showed that the reactor pressure was above 22.1 MPa at 400 °C with 33 mL of water in the reactor. Therefore, the mass of DSS added to the reactor was calculated from the required water volume (i.e., 33 mL) divided the moisture content of the DSS. The specific added mass of each sludge as well as the mass distribution of products after SCWG process was shown in Table 3.

In a typical experiment, 44 g of wet sewage sludge (with a water content of 74.8 wt%) was placed in the reactor, which was then sealed and placed in a salt-bath furnace kept at 400 °C. When the