



Full Length Article

In-situ removal of sulfur from high sulfur solid waste during molten salt pyrolysis

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ABSTRACT

In order to address the adverse effects of high sulfur content on the subsequent use of pyrolysis char, the removal of sulfur from high sulfur solid waste during molten salts pyrolysis was studied in this work. The results show that sulfur content of molten salts pyrolysis char was significantly lower than that of general pyrolysis char because molten salts catalyzed the decomposition of organic sulfur. Moreover, the removal efficiency of sulfur in molten salts pyrolysis char was obviously enhanced with the increase of temperature and time. Especially under the condition of 850 °C and 2 h, more than 33 wt% of the sulfur in molten salts pyrolysis char was successfully removed compared with ordinary pyrolysis char. Molten salts, which provided a larger contact area between char and volatiles, promoted a large amount of easily decomposed organic sulfur-containing compounds production by the cyclization reactions between char and hydrogen sulfide at higher temperatures. Due to the adsorption of H₂S by molten salt, the 'SH radical was released more into the molten salt in the form of H₂S rather than reacting with zinc oxide to form thermal stable zinc sulfide. Both of these reasons contributed to the removal of sulfur in the molten salt pyrolysis char.

1. Introduction

A large amount of solid wastes is produced every year in China. Statistics show that China produced up to 3,270,790,000 tons of solid waste in 2015 alone [1]. The storage of the solid waste occupies a lot of land and potential environmental pollution caused by the unreasonable disposal of solid waste becomes more serious [2]. Heat treatment technology offers a promising method for most solid waste treatment, which could fast reduce the volume of the waste and recover energy and resources at the same time [3]. Considered to be a very important heat treatment technology, pyrolysis can transform solid waste into useful gases, tar and char. So far, pyrolysis of solid waste has been broadly studied by using different kinds of reactors such as fixed bed, fluidized bed, rotary kiln and closed batch reactor [4–8].

Compared with general pyrolysis process, molten salts pyrolysis have several advantages: molten salts are excellent heat transfer media, the reactions are very fast, and there is good contact between the liquid and the samples [9]. These advantages have been confirmed in our previous study of Zhundong coal molten salt gasification [10]. So far, molten salt pyrolysis technology has been extensively studied in the field of solid waste treatment [11–14]. Yin et al. [15] harvested capacitive carbon by carbonization of waste biomass in molten salts. Studies have shown that alkaline metal-based molten salts can help catalyze the

pyrolysis process [16]. Jin et al. [17] further found intermixtures of Li₂CO₃, Na₂CO₃ and K₂CO₃ exhibited higher catalytic activity to the aimed reaction than the any simple ones by using molten carbonate salts catalyst for the wastepaper gasification. Therefore, it is feasible to use molten salt for catalytic pyrolysis of solid waste.

Moreover, molten salt pyrolysis can reduce the release of acid gases [18]. Siefert et al. [19] found alkali metal salt could capture acid gases such as H₂S by using alkali metal hydroxide to catalyze coal gasification. This property of molten salt is very important for the treatment of high-sulfur solid waste, such as waste tires and petroleum coke. Because sulfur-containing gases that will cause serious environmental pollution during the pyrolysis of high-sulfur solid waste will be captured by molten salt. Besides, the sulfur remained in the char would have a bad effect on the subsequent use of the solid products [20]. Therefore, the knowledge of sulfur removal and transformation is very important for the utilization of high-sulfur solid waste including waste tires by molten salt pyrolysis.

Recently, many studies focus on the behavior of sulfur in the pyrolysis process of waste tires. Unapumnuak et al. [21] found that half of the original sulfur was remained in the char rather than released as gases or condensed in the tar within the range of 350–850 °C during waste tires pyrolysis. According to our previous study, the sulfur in the char was mainly present in the form of sulfides during rapid pyrolysis of

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waste tires by using a vertical furnace, and ZnS was found as the most important sulfide source for the sulfur immobilization in the char [22]. H₂S was found as the main sulfur-containing component in gaseous products during waste tires pyrolysis [23]. During the pyrolysis process, the organic sulfur-containing compounds were gradually decomposed and their chemical forms also changed [24]. Most of the studies on the fate of sulfur in the pyrolysis process concerned on the general pyrolysis, while the removal and transformation mechanism of sulfur during molten salt pyrolysis of high-sulfur solid waste are rarely reported.

In this study, pyrolysis of high-sulfur solid waste in ternary molten salt (Li₂CO₃-Na₂CO₃-K₂CO₃) system was studied in the temperature range of 550–850 °C. The effect of molten salt on sulfur removal was studied by comparing the difference of sulfur content between molten salts pyrolysis char and general pyrolysis char. The migration and conversion behavior of sulfur in molten salt pyrolysis was revealed from the perspective of the change of sulfur form.

2. Experimental

2.1. Materials

Waste tires (WT) were provided by the nearby residents and petroleum coke (petcoke) was taken from a petrochemical plant in Qingdao, China. Before drying to constant weight at 105 °C by oven, the samples were broken and sieved to the sizes of 0.4–0.6 mm. The proximate and ultimate analyses were listed in Table 1. Waste tires have a large amount of volatile matter and ash. The content of fixed carbon in petroleum coke is up to 93.6 wt%, while ash is only 0.6 wt%. Especially, waste tires and petroleum coke all have a high content of carbon. Waste tires comprise 1.2 wt% of sulfur, while petroleum coke contains 7.8 wt% of sulfur. In the experiments, a ternary eutectic blend of alkali metal carbonates with a weight ratio of 32.1% Li₂CO₃, 33.4% Na₂CO₃ and 34.5% K₂CO₃ was used. In order to obtain homogeneous molten eutectics, the mixed salts were heated at 800 °C for 6 h in a muffle furnace. Then the salts were cooled and finely ground.

2.2. Experimental methods

The molten salts pyrolysis of high-sulfur solid waste was carried out in a homemade molten salt pyrolysis furnace as shown in Fig. 1. Prior to the experiment, about 300 g of the ternary salts were put into the reactor mentioned above and heated to the set temperatures ranging from 550 to 850 °C. In order to create an anaerobic environment, argon gas was continuously input into the reactor with a flow rate of 300 scem throughout the course of the experiment. After completely exhausting the air in the reactor, a basket containing about 2 g samples was immersed into the molten carbonates, and maintained for 0.5–2 h. After pyrolysis was finished, the basket was lifted from the molten salts into the upper part of the reactor. After cooling to room temperature under argon atmosphere, the basket was pulled out from the reactor. Then the products were washed with deionized water for 1 h. After drying at 105 °C for 12 h, the molten salts pyrolysis char was obtained (denoted as WT-X-Y and petcoke-X-Y, respectively, X represents temperature, Y

Table 1
Properties of high sulfur solid wastes.

Samples	Proximate analysis (wt%) ^a				Ultimate analysis (wt%) ^a				
	Moisture	Volatile matter	Ash	Fixed carbon	C	H	O ^b	N	S
WT	0.56	66.48	7.68	25.28	80.46	6.83	3.22	0.58	1.24
Petcoke	0.14	5.66	0.60	93.60	85.11	3.25	2.23	1.05	7.76

^a Dry basis.

^b Calculated by difference.

represents time).

The experimental results show that the removal of sulfur in pyrolysis char increases with time. In other words, pyrolysis char obtained at 2 h had the best desulfurization effect over the time range studied in this article. Therefore, waste tires general pyrolysis char was prepared by heating the sample in inert atmosphere at temperatures ranging from 550 to 850 °C for 2 h. The effect of molten salt on sulfur removal was obtained by comparing the difference of sulfur content between molten salts pyrolysis char and general pyrolysis char. To further understand the removal of sulfur in the molten salt pyrolysis, waste tires general pyrolysis char obtained at 450 °C for 40 min was endured another 0.5–2 h molten salt pyrolysis in the salts at 650 °C and 850 °C (denoted as WTGPC-X-Y, X represents temperature, Y represents time).

2.3. Analytical methods

The samples were ground into powder and dried at 105 °C for 6 h. To study the removal of sulfur in molten salts pyrolysis char, the sulfur contents in char were determined by using a Vario Micro cube elemental analyzer (GB/T 31391-2015). The proximate analyses of char were carried out by using a TGA2000 proximate analyzer and the results are given in Table 3 (GB/T212-2008). Moreover, mineralogical characteristics analysis of the char was carried out by X-ray powder diffraction (XRD). To obtain information of the mechanism of sulfur transformation, the sulfur speciation in waste tires and molten salts pyrolysis char were investigated by using a VG Multilab 2000 X-ray photoelectron spectrometer (XPS).

3. Results and discussion

3.1. Sulfur contents in molten salt pyrolysis char of high-sulfur solid waste

It can be seen from Table 2, char had a higher content of sulfur than the 1.24% sulfur content of the raw waste tires. The results were in good consistent with the conclusion mentioned above that most of the sulfur was remained in char during general pyrolysis. This was because sulfur-containing compounds with a certain thermal stability were formed in the molten salts pyrolysis process and the C–C bonds were broken down faster than the C=S bonds and C–S bonds in waste tires. This does not mean that molten salts had no effect on sulfur removal in char. On the contrary, compared with the general pyrolysis char, the sulfur content of molten salts pyrolysis char was significantly lower than that of general pyrolysis char. Especially, under the condition of 850 °C and 2 h, more than 33% of the sulfur in molten salts pyrolysis char was successfully removed compared with ordinary pyrolysis char. This was due to the catalytic effect of alkali metal ions in the molten salts on the cleavage of C–S bonds.

As Fig. 2 depicts, with the increase of temperature and time, the removal efficiency of sulfur in molten pyrolysis char was obviously enhanced in the temperature range of 550–850 °C and in the time range of 0.5–2 h. Taking 0.5 h as an example, the sulfur content in the molten salts pyrolysis char decreased from 2.99% to 2.27% as the temperature increased from 550 °C to 850 °C. Similarly, as time extended from 0.5 h to 2 h, the sulfur content decreased from 2.27% to 1.88% at 850 °C. This proved that as the pyrolysis process continued, the sulfur-containing compounds enriched in the char were gradually decomposed. Within the experimental range, the sulfur-containing compounds in the char were decomposed more thoroughly with the increase of temperature and time.

To better understand the removal of sulfur during molten salts pyrolysis, the changes of sulfur content of waste tires general pyrolysis char and petroleum coke after further molten salts pyrolysis were examined. The difference of sulfur content between molten salts pyrolysis char and raw materials above-mentioned was shown in Fig. 3. Petroleum coke sulfur removal rate stabilized at about 10%. As for the ordinary pyrolysis char of waste tires, the desulfurization rate was

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