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Product characteristics and kinetics of sewage sludge pyrolysis driven by alkaline earth metals

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ABSTRACT

Alkaline earth metals (AEMs) aggregated in sludge minerals influence the pyrolysis characteristics and product distribution. Sewage sludge pyrolysis behaviors driven by AEMs were first investigated using advanced thermogravimetry sequentially combined with Fourier transform infrared spectroscopy and mass spectrometry (TG-FTIR-MS). The AEMs represented by MgO and CaO affected the release of volatile products in different ways during sludge pyrolysis. Over 440 °C, CaO and MgO additions both enhanced total absorbance of pyrolytic volatiles, while the enhancement coming from CaO was stronger. Both additions reduced the release order of alkanes and olefins by varying degrees. The degree of reduction with MgO was more significant than that with CaO, while CaO addition promoted the release of CH_4, C_4H_8 and C_5H_{10} over 490 °C with respect to MgO. The addition of MgO more severely suppressed the release of pollutants including NH_3, HCN, NO_2, H_2S, CH_3SH, COS, SO_2 and nitrogen-derived aromatics than that of CaO. The catalytic effect induced by both species was evidenced by the related pyrolysis kinetics. The attained results revealed that AEM-containing minerals are promising candidates for pollution control during sludge pyrolysis for value-added products recovery.

1. Introduction

Sophisticated biological processes are widely adopted in municipal wastewater treatment for their efficiency and low cost; however, the large amounts of byproducts arising from the purification of wastewater, termed sewage sludge, are produced [1]. By 2015, 46.7 billion cubic meters of municipal wastewater were discharged in China [2], and the estimated production of sewage sludge with 70% moisture was approximately 28 million tons [3]. As both a carrier of wastewater-borne microbes and an aggregate of pollutants, sewage sludge not only contains bioavailable nutrient elements such as nitrogen, phosphorus and potassium but also includes dead microbe bodies, toxic organics not well degraded by microbes and heavy metals [1,4–6]. Due to the diverse composition, the bulk water remaining after mechanical dewatering and the quickly increasing generation of sewage sludge, conventional sludge management options such as incineration, composting, landfill and soil utilization are limited by varying degrees for widespread practice [7,8]. Thus, efficient, environmentally benign and cost-effective alternatives are needed.

The emerging pyrolysis technology, which is the underlying step of combustion and gasification, is a promising alternative for sludge treatment in terms of treatment efficiency [9,10], pollution reduction [4,11] and energy and resource recovery [12,13]. A current challenge in sludge pyrolysis for commodity recovery and energy saving involves the efficient catalytic interaction between the organic substances in sludge and the external or internal mineral source [14,15]. Previous studies demonstrated a hybrid effect induced by the minerals on the decomposition of sludge components and the physicochemical properties of the derived pyrolytic products [16,17]. Alkaline earth metals (AEMs, mainly magnesium (Mg) and calcium (Ca)) with the oxides are contained in the minerals, accounting for nearly 10% of the oxides in the dry sludge matrix [18]. Due to the substantial generation of municipal wastewater, the fractions of AEMs are prone to increase [7]. It has

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been acknowledged that AEMs have catalytic effects on the pyrolysis of coal [19,20] and biomass [21,22]. The type, valence, existing form and thermal stability of alkaline earth metals mainly dominate the effects induced during coal and biomass pyrolysis as well as the composition of the derived products, and the pyrolysis temperature affects the reactivity of the alkaline earth metals [23]. In addition, the nitrogen (N) transformation of coal or biomass suffers in the presence of alkali and alkaline earth metal species, and NH_3 and HCN have been found to be the two main nitrogen species evolved from pyrolysis reactions [24]. It should be highlighted that systematic investigations into the impact of AEMs on pyrolytic product generation and pollution control are still lacking.

A limited number of studies have investigated the effects of CaO on the product distribution and contaminant mitigation [25,26]. Sludge inherently containing CaO promoted the decomposition of sludge substances and prolonged the duration of sludge pyrolysis [16]. Gaseous products rich in H_2 can be attained with the addition of CaO, which favors the forward transfer of the water-gas shift reaction by capturing CO_2 [27], and the N in sludge can be transformed into non-polluting N_2 because CaO hinders the formation of NO_x [28]. Our previous study also found that CaO can catalyze the decomposition of the sludge matrix under high temperatures (over 700 °C). However, the effects of MgO on sewage sludge pyrolysis have not been well concerned; this topic is worth studying because Mg laying at the same group as Ca in the periodic table may be exhibit a similar effect on sludge pyrolysis to that from Ca. In studies on sludge pyrolysis, techniques such as thermogravimetry (TG) coupled with mass spectrometry (TG-MS) [29,30] or Fourier transform infrared spectroscopy (TG-FTIR) [14,31] are commonly used. Since the volatiles preliminarily generated during sludge pyrolysis are rich in aromatic compounds, characteristic of several phenyls, and thus easily condensed, there are limitations in terms of response sensitivity in using dual combinations for characterization. Thus, it was expected that triple combinations of those techniques would be attractive to attain a real-time map of the progress of sludge pyrolysis. To date, there are few studies focusing on the sewage sludge pyrolysis behaviors using a combined TG-FTIR-MS technique, especially with the presence of AEMs.

In this study, the individual roles of the AEMs in sewage sludge pyrolysis were systematically investigated. An advanced combined TG-FTIR-MS technique was first applied to track the evolution of pyrolytic volatiles as the pyrolysis temperature rose. The thermogravimetric performance, real-time infrared spectral absorbance of the volatile products and their released mass spectra were obtained. The sludge chars generated from the bench-scale pyrolysis of AEM-added sludge were characterized. A kinetic investigation of sludge pyrolysis in the presence of AEMs was conducted. Owing to the excellent response capacity, robust disturbance resistance and useful data on sludge pyrolysis, the TG-FTIR-MS technique is expected to increase the knowledge of sludge pyrolysis regulated by AEMs, which will greatly benefit the design and application of pyrolysis technology in sludge management practices.

2. Materials and methods

2.1. Sewage sludge pretreatments

The sludge feedstock used in the present study was sampled from a municipal wastewater treatment plant located in Beijing, China, in which the dewatered cake had a moisture of approximately 80%. After sampling, the obtained sludge was transported to the laboratory within several hours and then heated in an oven at 105 °C for two days. The dried sludge sample was sequentially crushed, screened and sieved to collect particles between 0.015 and 0.074 mm in size. The physicochemical properties, via proximate analysis, ultimate analysis and mineral composition analysis, of the sludge were determined, as shown in Table 1. It was found that the contents of the alkaline earth metals Mg and Ca expressed as the oxide form in the sludge were 2.99% and 5.30%, respectively.

AEM-impregnated sludge was prepared by mechanical dry mixing at a constant mass ratio of Mg/Ca-based chemicals to the mixed sludge. The Mg/Ca-based chemicals were MgO (analytical grade, Guangfu, China) and CaO (analytical grade, Guangfu, China), respectively. Considering the fact that the source of the municipal wastewater and the wastewater treatment process affect the content of alkaline earth metals in sludge, the studied addition mass ratios of Mg/Ca-based chemicals to the mixed sludge were 10%, 20%, 30%, 40% and 50%. Prior to mixing with sludge, these reagents were calcined at 700 °C for 4 h to remove adsorbed water and activate the reactivity. The AEM-added sludges were designated based on their addition ratios, for example, CAS10 and MGS10 represent the 10% addition ratio of CaO and MgO, respectively (Table S1). The sludge without addition was abbreviated RS and tested for comparison.

2.2. Sludge pyrolysis in TG-FTIR-MS

A combined TG-FTIR-MS device (TGA 800-Frontier FTIR-Clarus SQ 8 GC/MS, Perkin Elmer, USA) was utilized to conduct the pyrolysis experiments on the AEM-added sludges, which were heated from 30 to 900 °C at a rate of 30 °C/min under helium (99.99%, V/V) at a flow rate of 90 mL/min. In this device, the volatiles released from the TG furnace were directly pumped into the cell of the Fourier transform infrared spectrometer (wavenumber range of 4000-450 cm^{-1} and resolution of 4 cm^{-1}) and then analyzed (Both the accuracy and repeatability of the infrared spectrometer were verified using the standard spectra of polystyrene). After being detected by FTIR, the volatiles were immediately swept into the mass spectrometer. To avoid the condensation of volatiles, the temperature of the transfer lines (TL900, Perkin Elmer, USA) connecting the TG to the FTIR and FTIR with the MS were fixed at 290 °C. For RS pyrolysis, the amount of sample weighed was 20±0.5 mg. To rule out the interference arising from the amount of sludge sample, the mass of AEM-added sludge samples was in accordance with the addition mass ratios studied, meaning that the mass of sludge was constant in each run. It was confirmed that the mass change of the sludge materials with different amount of inorganic ash showed few influences on the progress of sludge pyrolysis (See Fig. S9-S13).

Real-time IR spectra related to the absorbance of volatile products generated from the pyrolysis of the sludge samples were recorded along with the mass spectra. In accordance with the results of the preliminary experiment, alkanes, olefins, aromatic compounds and inorganic compounds were detected in the derived volatiles. The mass-to-charge ratio m/z signals of alkanes included 16 (CH_4) and 30 (C_2H_6), those of olefins included 42 (C_3H_6), 56 (C_4H_8), 70 (C_5H_{10}) and 78 (C_6H_6), those of inorganic compounds included 18 (H_2O), 17 (NH_3), 27 (HCN), 34 (H_2S), 44 (CO_2), 46 (NO_2), 48 (CH_3SH), 60 (COS) and 64 (SO_2), and those of aromatic compounds with nitrogen substituted included 67, 79, 93, 94, 103, 105, 116 and 120, which are described in Table S2. It was found that the release characteristics of volatile products could be well measured by the TG-FTIR-MS device.

2.3. Characterization of the sludge-derived char

To investigate the difference in the sludge char derived from AEM-added sludge, MGS20 and CAS20 were pyrolyzed at 700 °C for 60 min in a silicon tube (Φ 60 mm × L 1000 mm) (NBD-1200O,