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Release of hydrogen sulfide during microwave pyrolysis of sewage sludge: Effect of operating parameters and mechanism

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HIGHLIGHTS

- Release of H_2S under different factors from microwave pyrolysis was studied.
- The evolution of sulfur-containing compounds in the chars was conducted.
- Temperature and catalyst were the main factors influencing the release of H_2S during pyrolysis.
- Organic sulfur accounted for 60% of total-S in sludge responsible for the formation of H_2S.
- The mechanism of H_2S formation from mercaptan, aromatic-S and sulfate was proposed.

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ABSTRACT

The effects of sludge characteristics, pyrolysis temperature, heating rate and catalysts on the release of H_2S and mechanism of H_2S formation during sludge pyrolysis were investigated in a microwave heating reactor (MHR). The evolution of sulfur-containing compounds in the pyrolysis chars obtained at temperature range of 400–800 °C was characterized by XPS. For a given temperature, the maximum concentration of H_2S appeared at moisture content of 80%. Compared to the influence of heating rate on the H_2S yields, pyrolysis temperature and catalyst played a more significant role on the release of H_2S during microwave pyrolysis process. The H_2S concentration increased with increasing temperature from 400 °C to 800 °C while decreased with increasing heating rate. Both the Nickel-based catalyst and Dolomite displayed significant desulfurization effect and Ni-based catalyst exhibited the larger desulfurization capability than that of Dolomite. The organic sulfur compounds accounted for about 60% of the total sulfur in the sludge which was the main reason for the formation of H_2S. The mechanism analysis indicated that the cleavage reactions of mercaptan and aromatic-S compounds at temperatures below 600 °C and the cracking reaction of sulfate above 700 °C respectively were responsible for the H_2S release during sludge pyrolysis.

1. Introduction

Energy and resource shortage is one of the greatest problems faced by the world nowadays and scientists worldwide have committed to find new alternatives to the fossil fuel energy. Sewage sludge as a misplaced biofuel rich in the organic substances (polysaccharides, lipids, proteins and nucleic acids) is increased on a relentless growth curve [1]. However, environmental quality requirements for sludge are becoming significantly stringent and economic pressures require low-cost solutions [2]. Recently, there has been increasing concerns about the thermochemical conversion of sludge into bio-fuels for energy recovery through pyrolysis and gasification technology. Compared to the recovery of heat from incineration and combustion, through pyrolysis and gasification, sludge can be transformed into high-quality biosyngas [3,4], combustible tar [5,6] and char [7] products under specific conditions. Pyrolysis/gasification is an effective technology for a clean conversion. During the sludge pyrolysis process, different malodorous gases will be released including volatile compounds [3], NH_3 and HCN [8] which also has been studied in the previous researches [9,10]. H_2S, an odorous gas to be harmful to human health, was reported to be the predominant sulfur-containing gas during sludge pyrolysis [11]. H_2S can be converted into SO_x compounds, contributing to the severe photochemical smog and acid rain pollutions. Consequently, research on the release of H_2S gas during the pyrolysis process is an issue of particular concern.

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Table 1
Characteristics of different sludge samples (wt%, daf).

Sludge samples	C	H	O	N	S
SS	24.17	4.57	24.63	4.24	0.70
LSS	35.02	6.75	16.98	6.13	0.55
ADS	22.16	4.17	20.13	3.89	0.54

daf, dried and ash-free basis.

Many efforts have been made to study the behavior of sulfur-containing compounds in relation to the formation of H_2S during the pyrolysis of sewage sludge [12–14]. It was reported that sulfur in the sludge was presented in the form of both inorganic and organic compounds. Especially, the organic-sulfur was considered as the main sources contributing to the release of H_2S during pyrolysis [11]. Gostelow reported that the reduction of sulfate was also the main reason for the formation of H_2S just like the desulfurization of sulfur-containing organic compounds [15]. Moreover, Ca-containing minerals have been proven to be able to affect the sulfur distributions in the pyrolysis solid, liquid and gas products, which further influencing the release of H_2S during the pyrolysis of sewage sludge [16]. It was also reported that sludge-derived adsorbents has been demonstrated to be efficient for H_2S removal at room temperature, mainly attributing to the oxides of iron and calcium remained in the sludge [17–19]. It was noted that lots of researchers focused on the pyrolysis of sewage sludge in conventional heating equipments such as fluidized beds, fixed beds or electric furnace. Actually, microwave has many advantages to carry out the sludge pyrolysis process with respect to its characteristics of rapid heating, low temperature of reactor wall and less PAHs yields [9,20]. Thus, microwave-induced pyrolysis is considered as a potential technology for the pyrolysis of sludge to recover energy efficiently. The difference on the heating mechanism of the conventional and microwave pyrolysis might result to different concentration of H_2S during the sludge pyrolysis process. However, the release of H_2S and its formation mechanism under microwave pyrolysis atmosphere was less reported as far as authors concerned. Pyrolysis behavior of sludge depends crucially on its physical and chemical characteristics as well as pyrolysis conditions, such as temperature, heating rate and additives [16,21]. An effect was found of the operation parameters on the yield and quality of pyrolysis products, while there is a lack of relevant literatures about the above factors on the release of H_2S during sludge pyrolysis.

Based on the problems mentioned above, a microwave heating reactor (MHR) was designed to introduce microwave in the sewage sludge pyrolysis [22]. The effects of various factors including sludge characteristics, pyrolysis temperature, heating rate and different catalysts on the H_2S yields were investigated in order to explore the important processing parameters. Moreover, the mechanism of H_2S formation during microwave pyrolysis of sewage sludge was also discussed at the final section.

2. Material and methods

2.1. Sewage sludge samples

The raw sewage sludge (SS) was supplied by a municipal wastewater treatment plant located in Harbin, China. This sludge had a moisture content of 78%, an ash content of 42% (on dry basis) and a volatile ratio of 55% (on dry basis). The lab-SBR sludge (LSS) and anaerobic digestion sludge (ADS) were obtained from the corresponding reactors in the lab. The dewatering of the sludge samples was according to our previous work [10]. The ultimate analysis of above samples was conducted in an Elemental Analyzer (Americas Vario EL III) and results were given in Table 1.

To ensure sample comparability, in the case of Nickel (SS-Ni) and Dolomite (SS-D) loaded samples, partial of SS was first mixed with the distilled water to form the sludge solution, and then Nickel-based catalyst or Dolomite (20 wt.%) was added to the sludge solution stirring for 24 h to ensure uniformity of the sample. The remaining mixture was dried in a vacuum at 106 °C for 24 h and then was ground and sieved to obtain a particle size of 106–150 μm.

2.2. Microwave-induced pyrolysis

Sludge pyrolysis was performed in a microwave heating device within a temperature range from 400 °C to 800 °C, and its detailed dimension information has been given before [22]. As displayed in Fig. 1, the experimental apparatus consisted of a microwave magnetron of 2450 MHz, a multiple mode cavity, a temperature controlling system, water-cooling circulation system, tar collection system. An infrared optical pyrometer was employed to measure the temperatures of the samples during the experiments. For each temperature test (final temperature), pyrolysis experiments were carried out by placing samples in the quartz reactor inside the microwave cavity first, and then the samples were heated from room temperature to the final temperature under the "isothermal mode" of microwave device. At the isothermal mode, the heating rate of microwave oven was variable with an average value of 300 °C/min during the pyrolysis. After attaining the required temperatures, the samples subjected to microwave radiation were held for 10 min under the fixed temperature until no significant release of gas was observed. To ensure an inert atmosphere, Argon (Ar) was injected into the system with a constant flow rate of 10 L/min for 20 min and then taken off before the start of the experiment. The microwave generator was turned off after reaching the designated reaction time. The carrier gas was reinjected into the system to purge out the residual gas for 20 min. In each experiment, the volatile substances evolved from the sludge pyrolysis passed through a number of dichloromethane-containing condensers placed in ice bathes. Then the non-condensable gases passed through for testing. The residual chars in the reactors were collected and stored in airtight containers until they were cooled to room temperature.

2.3. Product analysis

H_2S concentration was analyzed in a HP 5890 series II gas chromatograph fitted with a TCD detector. An HP 3 FT Molecular Sieve 13×, 45/60 column was used. The oven temperature was set at 70 °C and the carrier gas flow (H_2) was 20 mL/min. The gas samples (1 mL) were injected into the gas chromatograph and the injector temperature was 120 °C. The TCD was calibrated with a standard gas mixture at periodic intervals.

XPS analysis of the char-S compounds was performed according to the previous methods [23]. The experiment was performed on a PHI5700ESCA spectrometer equipped with Al Kα radiation (12.5 kV and 16 mA) at a base pressure of 5×10^{-7} Pa. The sludge samples were referenced to the C 1s peak at 284.6 eV. The areas of peaks reflected the relative contents of different components, which were normalized from dividing the peak area values by the total SS–S content for the semi-quantitative analysis.

3. Results and discussion

3.1. Effect of sludge characteristics

3.1.1. Sulfur content

Due to the different wastewater treatment process and water quality, the sludge properties of WWTPs are usually variable. In addition, in many cases sludge pretreatment was used to reduce the