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Nitrogen transformation among char, tar and gas during pyrolysis of sewage sludge and corresponding hydrochar

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ABSTRACT

Hydrothermal carbonization (HTC) is a promising thermochemical pretreatment to convert sewage sludge into the hydrochar prior to combustion or pyrolysis for energy generation. To investigate the effects of HTC on nitrogen transformation behaviors, pyrolysis of sewage sludge and the corresponding hydrochar were conducted. The results showed nitrogen in the hydrochar existed in more stable forms, making more nitrogen retained in the char for the hydrochar pyrolysis. Amine-N, heterocyclic-N and nitrile-N were detected in significant amounts for sewage sludge pyrolysis tar, which contributed to predominant (NH_3 + HCN)-N emission. Lower amine-N and heterocyclic-N content but higher alkyl nitrile-N content were observed in the hydrochar pyrolysis tar, which might explain the increase in HCN/NH_3 ratio. More importantly, the (NH_3 + HCN)-N yield from the hydrochar pyrolysis was considerably lower than that from sewage sludge pyrolysis, especially at temperatures higher than 650 °C. Taking account of the much lower nitrogen content, the total (NH_3 + HCN)-N emission from the hydrochar pyrolysis was only 35.6–48.2% of that from sewage sludge pyrolysis. The results suggested that HTC pretreatment of sewage sludge for energy production has the additional environmental benefit of mitigating nitrogenous pollutants emission.

1. Introduction

Sewage sludge, embedded with nearly all kinds of pollutants ranging from organic chemicals, heavy metals to pathogens, is increasing with rapid increase of wastewater treatment capacity [1,2]. As traditional methods of sewage sludge disposal including ocean dumping, landfill and land application are phasing out due to environmental issues and public concerns, efficient and environmental benign technologies should be developed for urgent challenge in sewage sludge disposal [3].

Combustion of sewage sludge is an excellent and proven disposal way, which can immobilize heavy metals in the solid residue, depredate highly toxic persistent organic compounds and reduce sewage sludge volume excellently as well as recovery energy [4,5]. However, high nitrogen content of sewage sludge supports the release of either NO_x or N_2O from combustion [6,7]. NO_x are main contributors to photochemical smog and acid rain, while N_2O will aggravate global warming and ozone layer depletion [8]. Pyrolysis is another attractive thermochemical conversion method to convert sewage sludge into bio-oil, combustible gas and the biochar [6]. Bio-oil and combustible gas can be used as potential chemical feedstocks and fuels and the biochar has been widely applied as either fuels or functional materials [9,10]. In addition, pyrolysis is the primary stage of the combustion, and understanding nitrogen conversion mechanisms during pyrolysis helps to reduce NO_x discharge in combustion process [11]. Consequently, extensive studies related to sewage sludge pyrolysis have been carried out over years. It has been demonstrated HCN and NH_3 were mainly originated from the second cracking of nitrogen-containing compounds including amine-N, pyrrole-N, pyridine-N and nitrile-N [6,9–14]. Increasing heating rate and shortening residence time decreased the emission of both NH_3 and HCN while increasing temperature facilitated NH_3 and HCN emission [6,9,12,13]. Additionally, iron/calcium-containing minerals were reported to catalyze the conversion of fuel-N/NH_3 into N_2 at high temperature [6,9,15]. By means of the analysis in terms of nitrogen existing forms and distribution, the nitrogen migrating pathways during sewage sludge pyrolysis were established and

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controlling intermediates generation was believed to be favorable in reducing NH_3 and HCN emission [6,9–11].

In addition to the emission of nitrogenous contaminants, the high moisture content and poor dewaterability of sewage sludge also limit the wide application of combustion and pyrolysis in disposing sludge due to energy-intensive drying process. Hydrothermal carbonization (HTC) is a notable thermochemical treatment which not only improve sludge dewaterability and but also convert sludge into a homogenized hydrochar with high energy density [16–18]. Moreover, HTC has the additional benefit of reducing nitrogen content through hydrolysis and deamination [19–21]. The outstanding advantages of HTC have made it increasingly important to convert sewage sludge into the hydrochar [18,22,23]. Nevertheless, more than 50% of nitrogen is still left in the hydrochar after HTC treatment of sewage sludge [20]. To control NO_x or its precursors emission during the hydrochar conversion requires better insight into the nitrogen transformation mechanism during hydrochar pyrolysis. However, related study is seriously insufficient compared to sewage sludge.

In the present study, nitrogen transformation during sewage sludge and corresponding hydrochar pyrolysis were investigated comparably. Specifically, the contribution of char-N and tar-N to NH_3 and HCN emission was evaluated and the effects of HTC and pyrolysis temperature on nitrogen distribution and nitrogenous compounds in the tar were determined. Furthermore, nitrogen conversion pathways of sewage sludge and the hydrochar during pyrolysis were also proposed. The purpose of this study is to investigate the effects of HTC on nitrogen transformation behaviors, which in turn provide possible strategy to reduce (NH_3 + HCN) and NO_x emission, and ultimately realize clean disposal of sewage sludge.

2. Experimental methods

2.1. Materials

In this study, digested sewage sludge was obtained from a wastewater treatment plant in Shandong Province. The digested sewage sludge (moisture content of 81%) was dried at 105 °C for 24 h and then crushed. The particles of 100–150 mesh were used for the pyrolysis in the present study.

The hydrochar was prepared through HTC of digested sewage sludge (without drying) using a stainless steel autoclave reactor equipped with thermocouple, pressure gauge and stirrer (Fig. 1). About 1.5 kg of raw sludge was loaded into the reactor and based on our preliminary experiment, the reactor was heated up to 200 °C holding for 30 min. After cooling the reactor down to ambient temperature, the solid-liquid mixture in the reactor was separated by vacuum centrifuge and the resultant solid residue was recovered as the hydrochar. Then the hydrochar was dried at 105 °C for 24 h and ground as raw sludge did. The dried hydrochar was weighed before stored in sealing bags for use. The main chemical properties of dried sewage sludge and the hydrochar are listed in Table 1.

Table 1
Characteristics of sewage sludge and the hydrochar (average ± standard deviations).

		Sewage sludge	Hydrochar
Proximate analysis (wt.%, db)	Fixed carbon	8.13 ± 0.20	10.13 ± 0.3
	Volatile matter	49.01 ± 0.30	31.33 ± 0.30
	Ash	42.86 ± 0.30	58.54 ± 0.36
Ultimate analysis (wt.%, db)	C	26.67 ± 0.18	23.40 ± 0.30
	N	4.00 ± 0.03	2.06 ± 0.06
	H	3.25 ± 0.33	2.36 ± 0.30
	S	1.17 ± 0.00	1.10 ± 0.00
	O[a]	22.05 ± 0.45	12.54 ± 0.53
Atomic ratio	H/C	1.46	1.21
	O/C	0.62	0.40
Metals contents (mg kg^{-1}, db)	K	4722.00 ± 56.67	4479.98 ± 60.49
	Ca	3314.39 ± 34.80	4400.19 ± 59.36
	Na	6340.87 ± 90.20	4180.66 ± 3.24
	Mg	6123.93 ± 64.13	7782.18 ± 40.44
	Al	20411.40 ± 92.91	28901.70 ± 99.20
	Fe	22384.10 ± 142.94	30371.00 ± 234.91
	Ni	2078.51 ± 24.93	2841.71 ± 28.21

Notes: db-dry basis.
[a] Calculated by difference.

2.2. Pyrolysis experiment

The pyrolysis of sewage sludge and the hydrochar were performed on a fixed-bed tubular reactor with a quartz tube of 1500 mm in length and 55 mm in inner diameter (Fig. 1). In each experiment, 3.0 g of fuel sample was loaded into a quartz boat and then was placed inside of the quartz tube appropriately. The quartz tube was pushed into the heating zone at the desired temperature (350–950 °C in an increment of 150 °C). After 30 min pyrolysis at final temperature, the quartz tube was pushed out of the heating zone and cooled down to ambient temperature using an electric fan. During the whole pyrolysis, a 500 mL min^{-1} of N_2 was introduced to maintain an inert atmosphere.

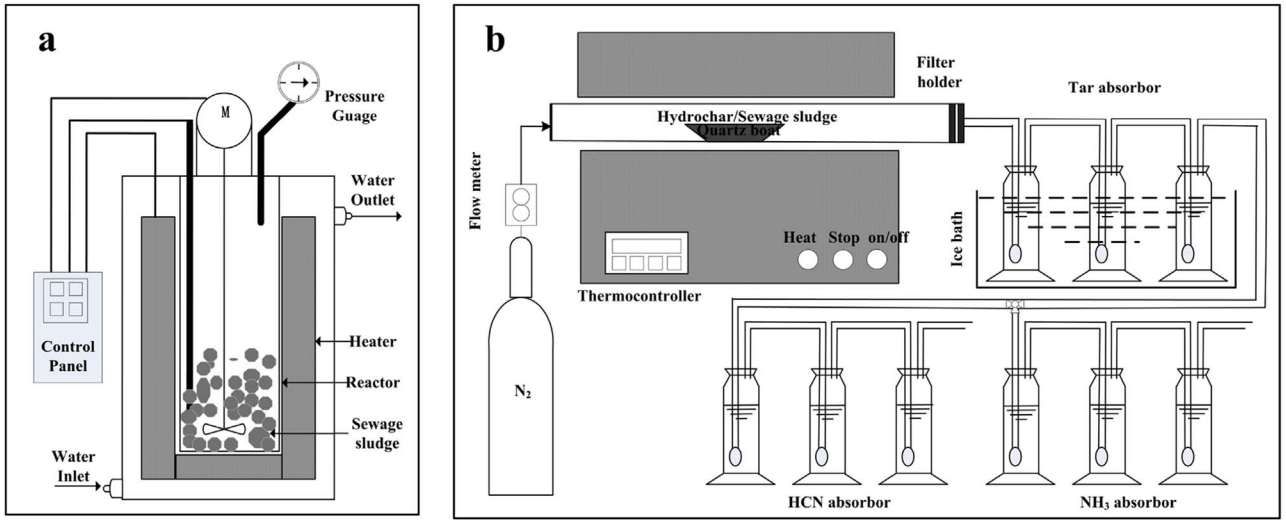

Fig. 1. Schematic diagram of the hydrothermal carbonization (a) and pyrolysis process (b).