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Catalytic role of conditioner CaO in nitrogen transformation during sewage sludge pyrolysis

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Abstract

Thermal disposal of sewage sludge is likely to cause serious nitrogen related environmental pollution since it contains considerable amounts of nitrogen, the species of which are quite different from those in coal. Considering that lime (CaO) is a widely applied chemical conditioner for sewage sludge dewatering, this study investigated the catalytic role of conditioner CaO in nitrogen transformation during sewage sludge pyrolysis in a drop-tube/fixed-bed furnace at 873 K, 1073 K and 1273 K, respectively. Model compounds were also used to further clarify the mechanisms involved. According to the results, conditioner CaO increased the fraction of more stable protein-N as well as amine-N. The solid phase reactions produced CaC_xN_y, thus enhancing the nitrogen retention in char. Correspondingly, decreased relative ratio of nitrates-N/nitrites-N and oxygenated organics in sludge conditioning contributed to less NO emission. Meanwhile, conditioner CaO promoted the conversion of HCN to NH_3, as well as the deamination of proteins, amine, and other N-containing compounds in tar and char, leading to increased NH_3 generation. Subsequently, CaC_x, the decomposition product of CaC_xN_y, captured NH_3, driving down the final production of NH_3. In addition, $Ca(OH)_2$ hindered the transformation of nitrile-N in char to HCN, decreasing HCN generation. CaO reacted with HCN, further reducing its releasing amount. CaC_xN_y derived from different sources decomposed to produce a very large amount of N_2. These indicate that reusing conditioner CaO is a promising strategy for reducing the productions of NO_x precursors efficiently and increasing the formation of non-polluting N_2 dramatically.

Keywords: Sewage sludge; Pyrolysis; Nitrogen transformation; Conditioner CaO

1. Introduction

In recent years, gasification and incineration have aroused increasing attentions for sewage sludge management and energy recovery [1–3]. However, sludge contains considerable amounts of nitrogen (2.4–9.0 wt.%), which is much higher than that of traditional fuel coal (<1.0 wt.%) [4–6]. Nitrogen exists mainly as protein-N in sludge [5–7], while pyridine-N and pyrrole-N are the dominant nitrogen functionalities in coal [8–10]. The nitrogen species in sewage sludge is likely more active than that in high-rank coal, and perhaps even more unstable than that in

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low-rank coal. Although thermal disposal methods indeed enjoy many significant advantages, they are not widely employed since oxides of nitrogen (NO_x and N_2O) emitted in these processes will eventually cause serious environmental pollution. The generation of NO_x/N_2O during gasification/incineration strongly depends on the types and yields of NO_x precursors produced in primary devolatilization stage, including N-containing gases (e.g. NH_3 and HCN), tar and char [11–12]. Tian and coauthors [5] found that HCN was the main NO_x precursor, accounting for 80% of total nitrogen when sludge was pyrolyzed in a fluidized-bed/fixed bed reactor. And NH_3 was the other important NO_x precursor at a fast heating rate. Cao et al. [13] provided a basic insight into sludge nitrogen transformation at 673 K to 973 K, and believed that HCN comes from the thermal cracking of volatiles above 823 K. Tian et al. [6] further demonstrated that deamination of amino-N derived from labile proteins decomposition led to NH_3 emission at 573 K to 773 K, and the ring-opening of heterocyclic-N compounds contributes to NH_3 releasing at 773 K to 1073 K. Simultaneously, the cracking of nitrile-N and heterocyclic-N is responsible for HCN generation.

In order to minimize the emissions of the NO_x precursors, in coal-related researches, various control technologies such as Ca-catalyzing have been developed [14]. It was reported that Ca-based catalyst (mainly refers to CaO) increases the N_2 yields when Yallourn lignite was pyrolyzed at 1123 K to 1273 K [15]. And mineral-Ca contained in low-rank coal has higher catalytic efficiency than additive-Ca [16,17]. At high temperatures, synergistic effects occur between nanoscale-CaO and iron minerals in coal [18]. Nanoscale-CaO can react with heterocyclic-N in char to form interstitial CaC_xN_y which is very easy to decompose to produce CaC_z and N_2, or further react with hydrogen radicals in solid and gaseous phase [12]. NH_3 generates accompanied by carbon crystallization [19]. In certain conditions, CaO was able to capture NH_3 [19]. It can also promote the conversion of HCN to NH_3, NO and H_2 [20]. Obviously, CaO is capable of participating in many processes of coal-N transformation, controlling the partitioning of volatile-N to HCN, NH_3, tar-N and pollution-free N_2. It should be borne in mind that reactivity of nitrogen structure is also an important guarantee for the N_2 formation [21].

For sewage sludge, as our previous study demonstrated, lime (CaO) is a commonly used chemical conditioner in dewatering process [22–24]. The calcium left in sludge dewatered with CaO as conditioner (S-CaO) is evenly distributed and presented as $Ca(OH)_2$, which will quickly decompose to produce highly active CaO during thermal treatment [24].

Considering that the content and species of nitrogen as well as calcium in sludge are quite different from those in coal, it is of importance and interest to investigate the effects of conditioner CaO on nitrogen transformation during the pyrolysis of sewage sludge. Unfortunately, little effort has been directed to it until now. Thus, this study aims to: (1) quantify the difference in nitrogen distributions in gases, tar and char between the cases of raw sludge (RS) and S-CaO pyrolysis; (2) elucidate the effects of conditioner CaO on the evolution of nitrogen species in three phases by using model compounds; (3) propose possible strategies for reducing the emissions of NO_x precursors and increasing the formation of non-polluting N_2.

2. Experimental

2.1. Properties of sludge samples

Raw sludge (RS) with moisture of 81.0 wt.% was obtained in a municipal wastewater treatment plant in Wuhan, China. With the same sample preparing process adopted by our previous study [24], 0.3 g/g (dry solids) CaO was applying to sludge conditioning, producing dewatered sludge with moisture of 69.4 wt.%. Afterwards, these two samples were dried at 378 K to constant weight and pulverized to 180–250 μm. As Table 1 lists, RS and S-CaO all have high contents of volatile matter and ash, but low content of fixed carbon. Especially, the content of volatile matter in S-CaO is 41.31%, whereas fixed carbon is only 0.75%. For this type of sludge, devolatilization is very important to the whole thermal disposal process. In addition, RS contains 4.78% of nitrogen, while S-CaO contains 3.10% of nitrogen due to increased solids amount caused by adding conditioner. The chemical compositions of ashes summarized in Table 2 demonstrate that further conditioning made CaO prevalenting in sludge particles with particularly high content of 46.75%.

2.2. Sludge pyrolysis procedure and sample analysis

Sludge pyrolysis was carried out in a drop-tube/fixed-bed furnace (750 mm long with a 120-mm internal diameter), as shown in Fig. 1. The reactor consists of four parts which were connected by grinding mouth: (1) injector (17 mm i.d.) with water-cooled wall, (2) intermediate reaction tube (38 mm i.d.) with sintered quartz filter installed on the sidewall and bottom quartz plate used to support the char generated, (3) the outer quartz tube (60 mm i.d.), (4) two special U-shaped tubes (10 mm i.d.) with a small flask for tar storage. Prior to each run, the quartz reactor was electrically heated to the required temperature (873 K, 1073 K and 1273 K, respectively) with three streams of argon (total of 1000 NmL/min) passing