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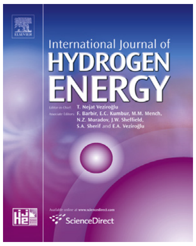

Influence of residual moisture on deep dewatered sludge pyrolysis

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ABSTRACT

Wet sewage sludge pyrolysis is an attractive method for producing H_2-rich fuel gas. To reduce energy consumption for excess moisture evaporation, deep dewatered sludge was used instead of traditional high-moisture sludge in this study. The emphasis was placed on elucidating the effects of residual moisture on tar, char, and on syngas generation, and clarifying the mechanisms involved. Results show that residual bound water exerted a stronger influence on products yields and distributions than free water, since the former could work inside sludge particles while the later only acted as steam outside. At low temperature (873 K), sludge moisture increased the relative ratio of cyclic, unsaturated, and hydroxyl, aldehyde or carboxyl-containing compounds in tar, in whose generation process H_2 and carbonaceous gas were produced. When the temperature rose, water in sludge increased the surface area of the char. The breaking of $\underline{C}$–C bonds caused by residual moisture would promote the macromolecular organic matters conversion to smaller ones, which were easy to undergo steam gasification, thus giving rise to the transformation of char–C to gas–C and enhancing H_2 yield. Therefore, the production of syngas, containing large amounts of H_2 and CO, was improved efficiently.

1. Introduction

The ultimate goal of sewage sludge management is to achieve the reduction of sludge volume, stabilization of organic matter, production of fuels, and minimization of the environmental impact. Among the different alternative disposal routes currently available for sewage sludge, pyrolysis has been proven to be one of the most promising methods, which can meet all the requirements mentioned above [1–3]. Since 1980s, numerous researchers have studied on the sewage sludge pyrolysis with different objectives [3–13]. For example, Urban and Antal [6], and Scott et al. [7] elucidated the pyrolysis kinetics of several dried sewage sludge samples, and developed models consisting of parallel competitive reactions. Besides on the kinetics, a large number of studies have focused on pyrolysis products, including solids, liquids, and gases. Tay et al. [8] prepared activated carbon from dry sewage sludge by pyrolysis and $ZnCl_2$-catalyzed activation. Others [9,10] applied similar sludge-based adsorbents to pollutants removal. Yang et al. [11] investigated the characteristics of pyrolysis oils derived from dry sewage sludge with a view to their application in a diesel engine. Shen and Zhang [12] optimized operating parameters for maximizing the fuel oil yield during dry sludge pyrolysis process. In addition, Inguanzo et al. [13] found that high pyrolysis temperature increases the yield of gas fraction with relatively high lower heating values (LHV). It must be noted that all the feedstocks are used in dry base so as to have high enough LHV. However, much of the energy contained in solids is consumed for removing the moisture during the sewage sludge drying process.

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To overcome this difficulty, in several researches [14–19], wet sludge was directly subjected to pyrolysis, combining drying and devolatilization together, which could be considered as a gasification process with steam as gasifying agent. Domínguez et al. [15–17] demonstrated that the residual moisture in conventional dewatered sludge increases gaseous production, as well as hydrogen content. The reason they supposed was that evaporated water might promote water–gas shift, steam reforming, and water–gas reactions. Zhang et al. [18] further revealed the decomposition process of dewatered sewage sludge, and suggested that the cracking and reforming of aromatic hydrocarbons at higher temperature (1273 K) give rise to the increase in H_2 yield. It should be pointed out that moisture favors gases generation within an appropriate range. According to Xiong's work [19], when the water content of sludge is higher than 51%, the LHV of gaseous product tends stable, while when it exceeds 47%, the amount of moisture participates in the reactions is close to saturation. In other words, the excess moisture not only does not work, but also consume energy for evaporation. This arouses urgent needs for effective technologies to reduce the water content of the dewatered sludge.

Traditionally, sludge was conditioned with polyelectrolyte and dewatered by centrifuge or belt press, through which the water content of sludge decreases from about 98% to 80%. Our previous study [20,21] has confirmed that sludge conditioned with Fenton's reagent and skeleton builders can easily achieve deep dewatering (water content is less than 60%) at a low chemical cost. Therefore, to solve the problem caused by the excess moisture, deep dewatered sludge was used instead of traditional high-moisture sludge in this work. It is worthy of study because conditioners function through changing sludge properties, which may exert a strong influence on subsequent pyrolysis process. Furthermore, wet sludge is the only object of study in research about related mechanism, resulting in the lack of direct evidence for the influence of moisture on sludge pyrolysis. Additionally, it is uncertain whether the residual internal water only plays role in generating a steam-rich atmosphere, which can be done by external free water. Thus, this study also aims to elucidate the effects of residual moisture on H_2-rich syngas, tar, and char generation, and clarify the mechanisms involved.

2. Experimental

2.1. Sample preparing

In this work, the sludge produced in a municipal wastewater treatment plant in Wuhan, China, was used as the raw material. At beginning, it was conditioned with Fenton's reagent and skeleton builders (0.3 g/g DS CaO combined with 0.4 g/g DS lignite) according our previous studies [20,22], followed by filter press dewatering with a pressure of 0.6 MPa. The characteristics of raw sludge, lignite and deep dewatered sludge were summarized in Table 1. Although the content of volatile matter reduced by almost 3%, the content of fixed carbon went up 5.32% after dewatering (see Table 1). More encouragingly, the water content of deep dewatered sludge has reached an extremely low value of 50.87%. All of this dewatered sludge was pulverized into fine powders and a large portion of fine wet sludge (evenly sampled) was then dried at 378 K to constant weight, so as to remove the tightly bound water or trapped water. Finally, part of this dry sludge (also evenly sampled) was soaked in the same amount of water as wet sludge.

2.2. Experimental apparatus and procedure

Three samples including dry sludge, wet sludge, and soaked sludge were pyrolyzed in a special horizontal quartz reactor (50 cm length × 3.6 cm i.d.) heated by an electrical furnace, as shown in Fig. 1. When the furnace temperature reached the set value (873 K, 1073 K and 1273 K, respectively), a quartz boat containing 2.5 g of sludge sample in dry base was placed in the water-cooled part of reactor for several minutes until an inert atmosphere was formed by introducing 60 NmL/min high purity N_2 and furnace temperature became stable. Then, the quartz boat was rapidly pushed into the reaction zone and sludge pyrolysis lasted for 60 min with the heating rate ranged from 5 to 24 K/s (4–7 K/s at 873 K, 8–14 K/s at 1073 K, 14–22 K/s at 1273 K). At the end of the whole process, the quartz boat was quickly pulled back to the water-cooled part and stayed for a period of time. Solid residue which had been cooled to room temperature was stored for testing. Volatile products passed through two condensers bathed in ice water and an impinger filled with cotton wool. In order to collect all the liquid products as far as possible, including tar, water, and hydrosoluble organic compounds, the above steps are repeated just replacing ice water with liquid nitrogen.

After each experiment, the non-condensable syngas pressurized in gas bag was analyzed by a Micro Gas Chromatograph (Agilent 3000A). The syngas yield was calculated by using the volume and density of each component. In addition, the LHV of dry syngas and the cold gas efficiency (CGE) were obtained through calculation. Meanwhile, the condensers (two special U-shaped tubes) were washed with dichloromethane. The tar obtained through dehydration with Na_2SO_4,

Table 1 – Characteristics of materials.

Materials	Proximate analysis (wt%)[a]			Ultimate analysis (wt%)[a]					LHV (kJ/kg$_{dry}$)
	Volatile matter	Ash	Fixed carbon	C	H	N	S	O[b]	
Lignite	53.98	10.04	35.98	65.27	4.16	0.91	0.37	19.25	22,537
Raw sludge	51.58	45.73	2.69	27.01	4.10	5.18	0.95	17.03	11,168
Deep dewatered sludge	48.62	43.37	8.01	29.68	3.53	2.92	1.45	19.05	10,126

[a] Dry basis.

[b] Calculated by difference.