



Effect of alkali addition on sulfur transformation during low temperature pyrolysis of sewage sludge

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Abstract

Odorous sulfur-containing gases released during sewage sludge processing cause significant environmental pollution. This study investigates the effect of alkali addition on sulfur transformation as well as the release of the sulfur-containing gases during sewage sludge pyrolysis at 150–450 °C. The presence of alkali can promote the transformation of unstable organic aliphatic and aromatic sulfurs into more stable sulfoxides and sulphonic acid at low temperatures (i.e., 250 °C). Alkalis also fix the inorganic sulfide and sulphate in char. Therefore, the release of the sulfur-containing gases can be greatly reduced with alkali addition. Stronger alkalis show more significant effect on the reduction of sulfur-containing gases, likely because of more OH radicals generated for the transformation of organic sulfurs.

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1. Introduction

Sewage sludge, a typical kind of municipal solid waste, has been produced enormously due to the rapid urban growth in China, creating serious environmental problems [1,2]. Several technologies such as anaerobic or aerobic digestion [3,4], incineration or co-combustion with coal [5–7] are currently used for energy production from sewage sludge. However, a low temperature drying/pyrolysis process is essential for the efficient utilization of sewage sludge in thermal processes

[8–11]. The inevitable odor emissions during pyrolysis can cause other concerns on environmental pollution and human health [12–14].

Sulfur-containing gases are the main odorous gases produced during low temperature pyrolysis, in addition to nitrogen gases and volatile fatty acids (VFAs) [1,13]. Our previous study reported that the sulfur-containing gases are mainly produced from low temperature decomposition of organic sulfur [8], such as aliphatic and aromatic sulfur compounds. Those organic sulfur compounds are easily decomposed at low temperatures via C–S bond cleavage, leading to the formation of odorous gases including H₂S and SO₂, COS, CS₂, CH₃SH [15–17].

Alkali addition has been considered as an effective method to reduce the emission of

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sulfur-containing odorous gases from low temperature pyrolysis of sewage sludge [18], because the presence of alkali may lead to the cleavage of C–S bond at higher temperatures [17]. It was also reported that CaO can catalyze ring-opening reactions of aromatic hydrocarbons followed by addition reaction of H₂O in solid phase, hence fixing sulfur in solid product [19]. Therefore, the purpose of this study is to study the alkali addition on the transformation of sulfur and the release of sulfur-containing gases during low temperature pyrolysis of sewage sludge.

2. Experimental

2.1. Sample preparation and properties

The raw sludge (RS) was obtained from a municipal wastewater treatment plant in Wuhan, China. To minimize the possible structural changes, the sludge was immediately dried at 105 °C to constant weight and pulverized to a size fraction of 106–125 μm. In order to minimize the effect of natural alkali species in the sludge the sample was then soaked in 1.0 M hydrochloric acid (HCl) and stirred for 24 h to remove the alkali and alkaline earth metallic (AAEM) species in the sludge. The acid-treated sample was filtered and continuously washed by distilled water until the pH was close to 7. The washed sample was further dried to prepare the acid-wash sludge (AS). The proximate and ultimate analyses results of the RS and AS are given in Table S1.

The AAEM contents of the RS and AS were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). As shown in Table S2, more than 80% of AAEM species were removed during acid treatment, apart from the silicon aluminate AAEM species which are stable [20]. The distribution of different sulfur compounds in RS and AS was also analyzed by X-ray photoelectron Spectroscopy (XPS), and the results are shown in Fig. S1. Compared to the sulfur in the RS, acid washing removed the inorganic sulphide and part of sulphonic acid, leading to relative increases in the contents of aliphatic and aromatic sulfurs. The total sulfur content also increases from 0.82 to 0.93% as the acid washing process removed the water-soluble and acid-soluble sulfurs.

Various alkalis such as Ca(OH)₂, Mg(OH)₂, KOH, NaOH were added into AS to prepare the alkali-added sludge samples at a metal-to-sulfur mole ratio of 30:1 by dry mixing [21,22]. The alkali pretreated samples were denoted as AS–Ca(OH)₂, AS–Mg(OH)₂, AS–KOH, AS–NaOH, respectively.

Two organic sulfur compounds including benzyl sulphide (BS), 4,4'-dihydroxydiphenyl sulphide (DHS) were also chosen to represent the typical aliphatic and aromatic sulfurs in sludge [8,17]. Their chemical structures are shown in Table S3. NaOH was also added into BS and DHS using

the dry mixing method to prepare the alkali-added samples, which were denoted as BS–NaOH and DHS–NaOH, respectively.

2.2. Pyrolysis experiments and sample analysis

Low temperature pyrolysis experiments were carried out at 150–450 °C in a fix-bed reactor detailed in Fig. S2. The reactor was pre-heated to the pyrolysis temperature with 1 l/min (measured under ambient conditions) nitrogen gas continuously flowing through the reactor. Then, ~0.5 g of sludge sample was loaded into the reactor and held for 20 min to ensure the sulfur-containing gases were completely released. The volatile products were passed through U-shaped tubes in an ice water bath to condense the tar and reduce gas temperature, and then gas products were collected by gas bags for further analysis. When collecting the volatile part of the pure organic sulfur compounds, the U-shaped tubes were replaced with helical tubes to ensure the complete condensation of volatiles. After each experiment, the char products were cooled down in inert atmosphere, and the char samples from repeated experiments were mixed together for subsequent sulfur determination.

The gas products were analyzed using a gas chromatograph (model no. HC-5) equipped with a flame photometric detector (FPD) to measure different sulfur-containing gases (i.e., H₂S, SO₂, CS₂, COS and CH₃SH). The sulfur content in char was determined by Vario Microcube analyzer (Elementar Company, Germany). The organic sulfurs were analyzed with XPS (VG Mutilab 2000). Approximately 5 mg of sludge/char sample was sent for XPS analysis with an X-ray source operated at 40 W (accelerating potential of 10 keV, current of 4 mA) after ground. According to method in our previous work [8,23], the S 2p spectra were fitted to 6 different peaks with different binding energies, which represent inorganic sulphate (170.0 ± 1.0 eV), sulphonic acid (168.2 ± 0.2 eV), sulphoxide (166.0 ± 0.5 eV), aromatic sulfur (164.1 ± 0.2 eV), aliphatic sulfur (163.3 ± 0.4 eV) and inorganic sulphide (162.2 ± 0.6 eV). After each analysis, all of these peak areas were measured to calculate the relative content for six sulfur compounds in the sample.

3. Results and discussion

3.1. Pyrolysis of the alkali-added sludges

3.1.1. Sulfur in the gas products from the pyrolysis of the alkali-added sludges

Pyrolysis experiments of AS and those added with NaOH, KOH, Mg(OH)₂, Ca(OH)₂ were first conducted at 150–450 °C. As shown in Fig. 1, this study compares the yield of total sulfur-containing gases at various temperatures for different alkali-added sludges. The yields was calculated by nor-

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